

PREFACE

Treatments of the double-layer have, hitherto, been concerned primarily with the electrical aspects of adsorption and distribution of ions and with the nature of the isotherms and equations of state for ion and neutral molecule adsorption. The role of solvent structure and orientation of solvent molecules at charged interfaces has been a relatively neglected subject in discussions of the double-layer. It has obvious importance in relation to the realistic representation of the interphase between an electrode surface and the solution. Watts-Tobin and Mott were the first to introduce explicit consideration of the role of the solvent, water, in terms of a two-state model for orientation of solvent dipoles in the double-layer field, in distinction to earlier theories in which continuum dielectric polarization treatments were employed. Their theory, and the derived treatment for adsorption developed by Bockris, Devanathan and Müller, is critically examined in relation to new experimental work reported in this thesis.

Studies of adsorption of neutral organic molecules have been stimulated by the effects these adsorbates have on electrochemical reactions such as corrosion, electrodeposition of metals and kinetic exchange currents. The problem of pollution of water by surfactants, and the resulting foaming, has provided added impetus to the study of adsorption of organic substances at liquid interfaces.

As in the case of bulk solutions of organic substances in the water solvent, rather specific solute-solvent and solute-solute interaction and structure effects may be anticipated in interphases, dependent upon the orientation of either or both species in the surface. Orientation effects associated with adsorption of organic substances in relation to the intrinsic orientation of solvent molecules must hence be understood. Especially at electrodes, where such effects will be charge-, or potential dependent, knowledge of solvent orientation is an essential requirement for quantitative treatments of the double-layer and electrode processes involving hydrated ions. When the surfactant is ionic, other long-range interaction effects arise and at appreciable coverages ($\theta > 0.2$), solvation co-sphere interaction effects become of major importance.

Meaningful interpretations of electrochemical adsorption depend very much on suitable choice of adsorbates, i.e., the molecular structure of the latter must be sufficiently simple and the molecule rigid enough to allow examination of a well-defined theoretical adsorption model.

In Chapter III and Part I of Chapter IV investigations on the adsorption of pyrazine and pyridine at the Hg-electrode/water and air/water interfaces in relation to quantitative evaluation of field-dependent orientation of solvent and adsorbate molecules are reported. Considerable attention has been given to the proper choice of an isotherm

based on rigorous statistical mechanical arguments as applied to the substitutional adsorption of organic molecules.

Adsorption results for pyrazine and pyridine have been compared with those for n-amyl alcohol, a flexible straight chain molecule, and 1,4-diazabicyclo-octane, a spherical aliphatic-type molecule with no π -electron density in the ring system.

In Chapter III and Part II of Chapter IV of this thesis, adsorption results for organic ions such as N-methyl pyridinium perchlorate, and the mono- and dications of diaza-bicyclo-octane are interpreted (a) in terms of interaction effects which take into account solvation co-sphere overlap effects, and (b) solvent and solute orientation at the interphase.

The work presented in this thesis has been prepared for publication in the following papers:

1. Molecular Orientation in Adsorption of Pyridine and Pyrazine at Water/Mercury and Water/Air Interfaces, B. E. Conway, H. P. Dhar and S. Gottesfeld, J. Colloid and Interface Science, In press, 1973.
2. Solvent Structure and Molecular Orientation in the Double-layer at the Mercury/Water Interface, B.E. Conway and H.P. Dhar, Croatica Chim. Acta, in press (Proc. Summer School on Surface Chemistry, Rovinj, Yugoslavia, 1972).
3. On the form of Adsorption Isotherms for Substitutional Adsorption of Molecules of Different Sizes, H. P. Dhar, B.E. Conway and K.M. Joshi, submitted to Electrochimica Acta.

4. Hydration Co-Sphere and Ion-Pair Interactions in Electrochemical Adsorption of Organic N-Cations, B. E. Conway and H. P. Dhar, in course of publication.
5. Solution Thermodynamic Properties and Orientation Behavior of Adsorbed Pyridine and Pyrazine at the Hg/H₂O Interface, B. E. Conway, J. G. Mathieson and H. P. Dhar, submitted to J. Phys. Chem.

ACKNOWLEDGEMENT

The author wishes to record his sincere thanks and gratitude to his research supervisor, Professor B. E. Conway, who generously gave his advise and direction throughout the course of this research project. Professor Conway has been always approachable and most understanding. It has been a great pleasure to work with him, because he possesses both great personal dedication and capability to provide guidance in research.

Grateful thanks are also due to Professor K. M. Joshi (Indian Institute of Science, Bombay) for many helpful discussions during his one year stay in this laboratory as a Royal Society Nuffield Research Fellow and Visiting Professor. Discussions with Drs. H. Angerstein-Kozłowska, J. G. Mathieson and other colleagues of the electrochemistry group have also been of great assistance.

Technical help received from Mr. R. Serrat of the University of Ottawa Computing Centre and the workshop staff of the Chemistry Department is acknowledged with gratitude.

Financial support for this research project was given by the Department of Energy, Mines and Resources through research grants to Professor Conway.

The work of Mrs. W. Storto in typing the thesis and Mrs. E. Szabo in drawing many of the diagrams for publication in the listed papers is also acknowledged.

TABLE OF CONTENTS

	<u>Page</u>
PREFACE	i
ACKNOWLEDGEMENT	v
TABLE OF CONTENTS	vi
LIST OF FIGURES	xiii
LIST OF TABLES	xxii
ABSTRACT	xxiii
CHAPTER I	1
INTRODUCTION	1
A. The Situation of Ions and Solvent at an Electrode	1
B. Structure of Liquid Water	2
1. Structure of a water molecule	2
2. General remarks on the structure of liquids	4
3. Early theories of water structure	5
4. Mixture models	6
5. Continuum models	8
6. Information on water structure from infra-red spectroscopy	8
7. Consistency of models with experimental data	9
C. Structure of Water at Metal Interfaces	10
D. Electrical and Chemical Factors in Adsorption	12
1. General	12
2. Gas/Solid interface compared to metal/ liquid interface	13

	<u>Page</u>
3. Adsorption of ions from solution:	
Structure of the double-layer	15
4. Adsorption of neutral molecules from	
solutions: Competitive adsorption	17
E. Theories of Adsorption	18
Part I: Adsorption Theories based on Di-	
electric Polarization	18
1. Introduction	18
2. Frumkin's theory	19
3. Butler's theory	21
4. Theory of Macdonald	23
Part II: Molecular Theory of Water	
Orientation and Displacement	24
1. Theory of Watts-Tobin and Mott	24
2. Theory of Macdonald and Barlow	26
3. Theory of Bockris, Devanathan and Müller	28
4. Theories of Bockris, Gileadi and Müller	31
5. Work of Hills and Payne	33
F. Choice of Adsorbate Molecules	35
G. Orientation of Adsorbate Molecules	37
H. Adsorption and Ionization	39
1. Hydration of adsorbate	39

	<u>Page</u>
CHAPTER II	41
EXPERIMENTAL	41
Part I: Adsorption at Mercury	41
A. Apparatus Assembly	41
1. Adsorption measurements by capillary electrometry	41
2. Location of meniscus in the capillary	42
3. Excess pressure measurements	46
4. Capillary design	46
5. Calibration of capillary	48
B. Experimental Conditions	50
1. Purification of materials	50
2. Reference electrodes	52
3. Counter electrode	53
4. Thermostasis	54
C. Sources and Estimation of Errors	54
1. Inherent error in the experimental measurements	54
2. Errors introduced in evaluating results	58
Part II: Adsorption at the Air/Water Interface	61
A. Method for Surface Tension Measurements	61
B. Apparatus and Procedure for Measurements of Δh	62

	<u>Page</u>
CHAPTER III	64
RESULTS	64
A. Adsorption at Hg/Water Interfaces	64
1. Computation of primary results	64
2. Adsorption of pyrazine	65
3. Adsorption of pyridine	69
4. Adsorption of n-amyl alcohol	72
5. Adsorption of 1,4-diazabicyclo(2,2,2) octane (DBO)	77
6. Adsorption of organic ions	81
(i) Adsorption of N-methyl pyridinium perchlorate	81
(ii) Adsorption of DBO mono- and dipositive ions	82
B. Adsorption at the Air/Water Interface	87
1. Adsorption of pyrazine and pyridine	87
CHAPTER IV	90
DISCUSSION	90
Part I: Adsorption of Neutral Molecules	90
A. Methods of Approach	90
B. Isotherms for Substitutional Adsorption of Molecules	92
1. Introduction	92
2. Thermodynamic treatment of substitutional adsorption	95

	<u>Page</u>
3. Statistical-mechanical basis of the isotherms	99
4. Properties of the isotherm relation (77)	103
5. Remarks on the isotherms of Bockris and Swinkells and of Schuhmann	108
6. Significance of surface coverage terms in isotherms	110
7. Standard states in isotherms	115
C. Adsorption of Pyrazine and Pyridine at the Hg Electrode	116
1. Free energy of adsorption	116
(i) Evaluation of $\Delta G_{\text{ads}}^{\circ}$ for pyrazine and pyridine	116
(ii) Comparison of theoretical and experimental $\Delta G_{\text{ads}}^{\circ}$ for pyrazine	120
(iii) Dependence of $\Delta G_{\text{ads}}^{\circ}$ on coverage θ	127
2. Entropy and enthalpy of adsorption of pyrazine and pyridine at the Hg surface	130
3. Esin and Markov effects	141
(i) Solvent and adsorbate orientation	141
(ii) Changes of χ potential due to replacement of oriented solvent dipoles	145
(a) Pyrazine	145
(b) Pyridine	148
(c) <u>n</u> -Amyl alcohol	154

	<u>Page</u>
(iii) Relation to evaluation of $(N_{\uparrow} - N_{\downarrow})/N_T$ and U_c/kT from the free energy of adsorption	156
(iv) Temperature coefficient of surface dipole potentials	158
4. Surface pressure relations for pyrazine and pyridine	160
D. Adsorption of Pyrazine and Pyridine at the Air/Water Interface	167
1. Comparison of isotherms for pyrazine and pyridine	167
2. Entropy and enthalpy of adsorption at the air/water interface	169
E. Adsorption of DBO at the Hg Electrode	171
1. Free energy of adsorption	171
2. Esin-Markov effects	174
3. Surface pressure relations	177
Part II: Adsorption of Organic Cations at the Hg Electrode	179
A. Introduction	179
B. Treatment of Data	181
1. Methods of approach	181
2. N-methyl pyridinium perchlorate	181
3. Mono- and dications of diazabicyclo-octane (DBO^+ and DBO^{++})	186

	<u>Page</u>
C. Dependence of ΔG_{ads}^0 on Coverage	191
1. N-methyl pyridinium perchlorate	191
(i) Partial loss of long-range Born solvation energy	194
(ii) Change of polarization in terms of dielectric decrement	199
D. Comparison of Adsorption Behavior of N-Me pyridinium perchlorate, DBO^+ and DBO^{++} Ions	202
APPENDIX I	209
CLAIMS TO ORIGINAL RESEARCH	227
REFERENCES	230

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Schematic diagram of apparatus. E, electrode connections; E', electrical contacts; W, water jacket; M, manometer; Bm, binocular microscope; O, capillary (see inset); L, lamp; B, bellows; R ₂ bulb; R ₁ , Hg reservoir; V, volt-ohmyst.	43
2	Schematic drawing of T.V. microscope and illumination arrangement for electrocapillary measurements by the method of determining excess pressures.	45
3	Plots showing curve-fitting in a 4th order polynomial for different compounds. X's are experimental points, and, —, smooth curves represent best fits through the points (for explanation of the axes see Chapter III).	60
4	Electrocapillary curves (based on γ values at 50 mV intervals) for adsorption of pyrazine from aq. 0.03 M NaClO ₄ solution. T = 293°K.	67
5	Plots of Γ versus q_M for various pyrazine bulk concentrations. T = 293°K.	68
6	Plots of Γ versus q_M for various pyridine bulk concentrations. T = 283°K.	71

<u>Figure</u>		<u>Page</u>
7	Electrocapillary curves (based on γ values at 50 mV intervals) for adsorption of <u>n</u> -amyl alcohol from aq. 0.3 M NaClO ₄ solution. T = 293°K.	74
8	Plots of Γ versus log C of <u>n</u> -amyl alcohol at various temperatures and <u>two</u> values of q_M .	75
9	Plots of Γ versus q_M for various bulk concentrations of <u>n</u> -amyl alcohol. T = 293°K.	76
10	Electrocapillary curves (based on γ values at 50 mV intervals) for adsorption of DBO (neutral) from aq. 0.3 M NaClO ₄ solution. T = 293°K.	79
11	Plots Γ versus q_M for various bulk concentrations of DBO (neutral). T = 293°K.	80
12	Electrocapillary curves (based on γ values at 50 mV intervals) for adsorption of N-methyl pyridinium perchlorate from aq. 1.0 M HClO ₄ solution.	83
13	Plots of Γ versus q_M for various bulk concentrations of N-Me pyridinium perchlorate. T = 298°K.	84
14	Plots of Γ versus q_M for various bulk concentrations of monopositive DBO ion. T = 293°K.	85

<u>Figure</u>		<u>Page</u>
15	Plots of Γ versus q_M for various bulk concentrations of dipositive DBO ion. $T = 293^\circ K$.	86
16	Experimental isotherms for adsorption of pyridine and pyrazine at the air/water interface at various temperatures. The dashed curve shows one isotherm after activity coefficient correction for pyridine.	89
17	Plot of the configurational $f(\theta) = \theta / (1-\theta)^x$ for various θ and x values.	104
18	Plot of the configurational $f(\theta) = \theta / e^{x-1} (1-\theta)^x$ for various θ and x values.	105
19	Plot of the configurational $f(\theta) = \theta / x e^{(x-1)} (1-\theta)^x$ for various θ and x values.	106
20	Plot of the difference between ΔG_{ads}^0 values calculated from equation (77) and from the Langmuir (L) isotherm for a given arbitrary solution concentration and various θ values.	107
21	Variation of ΔG_{ads}^0 of pyrazine at $20^\circ C$ as a function of q_M at various θ values (data for one coverage by pyridine ⁶⁰ is included for comparison).	118
22	Apparent standard free energy of adsorption ΔG_{ads}^0 of pyridine at Hg/H ₂ O interface at $40^\circ C$ as function of q_M and coverage (calculated for $x=3$).	119

<u>Figure</u>		<u>Page</u>
23	Variation of the function $\exp(-xB(\mu F - BUc)/kT)$ with surface charge $\pm q_M$ for values of $Uc/kT = 0, 3$ and 6 for $x = 1$ or 3 (calculated for $T = 298^\circ K$). Values of the orientation function B are also shown as $f(q_M)$.	122
24	Plot of $\exp(\Delta G_{chem}^o - \Delta G_{ads}^o)$ as $f(q_M)$ and θ for pyrazine (calculated for $x=3$ and $T=293^\circ K$).	124
25	Fit to the variation of ΔG_{ads}^o for pyrazine adsorption with q_M for $Uc/kT=2$, $x=3$, using equation (90); data for $308^\circ K$.	125
26	Variation of ΔG_{ads}^o with θ by pyrazine for several values of q_M at Hg at $293^\circ K$.	128
27	Variation of ΔG_{ads}^o with θ by pyridine for several values of q_M at Hg at $313^\circ K$.	131
28	ΔS_{ads}^o for pyrazine at the Hg electrode as a function q_M for various values of θ .	133
29	ΔH_{ads}^o for pyrazine at the Hg electrode as a function of q_M for various values of θ .	134
30	Compensation effect between ΔH_{ads}^o and ΔS_{ads}^o for various values of θ and q_M in pyrazine adsorption at Hg.	136
31	ΔS_{ads}^o for pyridine at the Hg electrode as a function of q_M for various Γ (or θ) values.	138
32	ΔH_{ads}^o for pyridine at the Hg electrode as a function of q_M for various Γ (or θ) values.	139

<u>Figure</u>		<u>Page</u>
33	Compensation effect between ΔH_{ads}° and ΔS_{ads}° for various values of θ and q_M in pyridine adsorption.	140
34	Esin and Markov effect for adsorption of naphthalene at Hg from methanolic Na_2SO_4 solution at $25^{\circ}C$ at the potential of zero charge.	142
35	Esin and Markov plots for pyrazine adsorption at Hg as a function of Γ at various q_M values in 0.03 M aq. $NaClO_4$. a) $293^{\circ}K$; b) $323^{\circ}K$; c) $338^{\circ}K$.	144
36	Evaluation of the solvent orientation distribution function $(N_{\uparrow} - N_{\downarrow})/N_T$ from data of Fig. 35a in relation to values calculated from equation (18) with various U_c/kT values. The distribution function from pyridine adsorption data of Fig. 37b is also shown.	147
37	Esin and Markov plots for pyridine adsorption at Hg as a function of Γ at various q_M values in 0.03 M aq. $NaClO_4$. a) $283^{\circ}K$; b) $298^{\circ}K$; c) $328^{\circ}K$.	149
38	Schematic representation of $\Delta E_q - \Gamma$ plots for (a) sudden change of orientation of a layer of dipoles; (b) a parallel orientation process and (c) typical experimental behavior with pyridine at negative q_M values.	150

<u>Figure</u>		<u>Page</u>
38A	Resolution of slope components in the Esin and Markov plots of Fig. 37, based on water and pyridine orientation contributions.	153
39	Esin and Markov plots for <u>n</u> -amyl alcohol adsorption at Hg at various q_M values in 0.3 M aq. NaClO_4 . a) 293°K ; b) 318°K ; c) 333°K .	155
40	(a) Temperature dependence of slopes of $d\Delta E_q/d\Gamma$ of Esin and Markov plots for pyrazine adsorption.	159
	(b) Temperature dependence of slopes of $d\Delta E_q/d\Gamma$ in the two regions of the Esin and Markov plots of Fig. 37 for pyridine adsorption.	161
41	ϕ_q - Γ plots for pyrazine in 0.03 M NaClO_4 at Hg for various q_M values.	162
42	ϕ_q - Γ plots for pyridine in 0.03 M NaClO_4 at Hg for various q_M values.	163
43	Variation of ΔG_{ads}^0 of DBO (neutral) at 20°C as $f(q_M)$ at various surface coverages.	172
44	(a) Esin and Markov plots for DBO (neutral) adsorption at Hg as a function Γ at q_M values $+8$ to $-2 \mu\text{C cm}^{-2}$.	175
	(b) Esin and Markov plots for DBO (neutral) adsorption at Hg as function Γ at q_M values -2 to $-8 \mu\text{C cm}^{-2}$.	175a
45	ϕ_q - Γ plots for neutral DBO in 0.3 M NaClO_4 at Hg for various q_M values.	178

<u>Figure</u>		<u>Page</u>
46	(a) Variation of ΔG_{ads}° with $\theta^{1/2}$ calculated from experimental data with the size factor $x=3$ for N-methyl pyridinium perchlorate.	182
	(b) Variation of ΔG_{ads}° with $\theta^{3/2}$ calculated from experimental data with the size factor $x=3$ for N-methyl pyridinium perchlorate.	182a
47	Esin and Markov plots for N-methyl pyridinium perchlorate adsorption at Hg for various q_M values.	184
48	ϕ_q - Γ plots for N-methyl pyridinium perchlorate in 1 M $HClO_4$ at various q_M values.	185
49	Dependence of ΔG_{ads}° on q_M for various Γ values for adsorption of N-methyl pyridinium perchlorate at Hg, calculated for $x=3$.	187
50	Dependence of ΔG_{ads}° on q_M for various θ values for adsorption of the monocation of DBO, calculated for $x=1$.	188
51	Dependence of ΔG_{ads}° on q_M for various θ values for adsorption of the monocation of DBO, calculated for $x=3$.	189
52	Esin and Markov plots for (a) the mono- and (b) the dications of DBO at various q_M values.	190

<u>Figure</u>		<u>Page</u>
53	(a) Dependence of ΔG_{ads}^0 on q_M for various θ values for adsorption of the dication of DBO calculated for $x=1$. (b) Dependence of ΔG_{ads}^0 on q_M for various θ values for adsorption of the dication of DBO calculated for $x=3$.	192 192a
54	ϕ_q - Γ plots for adsorption of DBO (a) monocation at Hg in 0.3 M KH_2PO_4 and (b) dication at Hg in 1 M aq. $HClO_4$.	193
55	Model for calculation of solvation energy in an interphase due to ion solvation co-sphere overlap (a) overlapping co-spheres (b) Integration over the spherical segment.	195
56	Co-sphere overlap energy W_h as a function of coverage θ or θ^2 for various types of calculation. Also coulombic ion-ion and ion/image-ion/image interaction energies are shown.	198
57	(a) Dependence of ΔG_{ads}^0 on θ for DBO monocation at various q_M values (calculated for $x=1$). (b) Dependence of ΔG_{ads}^0 on θ for DBO dication at various q_M values (calculated for $x=1$).	203 204
58	Models of adsorption and orientation of water and various N-containing ions at Hg. (a) DBO dication at negative q_M with some anion pairing.	206

<u>Figure</u>	<u>Page</u>
(b) DBO dication at positive q_M with interaction with adsorbed anions.	206
(c) DBO monocation at positive q_M with smaller interaction with adsorbed anions.	206
(d) Repulsive interaction between oriented DBO monocations at negative q_M .	206
(e) Orientation and solvent displacement by N-Me pyridinium ⁺ ion in the "flat" orientation at Hg.	206

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Values of $B (= \frac{N^{\uparrow} - N^{\downarrow}}{N_T})$ and U_c/kT as a function of q_M calculated from data for pyrazine and pyridine adsorption.	157
II	Activity coefficients for aqueous pyridine solutions.	169
III	Comparison of standard entropies of adsorption of pyrazine and pyridine at the air/water and Hg/H ₂ O ($q_M = 0$) interfaces.	170

ABSTRACT

Studies of the structure of the interphase in the electrochemical adsorption of selected neutral and ionic organic molecules at the mercury electrode have been carried out by electrocapillary measurements. Adsorption from solution occurs by solvent displacement in the interphase. When the adsorbate differs appreciably in size from the previously adsorbed solvent, the relative size factor, x , of adsorbate and solvent determines (a) the form of the relation for free energy of adsorption and (b) the form of the configurational function in the adsorption isotherm in terms of fractional coverage θ or site fraction X . Various types of isotherms that have been proposed for this situation are critically examined in relation to the statistics of the solvent-lattice replacement process that occurs in adsorption, e.g. for organic substances at electrodes. It is concluded that the correct configurational term to be used when $x > 1$ is $\theta/e^{(x-1)}(1-\theta)^x$. Using this term in an equilibrium adsorption isotherm then allows standard free energies of adsorption and derived quantities to be properly calculated from experimental coverage or surface excess measurements.

It is shown that it is incorrect to refer to an isotherm containing the configurational term $\theta/x(1-\theta)^x$ as the "Flory-Huggins" isotherm since Flory-Huggins statistics lead to an isotherm having a different form for the

configurational term, viz. that containing the $e^{(x-1)}$ factor, as above.

From the adsorption parameters calculated from a suitable isotherm, orientation effects at the water/mercury interface can be quantitatively evaluated in relation to the electrosorption of pyrazine and pyridine. Related conclusions can be made for the air/water interface.

Pyrazine being a chemically and electrically "symmetrical" molecule, provides an ideal basis for examination of electrochemical theories of adsorption of polar molecules in the double-layer at charged interfaces. It is shown to exhibit an almost symmetrical change of free energy of adsorption with field about a surface charge of $q_M = -2 \mu\text{C cm}^{-2}$, an observation which has been explained in terms of zero orientation of water molecules at that charge, and not at $q_M = 0$. This observation also enabled other solvent-solvent interaction effects, and the dependence of solvent orientation on surface charge, to be evaluated. By using pyrazine and pyridine in critical comparative experiments on (a) changes of surface dipole-potential difference (Esin and Markov effects), (b) surface pressure changes and (c) charge dependence of free energy of adsorption, it is shown how the surface dipole contribution from oriented solvent molecules may be evaluated together with the charge dependent distribution function for water orientation. In the case of pyridine, orientation of the adsorbate molecule itself occurs in a

manner dependent on surface charge on the metal and interaction with oriented surface- and bulk-solvent molecules.

Also, from the above information, it has been concluded that both pyrazine and pyridine adsorb in a similar orientation, probably "flat", on the positively charged surface, so that π -orbital interactions of the molecules with the surface are maximized. Important compensation effects are observed between heat and entropy of adsorption at various coverages and surface charges at mercury, and indicate the role of water structure (H-bonding) effects in the interphase.

1,4-Diazabicyclo-octane, referred to as "DBO", is an almost spherical molecule and has quite different adsorption characteristics which have been attributed to the high electron density on the N atoms. *n*-Amyl alcohol, like pyrazine, also adsorbs symmetrically around a surface charge of $q_M = -2 \mu C cm^{-2}$. Because of the strong hydrophobic character of the five carbon atom chain, the molecule perhaps adsorbs always with the carbon chain lying on the surface and the OH functional group oriented with neighboring water molecules in the inner Helmholtz plane.

The electrochemical adsorption of N-methylpyridinium perchlorate, and the mono- and dications of DBO has been studied at the Hg electrode in order to provide closely spaced data for an examination of specific solvation effects in interactions amongst specifically adsorbed cations in the

Hg/water interphase. Both solvation co-sphere overlap effects and cation-anion pairing are important, depending on the value of the surface charge.

A model and derived theoretical calculations for solvation co-sphere interaction effects show that these previously neglected effects can, in fact, be the main term in the two-dimensional interaction energy between specifically adsorbed ions of the same sign of charge.

Specificities in the adsorption of the three kinds of ions are considered in relation to surface pressure, coverage dependence of free energy of adsorption, and Esin and Markov effects.

CHAPTER I

INTRODUCTION

A. The Situation of Ions and Solvent at an Electrode

At an uncharged metal interface in solution, a double-layer can be set up with a corresponding local potential difference due to (a) solvent dipoles which have become oriented on account of specific interaction with the metal and (b) asymmetry¹ of electron distribution near the metal surface. In addition to these effects, there is the important contribution to the double-layer potential difference arising from any net electron charge on the metal and the corresponding accumulation of ions from the solution in response to this charge.

In the bulk electrolyte, under equilibrium conditions, the time-average forces are the same in all directions and at all points, and there are no preferentially directed electrical fields. The forces operating on particles near the phase boundary are, however, anisotropic, being different towards the boundary in comparison with the bulk electrolyte. Further, the forces due to the phase (e.g. the electrode) on the other side of the phase boundary (e.g. the electrode-electrolyte interface) vary with distance from the boundary; the further the ion is situated in the bulk, the smaller is the influence of the phase upon it and the more is the

situation of the ion characteristic of the bulk solution. Thus, the properties of the interphase region are different from those of either of the bulk phases.

The term electrical double-layer or simply double-layer is used to describe the distribution of charges and oriented dipoles constituting the interphase region at the metal/electrolyte boundary. The potential difference across the interphase is of the order of 1 V. The thickness of the interphase between the metal and the centres of ions in contact with the metal is about 3 to 5 $\text{\AA}$, and thus the field is very high, of the order of $3 \times 10^{+7} \text{ V cm}^{-1}$. This field produces electrostriction of the solvent molecules at the surface and causes appreciable dielectric saturation or orientation effects in the electrical double-layer, analogous to those arising in the primary hydration shells of ions².

Since a main feature of the present work is concerned with the role of solvent and associated structural problems in the interphase, it will be desirable first to review some background material on the structure and properties of the water solvent itself.

B. Structure of Liquid Water

1. Structure of a water molecule

Knowledge of the structure of a single water molecule and its electrical properties, such as its dipole and quadrupole moments, is useful in characterizing its charge

distribution and, therefore, understanding its association with other molecules in the liquid state. The Molecular Orbital picture³ for a water molecule shows that it has an approximately tetrahedral configuration. Besides the normal linear combination of atomic orbitals between the 1s orbital of hydrogen and the 2p orbitals of oxygen, it is suggested that the 2s orbitals of the oxygen atom hybridize with 2p_y and 2p_z orbitals involved in formation of the two O-H bonds in H₂O. This has the effect of enlarging the bond angle from 90° to ca. 105° and also of increasing the amount by which the oxygen orbitals overlap the hydrogen orbitals, hence creating stronger bonds. The hybridized 2s and 2p orbitals of oxygen form two lobes which accommodate the valence electrons. These lobes are symmetrically located above and below the molecular plane and project away from the two hydrogens forming a quasi-tetrahedral charge distribution. The two lone pairs of electrons on oxygen contribute to the dipole moment of water.

The water molecule has three nearly equal quadrupole moments, and seven non-vanishing octupole moments. Electron density contour maps for the molecule, and the values of the quadrupole moments, indicate that the overall charge distribution of the water molecule is not far from spherical.

2. General remarks on the structure of liquids

In general, liquids are more difficult to define than either crystalline solids or dilute gases. Therefore, statistical theories of the liquid state have lagged considerably behind those for solids and gases. In liquids, the potential energy (p.e.) of the molecules is approximately equal to their kinetic energy (k.e.) and since neither of these two terms is negligible, the mathematical treatment of liquids is very complex. Approximations⁴ in the statistical mechanical treatment of liquids such as liquefied inert gases have been developed. These approximations do not apply, however, to an associated liquid like water which is hydrogen bonded in a three-dimensional network.

The molecules of a liquid are assumed to occupy positions relative to their nearest neighbors, reminiscent of the positions they normally occupy in the corresponding solid. The structure lacks, however, a long-range order, and the short-range order that exists is also imperfect. At a fixed pressure and temperature, a molecule in a liquid may, to a fair approximation, be thought of as surrounded by nearest neighbors in almost the same relative positions and interacting through the same intermolecular potential as in the solid. One important difference, however, is that the relatively large k.e. allows individual molecules to change position. The relative positions of the molecules with

respect to a given reference molecule can be expressed in terms of the experimentally evaluated radial distribution function.

3. Early theories of water structure

The early X-ray diffraction work of Stewart⁵ on water showed that there was definitely short-range order in the liquid. This information provided the basis for the first quantitative theory of water structure by Bernal and Fowler⁶. They proposed that water consisted of a mixture of two forms which could be represented in terms of structures of ice I (hexagonal) and ice Ic (tetrahedral) (cf. ref. 3 for structures of ices). A change of temperature was regarded as producing a shift in the relative amounts of these species. Though their theory was successful in explaining the density maximum at 3.86°C, it did not reproduce the radial distribution curves for water⁷. From X-ray diffraction measurements, Morgan and Warren⁷ and, more recently, Narten et al.⁸ showed that, on the average, there are approximately four nearest neighbors to every water molecule over a wide range of temperatures (1.5 to 200°C). Morgan and Warren⁷ noted that at higher temperatures tetrahedral coordination is less sharply defined. On the basis of accurate X-ray data of Narten et al.⁸, Pauling's clathrate type model⁹ was rejected on the basis that it did not conform to the radial distribution function for water.

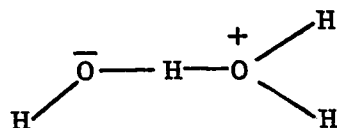
In the various theories presented over the last forty years or so, there is agreement on the basic physical phenomena involved which account for the properties of liquid water, but details of the representation differ. Generally, the models can be classified into two main groups: "mixture models" and "continuum models". Treatments based on these models have been reviewed in the recent literature^{10,3}.

4. Mixture models

In this model, water is considered as an equilibrium mixture of species that are distinguishable in an instantaneous picture in terms of their energy, orientation and association. In the mathematical treatment of mixture models, each species of water is considered to occupy a discrete energy level, commonly called a 'state'. Owing to thermal agitation, molecules experience frequent transitions between these states and consequently, in the time average, all molecules are equivalent. A change in P or T is regarded as shifting the relative populations of the states; the thermodynamic properties of the liquid are explained in terms of these shifts.

Many mixture models for water have been proposed. Two main classes of theories may be distinguished. In one class, at least one component is treated in terms of a known structure, e.g. ice, and is considered to exist as assemblies of at least some tens of molecules. The theories of Frank and Quist¹¹ and of Kamb¹² fall in this category. The

"flickering cluster" model proposed by Frank and Wen¹³ was derived on the basis that the following resonance structures contribute to the mutual attraction of a pair of water molecules:



Formation of one hydrogen bond was regarded as promoting cooperatively the formation of other hydrogen bonds in its vicinity.

In the second class of theories, the species are considered as differing simply in the number of broken and unbroken hydrogen bonds; extended structures may also be considered. The so-called interstitial model for water is a special class of mixture model. One species of water molecule is regarded as forming an hydrogen bonded framework containing cavities in which the other species (assumed to be single, non-hydrogen bonded water molecules) reside. Samoilov¹⁴ interpreted the radial distribution function of water in terms of an interstitial model. According to him, liquid water is similar to ice but has molecules in the cavities. As ice melts, some of the molecules break their hydrogen bonds with the lattice and move into neighboring cavities, as suggested by Bernal and Fowler⁶.

5. Continuum models

A continuum theory describes water as having essentially complete hydrogen bonding at all times except at relatively high temperatures, but as having a distribution of intermolecular distances, orientations and energies of bonding between the molecules, which may vary with temperature and pressure. Pople's¹⁵ treatment is the most modern continuum theory of water in which the majority of hydrogen bonds between neighboring molecules were regarded as distorted or bent. Water molecules in the liquid were considered to be four-coordinated into irregular and varied networks in contrast to the orderly networks of a few basic types that exist in the lattice structures of phases of ice. Bernal¹⁶ believed that five-membered rings are a frequent configuration in the liquid but that rings containing four, six, seven or even more molecules contribute to the network structure. Pople¹⁵ and Bernal¹⁶ showed that these models were consistent with the radial distribution function of water, and Pople demonstrated that his model could also account for the dielectric constant of water and for the decrease of volume of ice I on melting.

6. Information on water structure from infra red spectroscopy

From infra-red spectral studies of the uncoupled O-H and O-D stretching bands in liquid H₂O carried out by

Falk and Ford¹⁷ and by Frank and Roth¹⁸, it became apparent^{19,3} that (a) a range of O-H environments or, equivalently, of hydrogen bond strengths, is present in liquid water and the mean hydrogen bond strength decreases gradually as temperature increases; (b) water does not contain a small number of distinctly different molecular species; this was indicated by the observation of a smooth band contour that passes through a single maximum; (c) there are present in the liquid water, even below 100°C, some non-hydrogen bonded O-H groups which have environments distinctly different from the majority of the O-H groups. This has been supported by the discovery of Walrafen^{20,21} of an isosbestic point in the Raman-spectral studies of the uncoupled OD stretching vibrations, a phenomenon that is often associated with two absorbing species in equilibrium, the relative amounts of which change with temperature.

7. Consistency of models with experimental data

The basic idea of the mixture model, that liquid water is a mixture of distinctly different species, is not in accord with much of the experimental data (cf. ref. 3). Studies of uncoupled stretching bands show that the liquid contains a variety of molecular environments, and thus water cannot be described in terms of a small number of discrete states. A frequently cited justification for adopting a mixture model (e.g. the "significant structures" model of Eyring²²) is that with proper choice of parameters, a partition

function based on the model can reproduce a number of equilibrium properties. However, it should be noted that a correct average energy can be computed from a judiciously (or empirically) selected set of discrete energy levels, even if the true "spectrum" of energy states is continuous.

The continuum theories have received less attention to date, although these theories seem to be in accord with most of what is known about the structure of water from experimental data. Extensive hydrogen bonding can account for the large dielectric constant and energy of vaporization of water, the abnormal proton mobility in the liquid and the low quadrupole coupling constant for deuterons in liquid D_2O . Also the correct temperature dependence of dielectric constant can be calculated¹⁵.

C. Structure of Water at Metal Interfaces^{23,24}

In the absence of any directing forces between a metal electrode and water molecules, and allowing for the maximum contact adsorption (20%) of other ions on the surface, at least 70% of the metal surface is normally covered with water molecules in aqueous ionic solutions. There is, however, interaction between water molecules and the metal surface. Firstly, there are image forces^{1,23} operating between water dipoles and their corresponding images "in" the metal. A charge q_M at a distance d from a metal surface experiences an image force of magnitude $-q_M^2/4d^2$. In addition

to image forces, there are dispersion forces - attractive, non-directional forces, and also in some cases forces of a more chemical nature. All these forces operate even at an uncharged electrode which therefore has an attraction for water molecules and may provide forces which are comparable with those which bind water molecules into networks within the liquid phase. Of course, depending on site distribution (at solid metals) and temperature, various degrees of binding of water molecules to the metal surface can arise.

In addition to the above forces, charge on a metal surface will stimulate the water molecules to orient themselves so that their dipoles tend to lie parallel to the field of the charged surface. The net result is that the electrode is almost fully covered with a layer of water dipoles oriented to an extent dependent on charge. The degree of orientation of the water dipoles also affects the dielectric constant of this water layer. The dielectric constant of a fully oriented water layer is about 6^{25} , while bulk water has a dielectric constant of 78.

Apart from this oriented layer, equivalent to the primary hydration sheath at an ion, there is a secondary hydration region in which water molecules are somewhat uncertainly oriented toward the surface. Orientation of water molecules in this layer is restricted by thermal and hydrogen bonding influences of the particles in solution. The dielectric constant increases rapidly in the direction away

from the metal and, over a few layers, it reaches the value characteristic of the bulk electrolyte. The dielectric constant of the second layer has been taken as ca. 40^{24} .

Two limiting orientations of the water molecules are possible: at high positive charge on the surface, the molecules orient with oxygen atoms in contact with the electrode and the hydrogen ends towards the solution. At large negative charges, the hydrogens face the electrode and oxygen atoms are towards the solution²⁵ (see p.28).

D. Electrical and Chemical Factors in Adsorption

1. General

Usually molecules impinging on a surface remain there for sometime before re-evaporating, depending on various factors such as the actual site in the surface which the molecules strike, the nature of the surface and that of the molecule, the temperature of the surface and the k.e. of the molecule. This situation known, of course, as adsorption results in a higher concentration of the molecules being at the surface than the average in the bulk phase. Usually molecules exhibiting small intermolecular attractive forces, and therefore small surface tensions in the pure state, tend to concentrate at a surface; however, the adsorption does not usually proceed so far that the surface consists solely of that component.

The forces giving rise to adsorption are, in

principle, not different from those in any other interaction phenomenon involving atoms and molecules - like cohesion in solids and liquids, and Van der Waals and dispersion forces between molecules. All adsorption forces in an interphase are basically electromagnetic in origin but specific adsorption forces (chemisorption) arise from a certain amount of unsaturation in the bonding of the surface metal atoms.

2. Gas/Solid interface compared to metal/liquid interface

The principal distinction between gas/solid and metal/liquid interfaces lies in the presence of a solvent in the latter case which (a) gives rise to greater complexity of interactions in the surface layer, but (b) allows, in the case of metals or semi-conductors, control of the electrical field across the interface or the net charge at the surface.

While studies of adsorption at the gas/solid interface offer possibilities for use of sophisticated techniques such as i.r., Raman and Auger spectroscopy, as well as low energy electron diffraction which are inapplicable in most circumstances at the metal/liquid interface, the latter type of interface can be studied accurately with respect to other details of the adsorption process when the metal is a liquid electrode, e.g. Hg, Ga, especially with respect to the electrical factors in adsorption. Also, the recently developed techniques of in situ reflectance measurement³⁷ provide powerful new approaches for examination of metal (as an electrode)/liquid interfaces.

At a gas/solid interface, two types of adsorption may be distinguished, based on the relative energies involved in the metal-adsorbate bond. One is physical adsorption, the forces of attraction being the weak Van der Waals type associated with an heat of adsorption rarely exceeding 5 kcal mole⁻¹. The other is chemisorption in which the adsorbate layer is chemically bound to the surface by covalent forces. The heat of adsorption is usually in the range 10-80 kcal mole⁻¹ of adsorbate. Chemisorption is usually irreversible and generally proceeds until the surface is covered by a complete layer one molecule in thickness. Physically adsorbed layers can, however, be formed up to thicknesses greater than that of a monolayer. The first layer is usually rather more strongly adsorbed than the second and further layers.

In chemisorption, molecules or radicals can become oriented to give maximum overlap between adsorbate and surface metal orbitals and thus modify the intrinsic electrical field at the surface in the absence of adsorbate. Such variations in the electronic nature of the surface phase can be studied as a function of coverage, e.g. through electron work-function measurements. Any adsorption on the surface will be accompanied by a change in the surface potential χ which can be measured and which leads to changes in the electrical properties of the interfacial region of the metal such as conductivity and dielectric constant. Evidence can

also be obtained about redistribution of electrons within the adsorbate molecules by instrumental techniques such as i.r., e.s.r. and dielectric polarization studies.

3. Adsorption of ions from solution: Structure of the double-layer

As mentioned above, adsorption at the metal/liquid interface is unique due to the ubiquitous presence of a solvent, usually water. Unfortunately, in most earlier work on ionic adsorption at electrified interfaces, the role of solvent has been neglected. Helmholtz²⁶ regarded an electrified interface as equivalent to a condenser of constant capacity, i.e. with equal charges on the metal and the solution facing each other at a constant distance. Gouy²⁷ took into account the fact that there must be an equilibrium between the electrical forces which are responsible for the existence of the double-layer and the thermal or osmotic forces tending to maintain homogeneity of the ions. This representation is usually called the "diffuse double-layer" model. Chapman²⁸ extended Gouy's model of the double-layer by introducing Poisson's equation and Boltzmann's law to evaluate the distribution of ions in the diffuse double-layer and the corresponding variation of electrical potential. His calculations were similar to those made later by Debye and Hückel to determine the distribution of ions in the ionic atmosphere around a given ion in solution. The Gouy-Chapman theory

leads, however, to erroneous values of the double-layer capacity.

The next development was due to Stern²⁹ who took into account the possibility that the ions (a) have finite size and (b) that the ions may or may not be chemisorbed (or 'specifically' adsorbed) at the interface. The first layer of ions is regarded as being adsorbed directly at the metal and thus constitutes a layer analogous to that suggested by Helmholtz. Beyond this layer, the ions were regarded as diffusely distributed. Grahame³⁰ examined at length the consequences of the Stern model and considered specifically the effects of taking into account the different degrees of solvation of anions and cations in the double-layer. The following picture of the double-layer has emerged from Grahame's work on the metal-electrolyte interface.

(a) The metallic phase at potential ϕ_m bears a net electrical charge q_M which has a well-defined thermodynamic significance and can be measured absolutely.

(b) The closeness of approach of ions in the solution to the metal is determined by whether or not their hydration shells can be displaced or distorted on the side nearest to the metal. Centres of such distorted solvated ions which are regarded as being specifically adsorbed³¹ lie on a 2-dimensional locus called the Inner Helmholtz Plane (I.H.P.) at which the potential is ϕ_1 . Ions which retain their first hydration shells cannot approach the electrode so closely

and the locus of their centres of closest approach is termed the Outer Helmholtz Plane (O.H.P.), or Gouy Plane, at which the potential is ϕ_2 .

(c) The diffuse layer, or the ionic atmosphere conjugate to the charged interface, is bounded by the O.H.P. and extends into the bulk of the solution over a distance related to the Debye-Hückel $1/\kappa$ parameter; it contains non-specifically adsorbed ions which are attracted to the charged metal surface entirely by coulombic forces.

4. Adsorption of neutral molecules from solution:

Competitive adsorption

The above double-layer theories were developed specifically to account for the ionic distribution in the interphase. It is of considerable importance, however, to investigate also the adsorption of neutral molecules in order to obtain information about solvation and orientation effects. Also, since the electrode surface is almost fully covered with water dipoles, it is evident that for each organic molecule adsorbed on the surface, a number of water molecules must be displaced from the interface. This number will depend on the ratio $\times$ of the effective projected area of the organic molecule to that of a water molecule in the interphase.

Such adsorption should always be regarded as a competitive process. Some authors^{32,33} have considered the possibility that water molecules at the interface are grouped

in clusters, so that each cluster behaves as a single entity with respect to displacement by an adsorbate.

Giomini et al.³³ favored a cluster of 5 water molecules, while Parsons³² favored clusters of 3 to 4 water molecules. However, later Parsons³⁴ and other authors^{35,36,37} found increasing evidence for the role of discrete water molecules at the interface. The problem, however, seems not to have been resolved for very large adsorbate ions^{32,33} and the determination of the number of solvent molecules displaced is probably specific to the system under study, depending on the configuration of H₂O molecules in the neighborhood of the adsorbed ions in relation to the metal-solution field.

The form of the adsorption isotherm for competitive adsorption involving molecules of different sizes is an important matter in evaluation of experimental results. This topic will receive special consideration in a later section (p.92) where some original calculations are presented.

E. Theories of Adsorption

Part I: Adsorption Theories based on Dielectric Polarization

1. Introduction

In a series of papers, Gouy²⁷ examined the effect of organic substances on the electrocapillary curve (see Chapter III) for mercury in a solution of a surface-inactive salt such as sodium sulfate. He found, with rare exceptions,

that these substances caused depression of the curve which was greatest in the neighborhood of its maximum, falling off on each side and, in many cases, ultimately becoming zero. He ascribed this behavior to the effect of the electrical field on the adsorption of the added substance, the amount adsorbed being greatest when the electric field at the interface was small and becoming diminished as the field increased in either direction away from the potential of zero charge (p.z.c.).

Principally two types of theories have been advanced to explain quantitatively the adsorption of neutral molecules. In the first are the theories of Frumkin³⁸, Butler⁴⁰ and Macdonald⁴³ based on the macroscopic concept of the energy of the dielectric in the double-layer regarded as a condenser. The second group of theories centres around the idea of orientation of solvent and solute molecules near the interface. These theories were proposed by Watts-Tobin and Mott^{23,47,48}, Macdonald and Barlow⁵⁰ and developed further by Bockris, Devanathan and Müller²⁵.

2. Frumkin's theory

A quantitative theoretical treatment of adsorption of organic substances at Hg was first given by Frumkin³⁸ who considered the energy change of the double-layer when adsorption of a molecule occurs. The capacity of an element of double-layer of area S changes from the value C per unit area appropriate to the base solution to a value C' appropriate

to the electrode saturated with the adsorbed material. The energy change is (cf. ref.³⁹)

$$\Delta \bar{G}^0 = \Delta G^0 + \frac{1}{2} \phi_m^2 (C - C') S + \phi_m (\mu/\ell - \mu'/\ell') \quad (1)$$

where ϕ_m is the potential drop across the inner region of the double-layer of thickness ℓ in the absence of the adsorbate, and ℓ' in its presence; μ is the component of the dipole moment of the double-layer element normal to the electrode surface in the absence of adsorbate and μ' is the same quantity when the element is filled with adsorbate. The second term of the r.h.s. of (1) accounts for the variation of the energy of the interphase due to the smaller dielectric constant and greater breadth of the organic molecule than water when the surface is saturated with the adsorbed substance. The third term is associated with the change in the effective total dipole moment of the species in the interphase due to the adsorption process and consequent replacement of solvent dipoles. The first term, ΔG^0 , is the "chemical" component of free energy of adsorption, i.e. when $\phi_m = 0$. It follows from Equation (1) that $\Delta \bar{G}^0$ has a maximum value when

$$\phi_m = \phi_{m, \max} = - (\mu/\ell - \mu'/\ell') / (C - C') S \quad (2)$$

and the corresponding $\Delta \bar{G}_{\max}^0$ is defined as

$$\Delta \bar{G}_{\max}^0 = \Delta G^0 - (\mu/\ell - \mu'/\ell')^2 / 2 (C - C') S \quad (3)$$

so that equation (1) can be written in terms of directly measurable quantities, viz

$$\Delta \bar{G}_{\max}^0 = \Delta \bar{G}^0 - \frac{1}{2} (C - C') S (\phi_m - \phi_{m,\max})^2 \quad (4)$$

which is analogous to the relation derived by Butler.

In terms of charge q_M on the metal, Parsons³⁹ wrote equation (4) as

$$\Delta \bar{G}_{\max}^0 = \Delta \bar{G}^0 - \frac{1}{2} q_M^2 (1/C' - 1/C) - 4\pi q_M (\mu/\epsilon - \mu'/\epsilon') \quad (5)$$

where ϵ and ϵ' are the dielectric constants in the presence and absence of adsorbate.

In Frumkin's model, as the author himself pointed out, the change of capacitance from C to C' may arise as a result of changes of either the polarizability of the dielectric or the thickness of the condenser, or both.

3. Butler's theory

A different and more realistic treatment of adsorption of organic substances was given by Butler⁴⁰ who considered the distribution of solvent and organic solute in the field of the electrode. A quantity of solute is assumed to be brought up to the double layer where the field is F and a corresponding volume of solvent is displaced. The work, W , done in transferring an element of volume δv of the solute against an electric field F to displace an equivalent volume of solvent S at the interface is

$$W = -\frac{1}{2} (\alpha_A - \alpha_S) F^2 \delta v \quad (6)$$

W is then introduced into a Boltzmann distribution equation so that the extent of adsorption Γ is related to the field by

$$\Gamma = \Gamma_0 \exp \left\{ \frac{1}{2}(\alpha_A - \alpha_S)\delta v F^2 / kT \right\} \quad (7)$$

where Γ_0 represents the surface excess when $F = 0$, and α_A and α_S are the polarizabilities of the solute and solvent, respectively.

It is then assumed that $\Delta\gamma$ and $\Delta\gamma_0$, the depressions of surface tension when the fields due to excess charge at the surface are F and zero respectively, are proportional to Γ and Γ_0 , so that eqn. (7) becomes

$$\Delta\gamma = \Delta\gamma_0 \exp \left\{ \frac{1}{2}(\alpha_A - \alpha_S)\delta v F^2 / kT \right\} \quad (8)$$

In addition, the molecules may have polarization P per unit volume in the absence of an electric field arising from orientation of their dipoles at the surface; then the additional work of adsorption per unit volume of solute molecules replacing unit volume of solvent is $(P_A - P_S)$ so that eqn. (8) can be written as

$$\Delta\gamma = \Delta\gamma_0 \exp \left\{ \frac{1}{2}(\alpha_A - \alpha_S)\delta v F^2 / kT + (P_A - P_S)\delta v F / kT \right\} \quad (9)$$

Butler found satisfactory agreement between experimental and the theoretically calculated values of $\Delta\gamma$ for many organic compounds. However, the theory has been criticized⁵⁴ on the grounds that bulk dielectric constants are

used for interface calculations. The treatment of Butler was further improved by Lorenz and Möckel⁴¹ who took into account dielectric saturation in the interphase.

4. Theory of Macdonald

Based on the experimental capacitance data of NaF obtained by Grahame⁴², Macdonald developed⁴³ a theory of the electrical double-layer in which three main one-dimensional regions were considered along a distance coordinate d . An ideal polarized metallic electrode is placed at a position defined as $d=0$. Next to the electrode there is a charge-free layer extending to a distance $d=d_0$. Finally, polar material containing univalent positive and negative ions extends from $d=d_0$ to $d=\infty$. The dielectric constants in the two layers may be different and depend on electric field strength and position. Since the thickness d_0 of the charge-free layer may be a function of electric field strength, the theory of Macdonald included effects of high-field dielectric saturation in the double-layer and also the high-field compression in the inner layer which increases as the polarizing potential is increased.

The following expression for the differential capacitance of the electrical double-layer was obtained:

$$C_T^d = C_1^0 \left[\left(\frac{\kappa_1^0}{\kappa_1} + \frac{\epsilon_1^0}{\epsilon_1} \right) \left(\frac{z_0}{z_0^0} \right)^2 - \frac{\epsilon_1^0}{\epsilon_1} \left(\frac{z_0}{z_0^0} \right) + \gamma X_2^* (\sinh \phi_2^*)^{-1} \right]^{-1} \quad (10)$$

The superscript zero designates the value of a quantity at the p.z.c. (also called the electrocapillary maximum [e.c.m.] potential in other contexts) and potentials (V_0 , the so-called rational potentials³⁰) are

measured from the p.z.c. The subscripts 1 and 2 identify quantities defined in the charge-free and diffuse-layer, respectively. κ_1 is the differential dielectric constant and refers to any dielectric saturation effects arising at high fields, ϵ_1 is the static dielectric constant and z is a normalized distance, X^* and ϕ^* are the normalized field strength and potential, respectively; $\gamma = C_1^0/C_2^0$, where C is the capacity.

In this theory, calculation of C_T^d is not straightforward, even when all the constants are known, because of implicit relations between the variables. Taking $\kappa_1^0 = 14$, Macdonald found good agreement between the experimental and theoretically calculated values of C_T^d , particularly at negative potentials. Later²⁵, the value of dielectric constant for the charge-free region was taken as 6 (cf. ref.⁴⁴).

E. Theories of Adsorption

Part II: Molecular Theory of Water Orientation and Displacement

1. Theory of Watts-Tobin and Mott

Following the treatment of Macdonald⁴³, Watts-Tobin and Mott in a series of publications^{23,47,48} proposed a basis for explaining the sharp increase of capacitance at potentials positive to the p.z.c. Slightly on the anodic side of the electrocapillary maximum (e.c.m.) there is a hump in most capacity vs. potential curves. Watts-Tobin²³

suggested that the hump may be due to increase in the effective dielectric constant of the layer, marking the point where the average dipole moment of the water in the layer becomes reversed. This appeared²³ reasonable because at 300°K the field required to provide an energy of the oriented dipole equal to kT is $6.6 \times 10^6 \text{ V cm}^{-1}$ which is less than the applied field ($>10^7 \text{ V cm}^{-1}$). The water molecules probably lie²³ in contact with the metal and it was thought that the ions could partially shed off their primary hydration shell because of high field near the interface. On the basis of Kemball's work⁴⁵ on heat of adsorption of water molecules from the vapor at a mercury surface, Watts-Tobin suggested that water molecules form a close-packed monolayer on mercury and are only slightly affected by the presence of bulk water.

Conway et al.⁴⁶ showed that the dielectric constant of water rises rapidly on moving from the metal through the O.H.P. so that water molecules near the metal cannot be treated as a dielectric continuum. Polarization due to orientation of water also extends⁴⁸ beyond the layer of molecules in contact with the metal due to H-bonding with the innermost layer.

Mott and Watts-Tobin⁴⁷ deduced a relationship between the charge on the metal (q_M) and the potential drop ($\Delta\phi_m$) across the double layer when a very thin layer of water molecules is on the electrode:

$$q_M = \frac{\kappa_o}{4\pi\ell_o} \phi_m + \frac{N\mu}{\ell_o} \tanh \frac{\mu F}{kT} \quad (11)$$

where κ_o is the dielectric constant of the oriented water molecules, ℓ_o the distance between the metal and the O.H.P., N the number of water molecules per unit area, μ the dipole moment of water and F is the field across the double-layer. The capacitance hump could be reproduced reasonably well with the above $q_M - \phi_m$ relationship.

In order to explain the sharp rise of capacitance curves with potential on the anodic side of the p.z.c., the theory of Watts-Tobin and Mott suggests that mercury atoms are pulled out of the surface by the electric field to form ad-atoms. This was a new idea and was shown by them to be thermodynamically possible. The authors also proposed that adsorption of OH ions occurred at positive charges thus increasing the capacitance under those conditions. However, the latter suggestion has been disproved⁴⁹ on the grounds that the capacitance is unaffected by pH.

2. Theory of Macdonald and Barlow

Almost at the same time as the publication of the theory of Watts-Tobin and Mott, Macdonald and Barlow⁵⁰ improved the earlier theory⁴³ of Macdonald and obtained better agreement between the theoretical and experimental capacitance curves for NaF in water⁴² and KF in methanol⁵¹. The interface

was regarded as an hexagonally close-packed charge-free monolayer of solvent, physically adsorbed on the mercury surface by dipole-image forces. Neglecting association in the monolayer, the inner-layer dielectric constant and its dielectric saturation properties were calculated for three conditions: (a) where dipole image contributions are neglected, (b) where monolayer dipoles are imaged in the mercury electrode only, and (c) where they are additionally imaged in an equipotential plane on the solution side of the interface. All these treatments lead to much smaller dielectric constants than that of the bulk solvent.

The basic capacitance equation was derived as follows. The capacity of the charge-free inner layer is

$$C_1 = dq_M/d\phi_m = (dq_M/dF_1)(dF_1/d\phi_m) \quad (12)$$

where F_1 is the field in the inner-layer and ϕ_m the potential drop across it, and dq_M/dF_1 involves the differential dielectric constant κ_1 . $\phi_m = F_1 d = F d_o t$ where d is the thickness of the inner layer and t is the normalized thickness defined as $t = d/d_o$. Then it can be shown that

$$C_1 = \frac{1}{d_o} \frac{dq_M}{dF_1} \left\{ t \left[1 + \frac{d(\ln t)}{d(\ln F_1)} \right] \right\}^{-1} \quad (13)$$

The authors then derived expressions for the dielectric saturation, electrostriction and compression effects in the inner layer.

3. Theory of Bockris, Devanathan and Müller ("BDM")

These authors used²⁵ the model of Watts-Tobin and Mott and applied it to adsorption of ions and neutral molecules at the charged mercury/aqueous solution interface. Their treatment brought some consistency between a number of experimental facts and enables some properties of the double-layer to be predicted in fair agreement with experiment.

In formulating a model for adsorption of molecules on electrodes, Bockris et al.²⁵ regarded the solvent orientation treated by Watts-Tobin^{23,47,48} as of primary importance. In the latter work, the solvent molecules were regarded as being distributed between two states of orientation in which the dipoles are aligned with or against the field, i.e. in opposite directions. Water molecules having their oxygen ends towards the electrode can be called "down" dipoles designated by $N\downarrow$, and molecules with their hydrogen atoms towards the electrode can be called "up" dipoles, denoted by $N\uparrow$. The populations of the dipoles in "up" and "down" states are dependent (a) on the field and (b) on the mutual lateral interactions between the oriented dipoles²⁵.

The equilibrium between water adsorbed on the electrode in "up" or "down" orientations was derived from kinetic relations for adsorption at equilibrium, giving

$$\frac{\theta\uparrow}{\theta\downarrow} = \frac{k\downarrow}{k\uparrow} = e^{2y} \quad (14)$$

where k 's are the rate constants for "up" and "down" adsorption processes and kTy is the sum of the energies of the dipoles arising from orientation in the field and mutual interactions (note that $(kTy)^\uparrow = - (kTy)^\downarrow$). Hence

$$\frac{\theta^\uparrow - \theta^\downarrow}{\theta^\uparrow + \theta^\downarrow} = \tanh y = \frac{N^\uparrow - N^\downarrow}{N^\uparrow + N^\downarrow} = \frac{N^\uparrow - N^\downarrow}{N_T} \quad (15)$$

where $\theta^\uparrow = \frac{N^\uparrow}{N_T}$, $\theta^\downarrow = \frac{N^\downarrow}{N_T}$ and $N_T = N^\uparrow + N^\downarrow$. (16)

For the "up" water dipole, its energy is

$$kTy = \mu F + Uc \frac{N^\downarrow}{N_T} - Uc \frac{N^\uparrow}{N_T} = - (\text{energy of "down" water}) \quad (17)$$

where c is the coordination number in the interphase, U the lateral interaction energy between a pair of adjacent dipoles and F the electrode field, $-4\pi q_M/\epsilon$. Hence, from equations (15) and (17),

$$\frac{N^\uparrow - N^\downarrow}{N_T} = B = \tanh \left[\frac{\mu F}{kT} - \frac{Uc}{kT} \frac{(N^\uparrow - N^\downarrow)}{N_T} \right] \quad (18)$$

Adsorption of organic molecules at a metal surface covered by solvent dipoles can only occur by displacement of a certain number of solvent molecules previously oriented to an extent B in the field. Thus, if the adsorption of one organic molecule displaces x water molecules, and if there is no lateral interaction ($U = 0$) between the water molecules, then the electrical component of the free energy of adsorption of an average water molecule in the surface is given by

$$G_{w,ads}^o = \left(\frac{N_{\uparrow} - N_{\downarrow}}{N_T} \right) \mu F = B\mu F \quad (19)$$

The free energy of adsorption of organic molecules is given by

$$\begin{aligned} \Delta G_{ads}^o &= \Delta G_{chem}^o + x\Delta G_{w,ads}^o \\ &= \Delta G_{chem}^o + xB\mu F \end{aligned} \quad (20)$$

Then the isotherm obtained²⁵ is

$$\frac{\theta}{(1 - \theta)} = \frac{C_{org}}{C_w} \exp \frac{-\Delta G_{chem}^o}{kT} \exp \left(-x \frac{B\mu F}{kT} \right) \quad (21)^*$$

If the interaction energy amongst the water dipoles is included in the expression for energy of water molecules at the surface, equation (21) is written as

$$\frac{\theta}{(1 - \theta)} = \frac{C_{org}}{C_w} \exp \frac{-\Delta G_{chem}^o}{RT} \exp B \left\{ -x \left(\frac{\mu F}{kT} - \frac{U_c}{kT} \right) \right\} \quad (22)$$

Although in the BDM theory, an attempt was made to develop a molecular picture of adsorption, only qualitative agreement between theory and experiment has hitherto been demonstrated²⁵. Most electrostatic theories predict maximum adsorption at the p.z.c. but experimentally for most neutral molecules the maximum occurs between -2 to -5 $\mu C \text{ cm}^{-2}$.

* If the size factor x is included²⁵ in the term for free energy of displacement of solvent, it should also be included in the configurational term $\theta/1-\theta$ (see p.121).

Frumkin and Damaskin⁵² raised several objection to this theory on the grounds (a) that the distortion polarizability of the water molecules is omitted in the free energy calculations where only orientation polarization is considered and (b) that the increase in the electrical energy of the double-layer due to the substitution of water by organic substance at constant charge is not allowed for. Damaskin⁵³ argued that any theory taking account only of the effect of reorientation of adsorbed solvent dipoles while neglecting the energy change in the double-layer is at variance with thermodynamics. However, support for this theory has been recorded elsewhere^{54,55,37}.

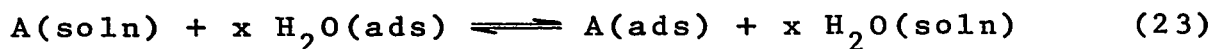
An interesting prediction from the BDM theory is that the capacitance hump is much reduced if lateral interactions (the U term) between the solvent dipoles are taken into account but the agreement between the theoretical predictions and Grahame's capacitance data at positive polarizations was still not very satisfactory.

4. Theory of Bockris, Gileadi and Müller

These authors⁵⁴ improved the BDM theory. They recognized that (a) "up" and "down" dipoles need not be oriented normal to the interface (a conclusion also indicated from the present experimental work); (b) chemical free energies of adsorption need not be equal in the different orientations; and (c) orientation of the adsorbate molecules can be determined by their interaction with the solvent, by

the number of solvent molecules displaced as well as by their interaction with the field in the electric double-layer itself.

Displacement adsorption occurs according to a quasi-chemical equation



From equation (23), when concentrations are expressed in mole fractions, a general adsorption isotherm:

$$f(\theta) = \frac{X_A}{X_S^x} \frac{K_A}{K_S^x} \quad (24)$$

was written where $K_A = \exp(-\Delta G_A^0/RT)$ and $K_S = \exp(-\Delta G_S^0/RT)$ and $f(\theta)$ was taken⁵⁴ as $\frac{\theta}{(1-\theta)^x} \frac{[\theta+x(1-\theta)]^{x-1}}{x^x}$ where x is the relative size of adsorbate and solvent molecules. The validity of choosing $f(\theta)$ in the form shown above is considered in Chapter IV, Section B, Part I. In eqn. (24), ΔG^0 terms are the average standard partial molar free energies of the indicated species in the interphase. The average free energies of solvent molecules in the "up" and "down" positions are considered to be sum of contributions from: (a) interaction of the molecule with its neighbors of like orientation, a term that is proportional to their relative surface coverage; (b) interaction with neighbors of opposite orientation, (c) the field energy of their dipoles which depends on the angle of inclination of the dipole to the field and (d) any field-independent interaction with the interface (i.e. a chemical energy term).

The average free energy ΔG_S^0 for all solvent molecules involving contributions $\Delta G_\downarrow^0$ and $\Delta G_\uparrow^0$ for ψ and $\uparrow$ molecules,

respectively, is given by

$$\Delta G_S^0 = \frac{N_{\uparrow}}{N_T} \Delta G_{\uparrow}^0 + \frac{N_{\downarrow}}{N_T} \Delta G_{\downarrow}^0 \quad (25)$$

where the subscript S refers to solvent and other notations are as defined previously. Bockris et al.⁵⁴ wrote explicit expressions for $\Delta G_{\uparrow}^0$ and $\Delta G_{\downarrow}^0$ in terms of the above four interaction contributions mentioned and examined ways for their calculation.

For the adsorbed solute, any solute-solute interactions are neglected, and the average free energy for a solute in "up" or "down" positions is written in terms of only two contributions, (c) and (d) above. The calculations were carried out by successively introducing the parameters contained in the general equation (24).

The authors showed that the revised theory substantially improved agreement between theoretical and experimental adsorption curves. The main achievement of this theory is that the maximum in the θ - q_M relationship need not occur always at a charge of $q_M = 0$. Bockris et al.⁵⁴ discounted a molecular theory proposed by Devanathan and Tilak⁵⁶, which the later authors claimed gave good agreement between experiment and theory for a number of compounds.

5. Work of Hills and Payne

Hills and Payne⁵⁷ attempted to provide new information on the structure of the double-layer by measuring temperature and pressure coefficients of the electrode capacity

of some salts. Such measurements lead to the surface excess entropy (Γ_s) and surface excess volume (Γ_v) of the interfacial region. Since these quantities are directly related to the properties of the inner layer, they should reveal valuable information on double-layer structure. Γ_s and Γ_v are given by

$$\left(\frac{\partial \Gamma_v}{\partial q_M}\right)_{T,\mu,P} = \left(\frac{\partial E}{\partial P}\right)_{T,\mu,q_M} \quad (26)$$

and

$$\left(\frac{\partial \Gamma_s}{\partial q_M}\right)_{T,\mu,P} = - \left(\frac{\partial E}{\partial T}\right)_{P,\mu,q_M} \quad (27)$$

where E is the electrochemical potential of the adsorbent measured against a reference electrode.

Evaluation of Γ_s and Γ_v calls for supporting information (e.g. partial molar entropies and volumes, and reversible electrode potentials) than is currently available, particularly for neutral molecules.

Hills and Payne found that Γ_v and Γ_s changed substantially with increasing anodic polarization where anion adsorption occurs. At cathodic polarizations, where specific adsorption of metal cations is usually negligible, Γ_v and Γ_s values are insensitive to q_M which suggests that the properties of water in the interphase are not varying significantly over the range $q_M = -5$ to $q_M = -20 \mu C \text{ cm}^{-2}$.

F. Choice of Adsorbate Molecules

Many types of molecules have been used in adsorption studies at electrode/solution interfaces. Shape, size and functionality of the molecules are among the important factors determining the choice of a particular adsorbate in order that a specific aspect of an interfacial phenomenon can be studied or a theoretical deduction verified.

Linear aliphatic molecules such as butyl alcohol⁵⁸ and valeronitrile⁵⁸, having hydrophobic and hydrophilic ends, adsorb with their hydrophobic (hydrocarbon) end towards the metal surface while the hydrophilic function tends to lie away from the surface thus maximizing hydrogen-bonding with solvent molecules. Butyl, phenyl and naphthyl compounds having different functional groups, e.g., OH, CHO, COOH, CN, SH, CO, NH_3^+ , SO_3^- all show⁵⁸ different adsorbability depending on metal-adsorbate and solution-adsorbate interactions. Aromatic-type molecules such as pyridine^{59,60} which have a completely different shape from most aliphatic molecules and a dipole moment associated with the whole ring structure of the molecule (in butyl alcohol, the dipole moment can be regarded as located in the functional group only) adsorb differently; pyridine, for example, shows a change of orientation with charge on the metal. On the other hand, studies of the adsorption of pyrazine³⁷ which is a symmetrical molecule without any net dipole moment, can reveal valuable information

on interactions among the solvent dipoles and, through the symmetrical $\Delta G_{\text{ads}}^{\circ} - q_M$ relationship, provide a more critical test of the adsorption theories, as will be demonstrated below.

Adsorption of thiourea⁶¹ and thiocyanate anions⁶², NCS^- , at the mercury electrolyte interface show peculiarities on the positive branch that have been attributed to short range interaction of the S atom with the mercury surface, leading to strong chemisorption.

Aromatic amines^{59,63} are thought to adsorb on the mercury surface through π -bond adsorbate-metal interaction forces.

Studies of 5-membered saturated and unsaturated ring compounds have been made⁵⁵ and the results were shown to support the BDM theory²⁵ of adsorption.

In the literature, there is a paucity of adsorption studies and evaluations of the various adsorption parameters with respect to the relative size of adsorbate and solvent, though the importance of taking into account the ratio of size of adsorbate and solvent molecules has been recognized^{36,64}. Conway and Gordon^{36,60} examined the effect of taking into account relative size in calculations of free energy of adsorption of pyridine at Hg. It is on this aspect of organic molecule adsorption that the main emphasis has been placed with regard to the choice of molecules investigated in the present work.

Specific reasons for choice of molecules employed here will be stated in a later section (see Results, Chapter III).

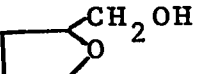
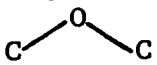
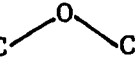
G. Orientation of Adsorbate Molecules

While solvent molecules are considered to be oriented in the "up" or "down" direction according to the charge in the electrode surface, little consideration has hitherto been given to the question of orientation of the adsorbate. Butanol and valeronitrile⁵⁸ have been regarded (perhaps improbably) as adsorbing always with their polar group outside the intense inner layer field. In the case of pyridine^{36,59} the molecule is adsorbed much more strongly on the negatively charged electrode surface than on the positive one, an effect that has been attributed to preferential interaction⁵⁹ of the nitrogen end of the adsorbed molecule with the water solvent when the molecule is oriented with the hydrophilic N atom away from the mercury surface, i.e., when the latter is negatively charged.

Conway and co-workers^{59,60,65} related the sudden changes of potential of zero charge ($\Delta E_{p.z.c.}$) observed in studies of pyridine adsorption with increasing surface concentration (Γ) of the adsorbate, with the orientation of pyridine molecules.

In the case of ' π -excessive' aromatic-type molecules, it has been concluded that they tend to lie flat on the Hg surface - on the negative branch, due to ordinary electrostatic polarization effects and on the positive branch, due to π -orbital interaction with the positive mercury surface. For saturated six-membered heterocyclic compounds, e.g.,

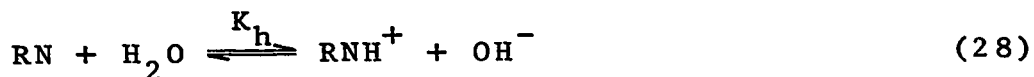
dioxane, morpholine and piperidine, no significant orientation effects have been noticed⁶⁵, because of the similarity of the projected molecular areas of the four possible orientational configurations.

Barradas and Sedlak⁵⁵ examined adsorption of tetrahydrofurfuryl alcohol (THFA),  on the Hg electrode surface. They concluded that the molecule adsorbs sideways with the OH group away from the electrode, so that the  segments of two adsorbed THFA molecules can overlap two H atoms of an adsorbed water molecule. This arrangement was thought to be stabilized by the presence of hydrated SO_4^{--} ions from the supporting electrolyte. These conclusions were based on the Γ - q_M relationships for the furan derivatives, whose breadth they qualitatively connected with the U_c/kT term, the energy parameter for interactions between adjacent water dipoles (actually in their paper⁵⁵ they wrongly associated this term with the interaction energy between adsorbate molecules). Their assumed orientation of THFA is favored by overlap of OH dipoles with the  end of the molecule; this is only possible when q_M is positive, i.e., when most of the water molecules have their hydrogen atoms oriented away from the electrode. At negative polarizations, therefore, the supposed orientation of THFA is not possible.

H. Adsorption and Ionization

1. Hydration of adsorbate

Organic bases (RN) in solution become ionized to some extent because of the reaction



but the adsorbate species in neutral or alkaline solvent will be predominantly RN depending on the extent of hydrolysis.

The hydrolysis constant, K_h , is

$$K_h = \frac{[\text{RNH}^+][\text{OH}^-]}{[\text{RN}]} = \frac{K_w}{K_a} \quad (29)$$

where K_w is the ionic product of water and K_a the acid dissociation constant of RNH^+ . For weak bases such as pyridine and pyrazine having $\text{p}K_a \approx 5$, K_h is negligible ($\approx 10^{-8}$). However, for strong bases, the pH of the solution has to be adjusted to minimize ionization. For reaction (28)

$$\frac{\alpha_h^2 C}{(1-\alpha_h)} = K_h \quad (30)$$

where α_h is the fraction of the base dissociated and C its concentration. If OH^- ion is present in excess of that arising from reaction (28) alone,

$$\frac{\alpha_h [\text{OH}^-]}{(1-\alpha_h)} = K_h \quad (31)$$

If K_h is known from eqn. (29), it is readily found that in added inorganic base, α_h becomes entirely negligible.

Blomgren and Bockris⁶³ gave a thermodynamic analysis for adsorption from ionized base systems and showed that the measured surface excess Γ_A must necessarily refer to the sum of Γ 's for the ammonium-type ion, RNH^+ , and the neutral base, RN , so that the apparent surface excess measured is

$$\left(\frac{\partial \gamma}{\partial \mu_{\text{RN}}}\right)_{q_M} = - (\Gamma_{\text{RNH}^+} + \Gamma_{\text{RN}}) \quad (32)$$

However, as shown above, in basic solution $C_{\text{RN}} \gg C_{\text{RNH}^+}$ so that the total surface excess determined is practically identical with that, Γ_{RN} , due to the organic base itself. In acid solution, the reverse is true. In the case of quaternary ammonium salts, no ambiguity, of course, is involved in Γ since no proton equilibrium arises.

Conway and Barradas⁵⁹ considered in detail the role of hydration in adsorption of organic bases by comparing the free energies of adsorption of N-compounds in the predominantly neutral or predominantly ionized cationic forms.

CHAPTER II

EXPERIMENTAL

Part I: Adsorption at Mercury

A. Apparatus Assembly

1. Adsorption measurements by capillary electrometry

Adsorption of organic neutral molecules and organic cations was studied by determination of the surface tension, γ , of mercury using a capillary electrometer with recently described^{66,67} improvements of technique. Experimentally, in the electrocapillary technique, the interfacial tension between a mercury electrode and an electrolyte is measured at various electrode potentials E . A mercury-solution interface is established in a fine, tapering capillary and by means of controlled external pressure, the meniscus is brought to a fiducial mark towards the end of the tube ca. 1 mm from the bulk solution into which the tip dips. Variation of potential and concentration cause changes of γ so that a varying pressure P is required to force the meniscus to the fiducial mark. These pressure changes are measured and converted to surface tension values using the relation

$$k_c \gamma = P \quad (33)$$

where k_c is the capillary constant determined in calibration measurements of surface tension of a known interface (Hg/aq.KCl).

By applying the Gibbs adsorption equation to surface tension measurements as a function of E and solute activity a , the surface excess Γ of the additive can be evaluated from the following equation³⁰

$$\Gamma_E = - \left(\frac{\partial \gamma}{RT \partial \ln a} \right)_E \quad (34)$$

When Γ is to be evaluated as a function of charge q_M on the metal, the thermodynamic equation is

$$\Gamma_q = - \left(\frac{\partial \xi}{RT \partial \ln a} \right)_{q_M} \quad (35)$$

where⁶⁹

$$\xi = \gamma + q_M E \quad \text{and} \quad q_M = - \left(\frac{\partial \gamma}{\partial E} \right)_a \quad (36)$$

the Lippman relation³⁰.

2. Location of meniscus in the capillary

The lower meniscus of a column of mercury supported in a fine capillary is adjusted in the usual way^{59,70} to a fiducial position by means of a gas line containing an accurate pressure regulator and communicating to the upper meniscus of the column of mercury (Fig. 1) and to one side of a 1-inch diameter thermostatted U-tube manometer. Final adjustment is made by the procedure of Parsons and Joshi⁷¹ by manipulating a screw-operated copper bellows connected by glass-metal seals to the gas line.

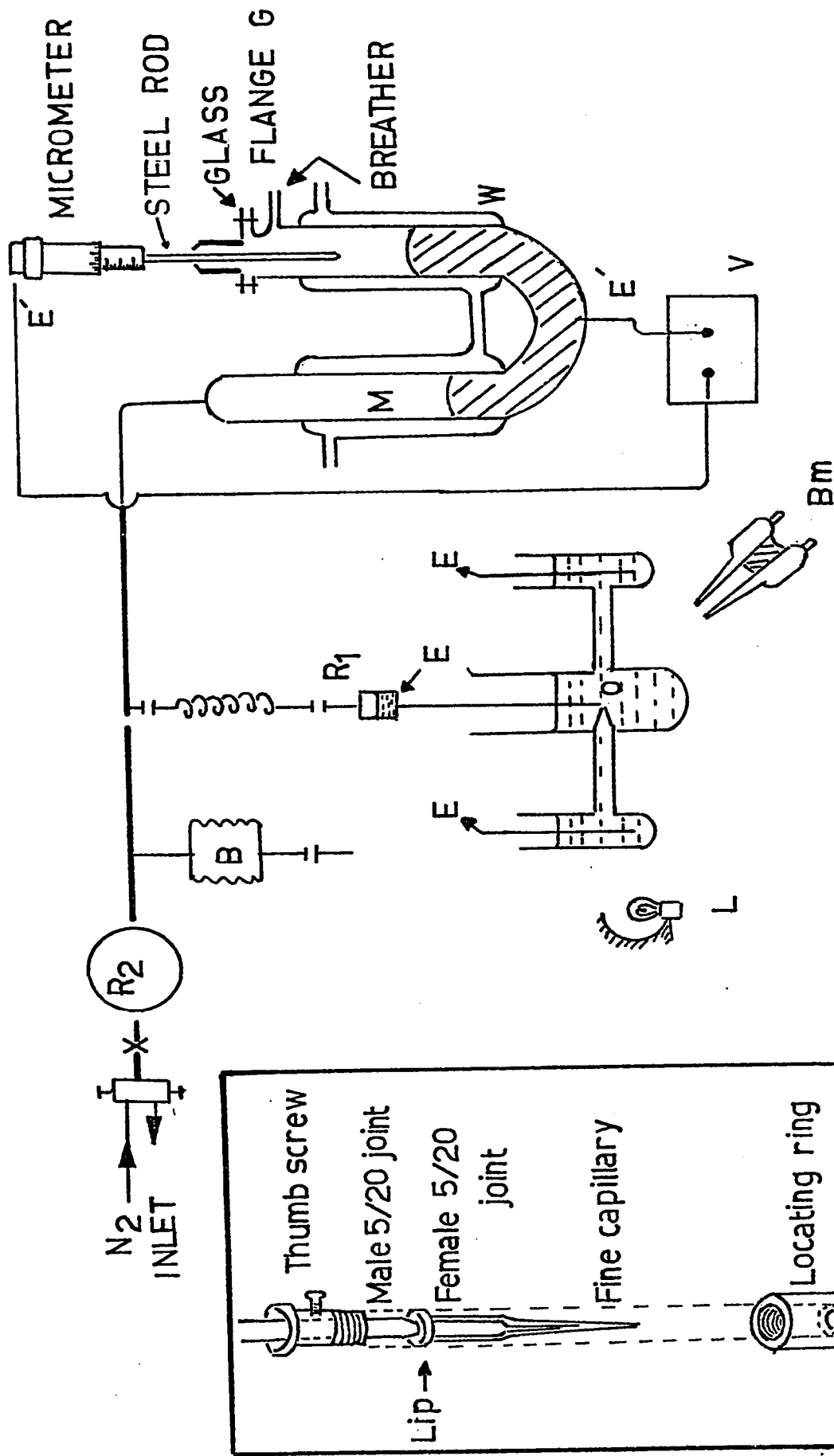


Fig. 1 Schematic diagram of apparatus. E, electrode connections; E', electrical contacts; W, water jacket; M, manometer; Bm, binocular microscope; O, capillary (see inset); L, lamp; B, bellows; R₁, Hg reservoir; V, voltmeter; ohmyst.

Further improvement⁶⁷ in the technique includes use of a small television camera which views the meniscus down one lens of a binocular zoom stereo-microscope and communicates the scanned image to a 25" t.v. monitor screen. The second lens of the microscope can be conveniently used to line up the optics of the system. The general layout of the television assembly is shown in Fig. 2.

The capillary and mercury thread are illuminated from the side by means of a microscope lamp having a 100W bulb and adjustable mirrors. The Hg thread can be made to appear as a clear dark image on a bright background or vice versa. The fiducial mark is fixed on the outside of the monitor screen to provide a reference point for the lowest level to which the mercury is brought in each measurement. The magnification is such that the full width of a very thin capillary appears as a 15 cm image in the screen and the mercury thread itself is seen as an image approximately 5 mm wide.

The electrical circuit comprises the usual d.c. polarization arrangement⁶⁶ using a helipot potential divider and a Radiometer pH-millivoltmeter for measurement of the potential of the mercury electrode with respect to that of a standard reference electrode in a third compartment of the cell.

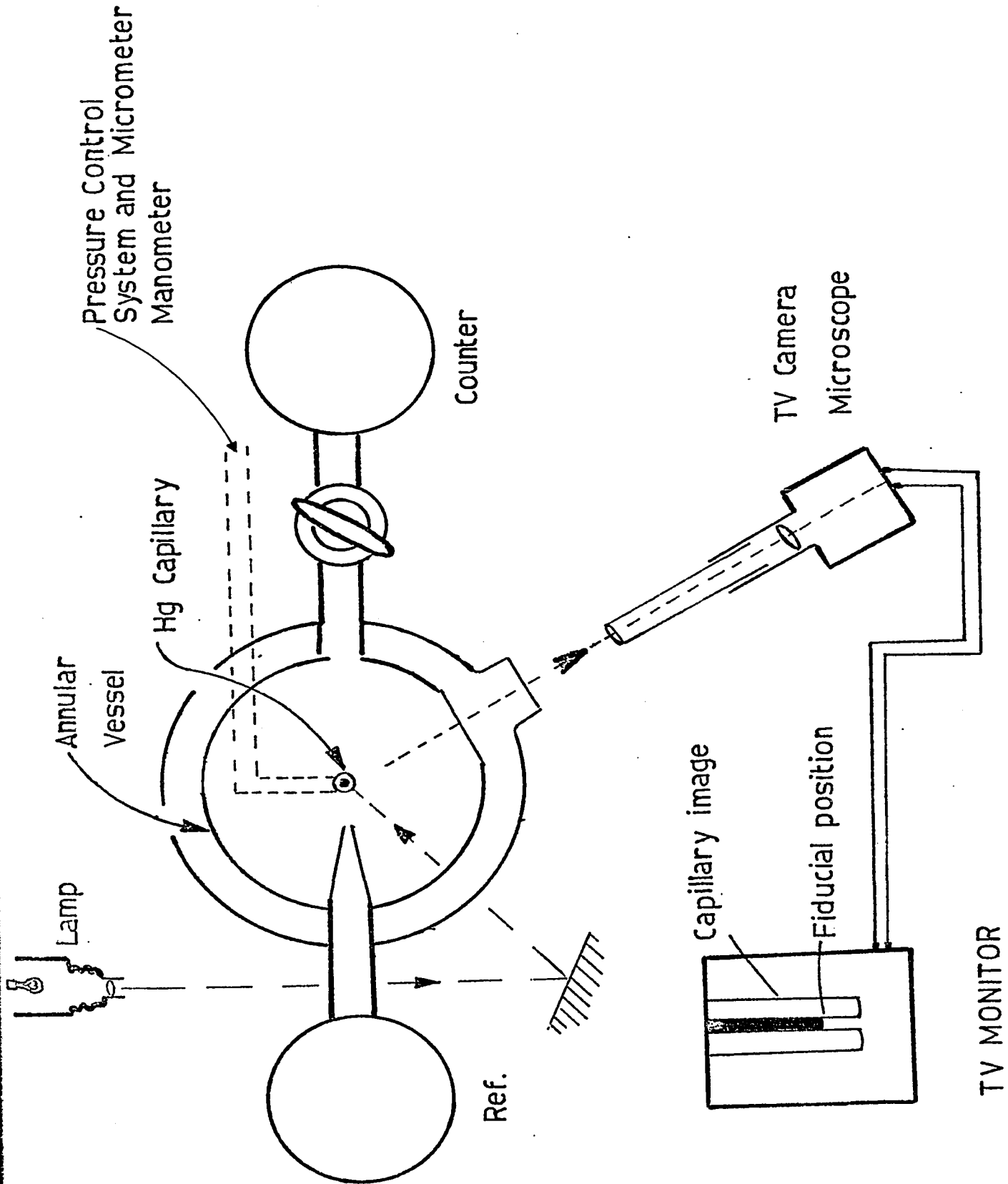


Fig. 2 Schematic drawing of T.V. microscope and illumination arrangement for electrocapillary measurements by the method of determining excess pressures.

3. Excess pressure measurements

The surface tension of mercury at the interphase is obtained from accurate pressure measurements made in the following way. The U-tube manometer is provided with a thermostatted water jacket, W, on each side and a $2\frac{1}{2}$ -inch glass flange (Fig. 1) at one of the ends. The other side of the manometer was connected in the usual way to the gas pressure and metal bellows assembly, and to the upper end of the capillary electrode by means of a flange seal joined to the glass-metal seal. The flange, G, was connected with metal clamps to a brass head in which was fixed a single-ended micrometer capable of measuring a displacement of 0.001 cm, with a 5 cm traverse. The shaft of the micrometer was securely connected to a 1/4-inch diameter stainless-steel rod machined to a sharp 60° -bevel at the end. Adjustment of the micrometer allowed the point of the bevel to be brought into contact with the mercury meniscus in the manometer tube, a condition which could be exactly indicated by completion of an electrical circuit through the mercury, the micrometer and its shaft, and 1.2 V battery operating through 100 K Ω resistance. Contact was shown by a sudden deflection of the needle of a "Volt-Ohmyst" multirange meter included in the circuit.

4. Capillary design

Pyrex capillary tubing 0.5 or 1 mm in diameter was first thoroughly cleaned for at least 12 h. in potassium

dichromate and concentrated sulphuric acid mixture and washed with conductivity water for an equally long period of time. The capillary was constructed from these cleaned tubes on a trial and error basis until one of diameter 0.002 to 0.004 cm with a tapering end approximately 2 cm in length is obtained. The drawn capillary is annealed in a low temperature, yellow flame for a minute. The capillary was then attached to a short piece of glass joint (5/20) which could be attached to the main reservoir of mercury. It was necessary that the final length of the tube from this joint to the tip of the capillary be of fixed length (18 cm), within ± 1 cm, so that the tip could be seen through the cell-window. The tip is cut with a very sharp glass knife so that microscopic jaggedness is avoided. The final capillary, at the fiducial position, should be able to support a pressure of 50 to 60 cm of mercury. The capillary is joined to the reservoir by means of a teflon sleeve and collar provided with a screw thread to maintain a tight seal. This is shown in the inset of Fig. 1. The mercury reservoir is a thermostatted 50 ml cylindrical flask sealed to the column tube below and to a flange above through a glass-metal seal.

After satisfactory construction, the capillary tip was always kept immersed in doubly-distilled water or in a dilute electrolyte solution.

5. Calibration of the capillary

The tip of the capillary was immersed in distilled water for 4 to 5 days before using it as an electrode. It was then calibrated at room temperature at a fixed point towards the end using 1N aq. KCl solution with respect to which Hg has a surface tension of $424.2 \text{ dyne cm}^{-1}$. The calibration was based on the following relationship⁶⁸ (cf. eqn. 33)

$$\frac{2\gamma}{r} \cos\theta = P \quad (37)$$

where r is the radius of the capillary at the fiducial point, θ is the contact angle of mercury with the capillary wall. θ is zero when there is complete wetting of the wall at the interface. When θ is 0° or 180° , or when θ is constant,

$$\frac{2\gamma}{r} \cos\theta = \text{constant} = k_c \gamma$$

Thus, eqn. (37) becomes the same as eqn. (33). Once k_c for a given capillary is determined, pressure data for any mercury-solution interface can be converted easily to surface tension values, assuming, in the usual way, that θ remains 180° .

It is generally assumed^{52,119} that the contact angle between mercury and the glass capillary electrode remains constant with respect to potential at the Hg/solution interface. Measurements of surface tension at liquid metal/solution interfaces using other procedures, such as the sessile drop method¹²⁰ which is free from uncertainties of contact angle,

have been shown to give results in good agreement with those obtained from electrocapillary measurements at the p.z.c. This is consistent with the fact that data derived from capacitance and electrocapillary measurements are almost in quantitative agreement^{72,73} over a range of electrode potentials and the capacity data do not involve contact angle except in the respect that an integration constant is obtained at one potential, that of the e.c.m. In the case of solid metals, the contact angle between an electrode and solution is known^{52,121} to change somewhat with potential in a manner which resembles an electrocapillary curve.

For experiments at different temperatures, it was assumed that the radius of the capillary changed negligibly so that the same capillary constant could be used at other temperatures as well. An estimate of the error involved in this assumption can be made from knowledge of the coefficient of expansion of glass. Assuming the coefficient of expansion remains the same over the range 5° to 60°C (the temperature range used in the experiments), the ratio of the radii at two temperatures r_{50}/r_5 is found to be equal to 1.0003, i.e. a negligible deviation from unity. The above ratio incurs an error of 0.02 dyne cm⁻¹. Further discussion regarding this point will be given in Section C of this Chapter.

Manometer readings at different temperatures were normalized to 25°C by multiplying the measurements by the ratio of the densities of mercury at the two temperatures before converting the readings to surface tension values.

B. Experimental Conditions

1. Purification of materials

(a) Water: Doubly-distilled water was used throughout the experiments wherever aqueous solutions were employed. However, no difference, in terms of adsorption, was observed between solutions prepared from singly-distilled and doubly-distilled water.

(b) Mercury: Purification was effected as follows: triply distilled, commercial grade mercury was passed first through a pinhole in a filter paper to eliminate any impurities gathered on the surface. The mercury was then passed through a 10% solution of nitric acid in a glass tube one meter in length connected to a narrower tube bent in a U-shape at the bottom. This mercury was then washed several times with water and then mixed with conc. H_2SO_4 in a conical flask through which air was drawn for at least 6 h. The cleaned mercury was finally dried overnight in an atmosphere of nitrogen before being doubly distilled in vacuo.

(c) Sodium Perchlorate: "Purified" (Fisher Scientific) sodium perchlorate monohydrate was dehydrated under vacuum at 110°C for 24 hrs. This salt, in aq. solution, was used as the supporting electrolyte for most adsorption experiments; it was chosen because of the minimal specific adsorption which the ClO_4^- anion exhibits.

(d) Perchloric Acid: BDH analytical reagent grade perchloric acid was used without further purification.

(e) Pyrazine: Pyrazine is a low melting (m.p. 54-56°C) compound which sublimes when left open to the atmosphere. "Puriss" grade pyrazine from Aldrich Chemical Co. was crystallized from 10% solution in 30-60°C petroleum ether. The filtered solution was evaporated at 50°C to 40% of its initial volume in a water bath. The solution was stirred manually to facilitate evaporation of the solvent. The resulting concentrated solution was cooled slowly at room temperature and then in ice-cold water. Well formed transparent crystals were separated by decantation of the mother liquor and dried at room temperature. About 70% of the pyrazine was recovered in this way.

(f) Pyridine: AnalaR pyridine from BDH Ltd was distilled under nitrogen which provided an inert atmosphere so that aerial oxidation was minimized.

(g) Potassium Chloride: 'Analytical Reagent' grade potassium chloride was recrystallized from twice distilled water before using it in solution for standardization of capillaries.

(h) 1,4-Diazabicyclo(2,2,2)octane (DBO): The compound (m.p. 157-159°C) was obtained from Aldrich Chemical Co. A 15% solution was made in 80-100°C range petroleum ether at the boiling point of the solvent. Small needle-shaped crystals

were recovered after cooling in ice-cold water. The mother liquor was decanted off and the product washed with ice-cold petroleum ether before being dried at room temperature under vacuum for ca. 20 minutes. Recovery of the compound was about 80%.

(i) n-Amyl alcohol: Fisher Certified Reagent grade n-amyl alcohol was distilled using a 1.5 ft Vigreux column. The middle fraction of the distillate in the boiling range 136-137°C was used for the adsorption studies. A saturated aq. solution was prepared from which other solutions were prepared by dilution.

(j) Potassium Dihydrogenphosphate: This salt, obtained from Fisher Scientific Co., was used without further purification. 0.3M solutions of the compound provided a buffer electrolyte for the experiments on adsorption of DBO in the singly ionized state.

2. Reference electrodes

The main consideration in choosing a reference electrode was that the liquid junction potential between the electrode and the solution should be a minimum. In some cases, it was possible to completely eliminate the liquid junction potential; in others, care was taken that the liquid junction potential remained constant in each series of experiments.

(a) Calomel electrodes: These electrodes were prepared by covering a mercury surface with a paste of calomel and mercury, and shaking slightly to obtain an even coverage. A sodium or potassium chloride solution of known concentration was then added slowly. When sodium perchlorate was used as the supporting electrolyte, the calomel electrode was made up from Hg, Hg_2Cl_2 and NaCl of strength equal to that of the supporting electrolyte. The electrical contact with the calomel electrode, as in the case of other reference electrodes employed, was made through a solution-wetted 10/30 ground joint to minimize diffusion of ions out of the electrode container. When not in use, the calomel electrodes were stored in aq. solution of the same salt at the same concentration as that inside the electrode.

(b) Mercury-mercuric oxide electrode: In adsorption studies from alkaline solution, the Hg-HgO electrode was employed. The electrode was prepared from a paste of HgO and Hg and the potential-determining electrolyte was the same solution as that employed in the particular adsorption experiments.

3. Counter-electrode

An hydrogen electrode set up at a platinized platinum gauze was used as the counter electrode in all the adsorption studies reported in this thesis. Steady readings were obtained after hydrogen had been passed for only 2 to 3 minutes at fresh

electrodes or for 10 to 20 minutes at older electrodes. The reason for using the Pt/H₂ electrode as a counter electrode was that this provides a non-polarized counter-electrode which maintains a stable potential as the potential of the Hg capillary electrode is varied. The latter is thereby better controlled.

4. Thermostasis

The working and reference electrode compartments of the capillary electrometer cell, the mercury column and the manometer were all double-walled so that thermostatted water could be circulated through the whole system. Above room temperature, temperature could be controlled within $\pm 0.1^{\circ}\text{C}$ and below room temperature to $\pm 0.3^{\circ}\text{C}$.

C. Sources and Estimation of Errors

Sources of error can be grouped into two main classes: (a) those inherent in the experimental set up and (b) those arising in the subsequent reduction of the primary experimental results, e.g., through use of some approximation of the exact theory or through calculations in which curve fitting of the experimental points was an essential step.

1. Inherent error in the experimental measurements

In measuring the pressure changes required to bring the mercury meniscus to the fiducial position, it was necessary

to know the height of the mercury column above the end of the meniscus, and also the manometric height up to the point of the bevel of the steel rod (see Section A.3 of this Chapter), attached to the micrometer screw when it is at the zero position. A cathetometer was used for these purposes. The error of such measurements was within ± 0.003 cm ($\approx \pm 0.02$ dyne cm^{-1}), and arises mainly from the uncertainty in precisely locating the top of the mercury columns. However, since the mercury height remained almost constant for a particular run, and the necessity of changing the steel rod arose only infrequently for a given set of results, errors of this kind remained constant and unidirectional. Since, in standardizing the capillary, similar errors could arise, it was reasonable to expect that no significant error was, in fact, introduced in the evaluation of γ from the pressure measurements themselves.

The most important error in capillary electrometry normally arises in making accurate adjustment of the meniscus in the capillary to the fiducial position*. Such errors were very much reduced in the present technique on account of the observation of the position of the minimum in relation to the end of the capillary in the highly magnified t.v. microscope image. Also, once a suitable position of the fiducial mark in the capillary was found with respect to the electrochemical cell and on the t.v. screen, that position was kept fixed by marking the positions of the cell on the supporting table, the mercury reservoir above the cell and the t.v. camera in all

* Cf. Fig. 2.

the runs for a particular compound. It minimized errors due to uncertainty of the exact location of the capillary end, and any variation in illumination of the capillary producing the image on the t.v. screen. Any such uncertainty was equivalent to an error in γ of within $0.1-0.2 \text{ dyne cm}^{-1}$.

Throughout the work it was observed that a particular fiducial position when used for a long time (2 to 3 months) became either quite sticky to mercury or it was difficult to adjust the meniscus at that position. If such a situation arose, the fiducial position was changed or the capillary was remade. It was also observed, particularly in work over a range of temperatures, that the capillary constant at 25°C for a given fiducial position changed significantly after several runs were performed at different temperatures. This became the main reason for irreproducibility in the work at various temperatures in the early part of this research project. Usually the capillary constant decreased, which was equivalent to an increase in the effective radius. It is unlikely that the radius of the capillary would change with time. The other possibility that mercury atoms could stick on the capillary walls and make them hydrophobic, seemed more reasonable. It is possible that with varying degrees of hydrophobicity of the capillary wall, the contact angle of the mercury-solution interphase could change, and thus explain the change of the capillary constant with time. It was necessary, therefore, to check the capillary constant quite

frequently. Sometimes, when the capillary constant changed significantly, values measured at intermediate concentrations were calculated from the average of two measured capillary constants. Such calculations were then found to be consistent with γ values derived for the entire concentration range studied in the experiment.

The use of the same capillary constant at all temperatures implied, besides assuming constancy of radius (see Chapter II, Section A.5), the assumption of constancy of contact angle. The magnitude of any error from this assumption is unknown, but data from electrocapillary and capacity measurements (which do not involve contact angles) in other work is usually in adequate agreement^{72,73}.

Another source of error was the change of potential of the reference electrode when solution containing an organic substance was used. It was observed that the potential of the reference electrode changed with time; the Hg-HgO electrode was found to be rather more unstable than the calomel electrode. Any change of potential of the reference electrode could shift the electrocapillary curve sideways on the potential scale which could ultimately introduce error in the calculations of the charge on the electrode in relation to potential.

In almost all the measurements, the cell reference electrode was checked against another electrode of the same composition which had not been used for measurements in the solution containing an organic substance. If the difference

of potential between the two electrodes was more than 1 mV, a fresh reference electrode was made.

An electrocapillary curve could be reproduced for all the compounds (except n-amyl alcohol, see below) in the potential range -0.15 to -1.2 V within 0.1 to 0.2 dyne cm^{-1} . The points were found equally reproducible at the extreme ends of the electrocapillary curves as they were at the electrocapillary maximum. For n-amyl alcohol, which adsorbs primarily around the e.c.m., reproducibility of a particular run was within 0.5 dyne cm^{-1} . Provided the capillary constant was checked, an electrocapillary curve could be reproduced even after a few months to within 0.5 dyne cm^{-1} or better.

2. Errors introduced in evaluating results

Evaluation of the surface excess quantities from the surface tension results requires knowledge of the activity coefficients of the solution. For organic compounds, activity coefficient data are not usually available. For all calculations, activity was replaced by the molal concentration with the assumption that the activity coefficients of dilute solutions of the organic compounds (maximum conc. being usually 0.5 molal) are unity. Further discussion of this point will be given in Chapter IV.

Other sources of error can arise in the computation of results. Since a computer program was used (see the following Chapter) for calculations of different parameters,

it was necessary that curve fitting of experimental points was as accurate as possible. In most of the present work, the number of concentrations studied for each compound, at a particular temperature, ranged from 12-18 (about 6 points per decade of concentration change). Special attention was given to obtaining measurements at more closely spaced concentration intervals than had been the case in previous work⁵⁸⁻⁶⁰. This is important in regard to the question of fitting results to various forms of adsorption isotherms. A sufficient number of points was therefore obtained to enable an accurate fit to a polynomial over the experimental points. A fourth-order polynomial was found to provide the best fit for the experimental data. This was judged by comparison between a third-order and a fourth-order fit. Lawrence et al.⁷⁵ mentioned that a third-order polynomial gave best fit for their data but they obtained only 3 points per decade of concentration. The fourth-order fits over some of the present data for a few compounds are shown in Fig. 3. Since only the concentrations at which the maxima occurred in the curves were required (see the next Chapter), the fit of the polynomial was considered very good.

The differences between p.z.c. data evaluated graphically and from best-fit computer calculations were within 2 mV. At extreme positive and negative charges (around $10 \mu\text{C cm}^{-2}$) and for the highest and lowest concentrations, the accuracy of the derived quantities was less than

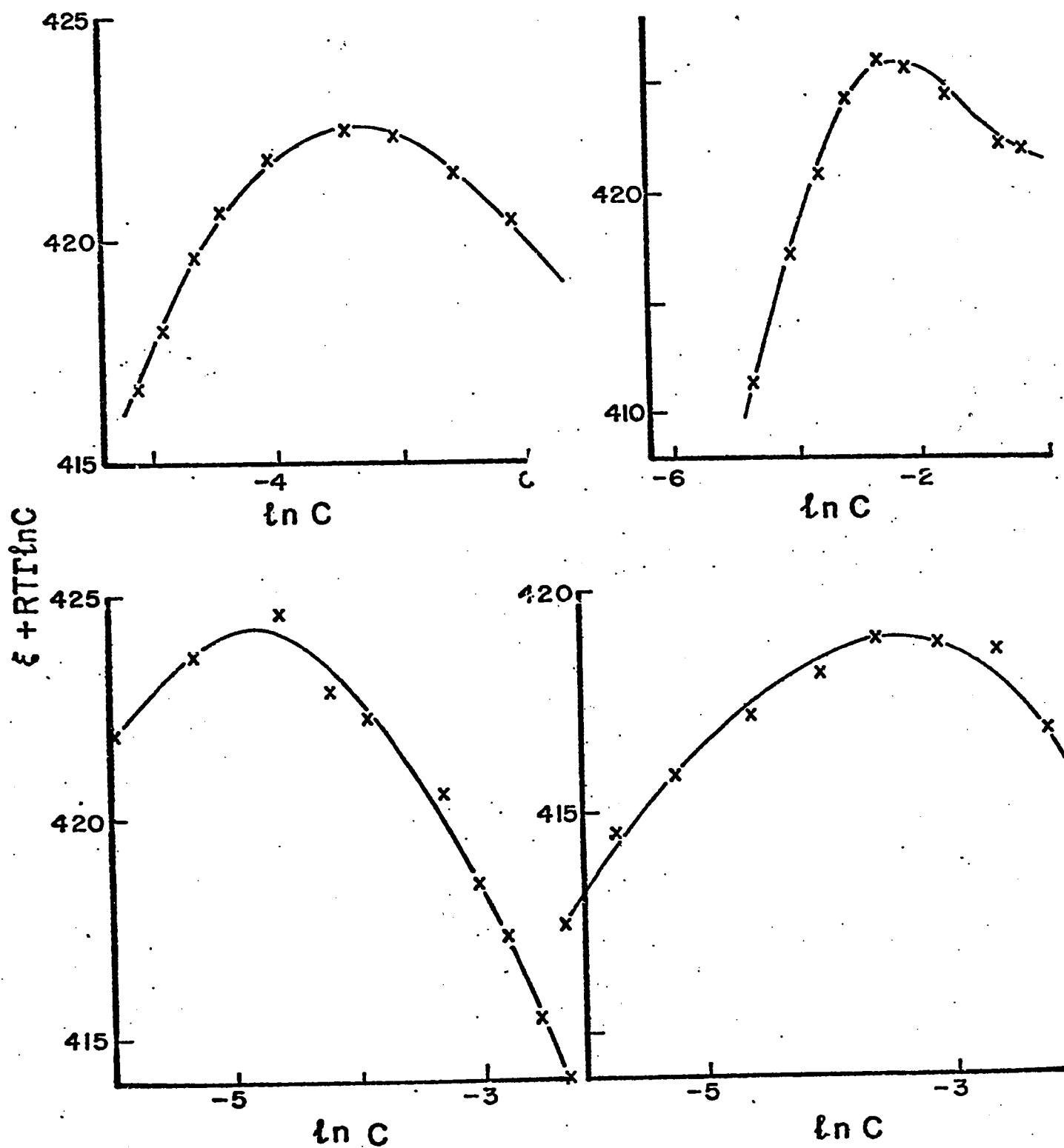


Fig. 3 Plots showing curve-fitting in a 4th order polynomial for different compounds. X's are experimental points, and, —, smooth curves represent best fits through the points (for explanation of the axes see Chapter III).

for the intermediate values. Since, throughout the concentration range, there was a random distribution of errors, the smallest values of Γ would carry the largest percentage errors. Values of Γ below 0.4×10^{-10} mole cm^{-2} were considered unreliable.

Part II: Adsorption at the Air-Water Interface

A. Method for Surface Tension Measurements

Jaeger's method⁷⁶ for determination of surface tension at the air-aqueous solution interface was used. The procedure is based on the formation of air bubbles inside the liquid. When a bubble forms at the end of a capillary tube, the excess pressure P above that of the atmosphere indicated by a manometer is equal to the hydrostatic pressure plus the pressure due to curvature of the drop, i.e.

$$P = \rho gh + \frac{2\gamma}{r} \quad (38)$$

where ρgh is the hydrostatic pressure at a depth h of a liquid of density ρ and $2\gamma/r$ is the pressure inside the spherical air bubble. The experiment consists in finding the minimum pressure at which bubbles will continue to form and detach themselves from the tube. Two tubes of different radii are attached to vertical rods so that they can be moved

up and down a vertical scale. The tubes are attached to the same air reservoir and the heights are adjusted until bubbles slowly detach themselves from both tubes simultaneously.

The surface tension of the liquid is given by

$$\gamma = \frac{r_1 r_2}{2(r_1 - r_2)} \rho g \Delta h \quad (39)$$

where r_1 and r_2 are the radii of the two tubes, Δh the difference of the depths of the ends of the two tubes and other parameters are as defined previously.

The method of Jaeger⁷⁶ is particularly useful for measuring the relative surface tension between two liquids of different densities, ρ_1 and ρ_2 , because in such a case the radii of the tubes do not enter into the mathematical formula since

$$\frac{\gamma_1}{\gamma_2} = \frac{\rho_1 \Delta h_1}{\rho_2 \Delta h_2} \quad (40)$$

If the height Δh_2 of one liquid (usually water) is known from experiment and its surface tension is found from tables, the surface tension γ_1 of another liquid or solution can be calculated from knowledge of Δh_1 .

B. Apparatus and Procedure for Measurements of Δh

The essential details of the apparatus used are given in ref. 76. Capillary tubes of uniform diameter were found suitable for the entire range of concentrations and

temperatures. Two capillary tubes of internal diameter 0.5 mm and 1 mm were chosen. Drawn capillaries with tapering ends were found insensitive to pressure changes.

The minimum pressure for simultaneous appearance of bubbles at the two tubes was measured in a differential manometer (Hg and silicone oil). The rate of bubbling in the wider tube was about one per second. The pressure as shown on the manometer was kept constant in all the measurements, so that when the concentration of the solution was changed, the heights of the capillary tubes had to be adjusted until air bubbles simultaneously appeared in both the tubes at the previously recorded minimum pressure.

Even with a very carefully cut capillary tube, it may be difficult to obtain an exactly plane end. In such cases, and in general, it was considered necessary to keep the orientation of the capillary fixed with respect to the entire experimental set up, otherwise errors due to slight uncertainty of the capillary end position, if it became rotated, would be introduced and the cathetometer readings become erroneous.

The accuracy in the evaluation of γ was estimated to be within 0.3 dyne cm^{-1} .

CHAPTER III

RESULTS

A. Adsorption at Hg-Water Interfaces

1. Computation of primary results

A computer program similar to that outlined by Lawrence et al.⁷⁵, was used to calculate the surface charge density, q_M , relative surface excess, Γ , and surface pressure, ϕ_q , from the experimental surface tension results.

q_M was determined by taking the experimental values of γ at various values of E for a particular electrocapillary curve and then the new variable defined by $y = \gamma + kE$ was computed; k in this equation is a constant. The curve $y = f(E)$ has a maximum at the value of E for which k is the slope of the electrocapillary curve. Thus, differentiating $y = f(E)$,

$$\frac{dy}{dE} = \frac{d\gamma}{dE} + k = 0 \quad \text{at the maximum}$$

or

$$k = \frac{-d\gamma}{dE} = q_M. \quad (41)$$

Thus instead of choosing E and differentiating the electrocapillary curve at that point to obtain q_M , a value of q_M is selected for which E and γ are then determined.

Similarly, at a constant value of q_M , the maximum of the curve $y = \xi + RT\Gamma \ln C$ gives the value of C at a chosen value of Γ , where $\xi = \gamma + q_M E$. Hence Γ vs. C or Γ vs. $\log C$ relations may be computed at different q_M values.

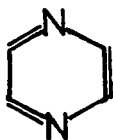
The surface pressure ϕ_q at constant q_M is defined as $\phi_q = \xi_b - \xi$ where the subscript b refers to the quantity for the adsorbate at zero concentration (base solution).

Errors introduced in the computation were discussed in Section C.2 of Chapter II.

2. Adsorption of pyrazine

Pyrazine is a symmetrical heterocyclic conjugated molecule containing two nitrogen atoms at the para positions:

Pyrazine



The electrical and structural symmetry of the molecule, and its rigidity, provides one of the best bases for application and examination of recent representations of adsorption in terms of isotherms^{25,59} for solvent substitution.

The adsorption of this molecule was studied from a supporting electrolyte of 0.03M aq. NaClO_4 solution. Electrocapillary curves based on about 24 points were obtained for this and all other molecules in the potential range -0.1 to -1.2 V. Measurements were made at the following temperatures and molal concentrations: 281, 293, 308, 323 and 338°K; 0.003,

0.006, 0.008, 0.012, 0.020, 0.035, 0.055, 0.090, 0.130, 0.180, 0.250, 0.350, 0.50 m.A 0.03 M NaCl/calomel reference electrode was used in all measurements of potential. In experiments where runs were made at various temperatures both the reference and the capillary electrodes were maintained at the same temperature, thus eliminating any thermal junction potential in the electrolyte.

Typical electrocapillary curves for this compound are shown in Fig. 4. Though it is not easy to interpret the adsorption behavior directly from inspection of the electrocapillary curves, it can be seen in a general way that adsorption of pyrazine is symmetrical around the electrocapillary maxima for various concentrations.

Fig. 5 shows plots of Γ vs. q_M for pyrazine at various bulk concentrations. Quantitative details of these results at different temperatures, and other results for various compounds, are given in tabular form in Appendix I. Closer inspection of the Γ vs. q_M curves in Fig. 5 shows that they are symmetrical around a surface charge of $q_M = -2 \mu\text{C cm}^{-2}$ and, for a given bulk concentration, the surface coverage decreases symmetrically with increasing positive and negative q_M . In terms of the solvent displacement theory of adsorption²⁵ of organic molecules this result implies that water molecules can be most easily displaced from the surface when q_M is near $-2 \mu\text{C cm}^{-2}$, while for charges positive or negative to $q_M = -2 \mu\text{C cm}^{-2}$, water molecules are energetically more difficult

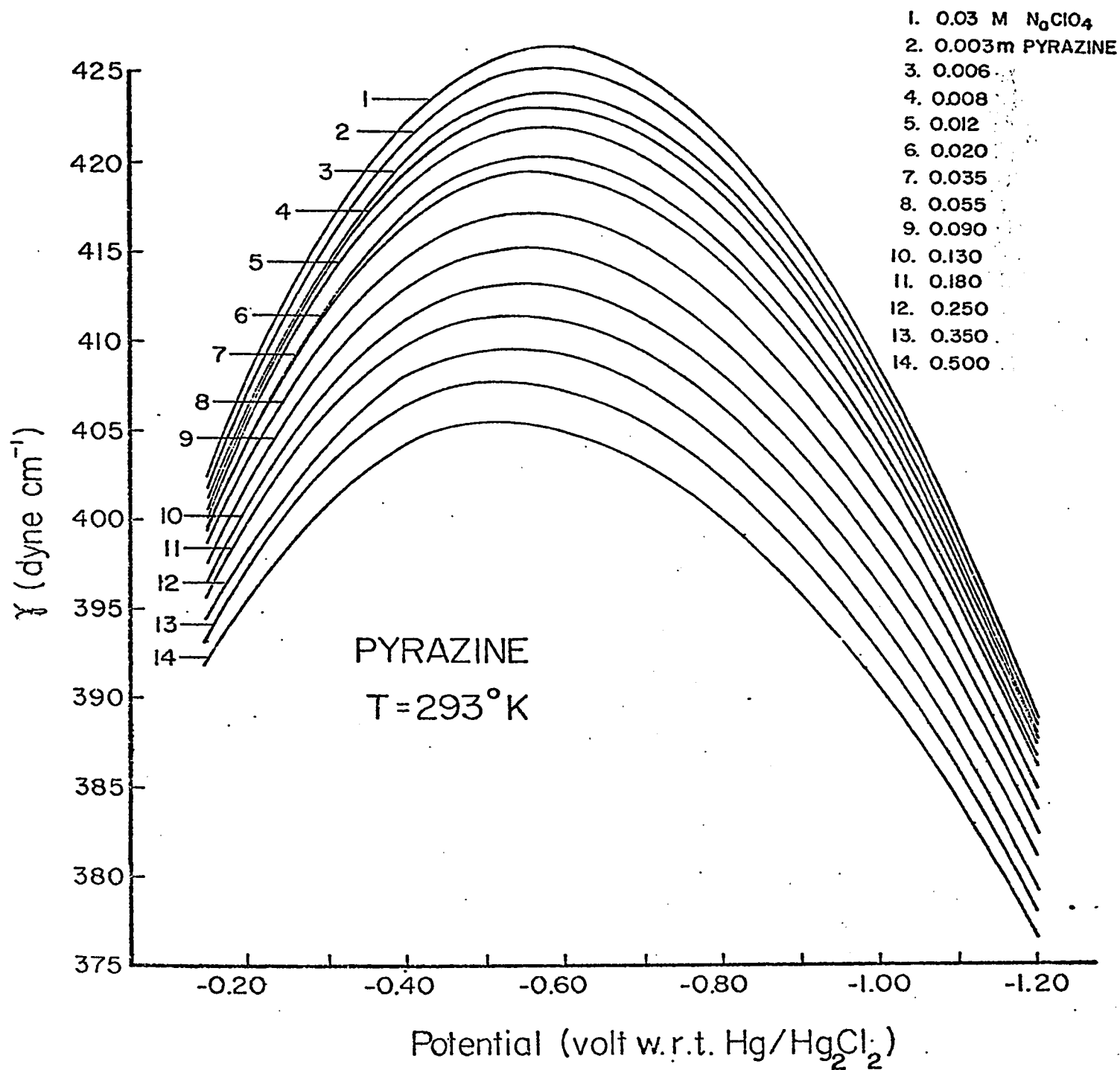


Fig. 4 Electrocapillary curves (based on γ values at 50 mV intervals) for adsorption of pyrazine from aq. 0.03 M NaClO_4 solution. $T = 293^\circ\text{K}$.

PYRAZINE
T = 293° K

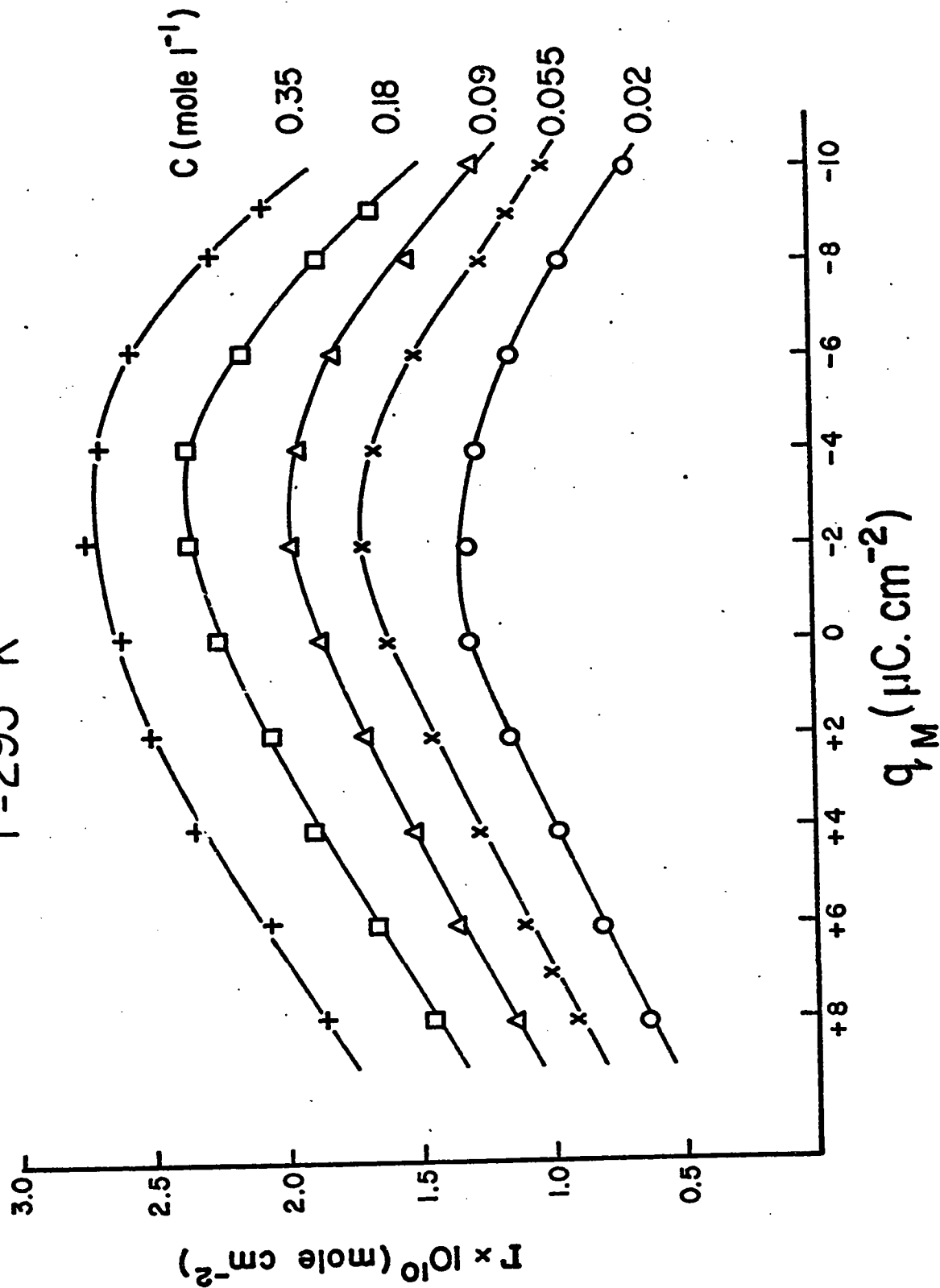


Fig. 5 Plots of Γ versus q_M for various pyrazine bulk concentrations. T = 293°K.

to displace. It is also to be noted that given displacements arise at the same differences of positive and negative charge about $q_M = -2 \mu C \text{ cm}^{-2}$.

Temperature effects in adsorption will be discussed in a later section dealing with evaluation of the free energy, entropy and enthalpy changes in adsorption.

3. Adsorption of pyridine

Electrochemical adsorption of pyridine had been studied in this laboratory^{59,60} previously but the number of concentrations had been limited to 2 to 3 points per decade so that the accuracy of the results was not sufficient for conclusive evaluation of e.g., ΔE_q^* with respect to Γ^{60} . The interesting results previously found indicated that it was necessary to make further studies of this molecule over a larger number of closely spaced concentrations and corresponding coverages. It was anticipated that the new results together with the fact that the molecule has an appreciable net dipole moment, and is virtually identical in size with the non-polar pyrazine molecule would allow a basis for direct comparison of adsorption results for the two molecules, especially with respect to orientation effects.

Pyridine was adsorbed from a supporting electrolyte of 0.03 M NaClO_4 in 0.01 M NaOH solution in order to keep the molecule in the un-ionized form. A Hg-HgO electrode in a solution of 0.03 M NaClO_4 and 0.01 M NaOH was used as the

* ΔE_q is defined (see p.141) as the difference of potentials for a given q_M to be attained in the adsorbate and in supporting electrolyte solutions.

reference electrode. Measurements were made at the following temperatures and molal concentrations: 283, 298, 313 and 328°K; 0.001, 0.002, 0.003, 0.005, 0.009, 0.016, 0.025, 0.040, 0.065, 0.110, 0.170, 0.240, 0.340, 0.460, 0.750 m.

In Fig. 6 are shown the plots of Γ vs. q_M for several bulk concentrations at 283°K. In contrast to the corresponding plot for pyrazine (Fig. 5), Fig. 6 shows that the coverage increases with increasing negative charge, while desorption arises only to a limited extent in the range of surface charge -2 to -8 $\mu\text{C cm}^{-2}$, depending on bulk concentration. Reflectance measurements with pyridine have shown that the molecule desorbs completely and suddenly at high negative potentials³⁷ (-1.8 V) in alkaline solution. The results in Fig. 6 are consistent with the fact that pyridine has a net dipole moment.

The fact that pyridine is more strongly adsorbed at the more negatively charged surface appears to be due to the tendency for the N-end of the molecule (the negative end of its dipole) to be oriented towards the solvent under these conditions where it can become H-bonded with solvent molecules more effectively than when it is oriented in the opposite direction, or lies flat (see p.120) at less negative charges. In the "flat" state, the hydrocarbon ring of the molecule is relatively displaced out of the solvent towards the metal surface (hydrophobic effect).

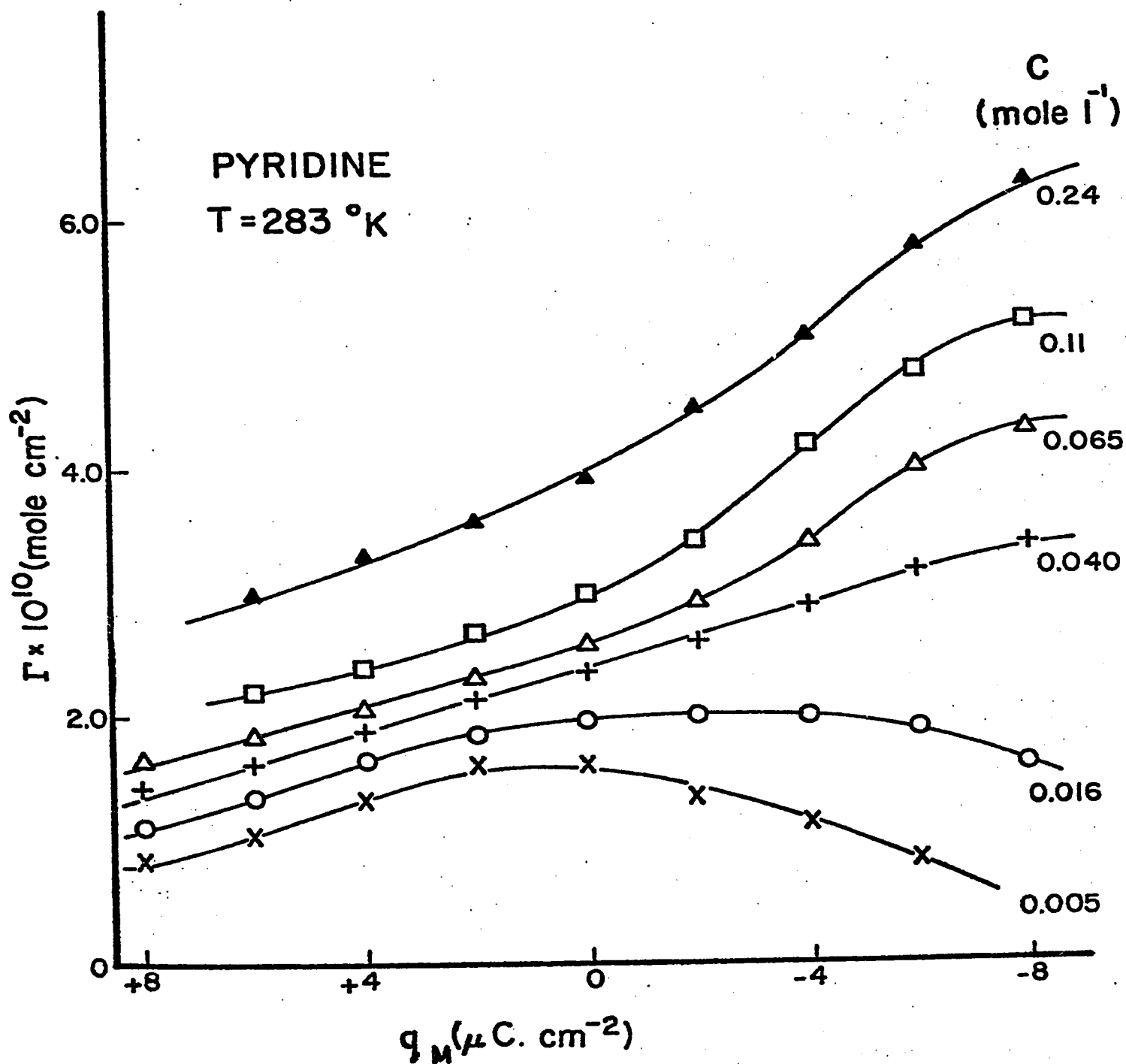


Fig. 6 Plots of Γ versus q_M for various pyridine bulk concentrations.
T = 283°K.

4. Adsorption of n-Amyl alcohol

There have been^{77,78} several previous studies of n-amyl alcohol adsorption at Hg but only at a single temperature. The purpose of the present work on this substance was to evaluate the entropy and enthalpy components of the free energy of adsorption for a molecule that was structurally much different from pyrazine and pyridine. Also the temperature dependence of the Esin and Markov effect (p.154) could be evaluated in relation to solvent orientation and orientation of the OH group.

In the literature, it is reported⁷⁹ that n-amyl alcohol is soluble in water to the extent of 2% (ca. 0.2M) at room temperature. A saturated stock solution of the alcohol in 0.3 M aq. NaClO_4 was made up at a constant temperature of 25°C by shaking the mixture for at least 6 h. Diluted solutions for the adsorption studies were then prepared from the saturated solution. The strength of the saturated solution was determined by means of refractive index measurements using an Abbé refractometer. Solutions at known concentrations, lower than the saturation solubility limit, were made up gravimetrically and their refractive indices determined. By extrapolation to the measurable refractive index of the saturated solution, the exact concentration of the latter could be determined. The molality of the saturated solution thus obtained was found to be 0.19 at 25°C.

Surface tension measurements were recorded at the following temperatures and molal concentrations: 283, 293, 303, 318 and 333°K; 0.0025, 0.0047, 0.0095, 0.0125, 0.019, 0.028, 0.038, 0.047, 0.0617, 0.076, 0.095, 0.124 m. A 0.3 M aq. NaCl/calomel half-cell was used as the reference electrode.

Adsorption of n-amyl alcohol by the electrocapillary technique was found to be dependent on time. Time dependency was also mentioned by Blomgren et al.⁵⁸ for butyl alcohol adsorption. A period of two minutes was allowed for each reading at a given controlled potential. The difference between the readings for 1 and 2 minute periods was less than 0.3% of the maximum surface tension of the interphase.

Electrocapillary curves for n-amyl alcohol are shown in Fig. 7. As observed in earlier work, at sufficiently positive and negative potentials, the curves tend to coincide with that of the base electrolyte. Adsorption tends to be greatest around the middle of the electrocapillary curves where the depression of the surface tension is much greater than at the two extremes of the curves. In Fig. 8 are shown the Γ vs. $\log C$ plots for various temperatures and q_M values. The important feature of these plots is that the surface coverage for the molecule reaches saturation at a low bulk concentration of 0.032 m, indicating relatively strong adsorbability of n-amyl alcohol at Hg in relation to that of pyridine or pyrazine. From the plots of Γ vs. q_M at constant C (Fig. 9), it is seen that the surface coverage changes

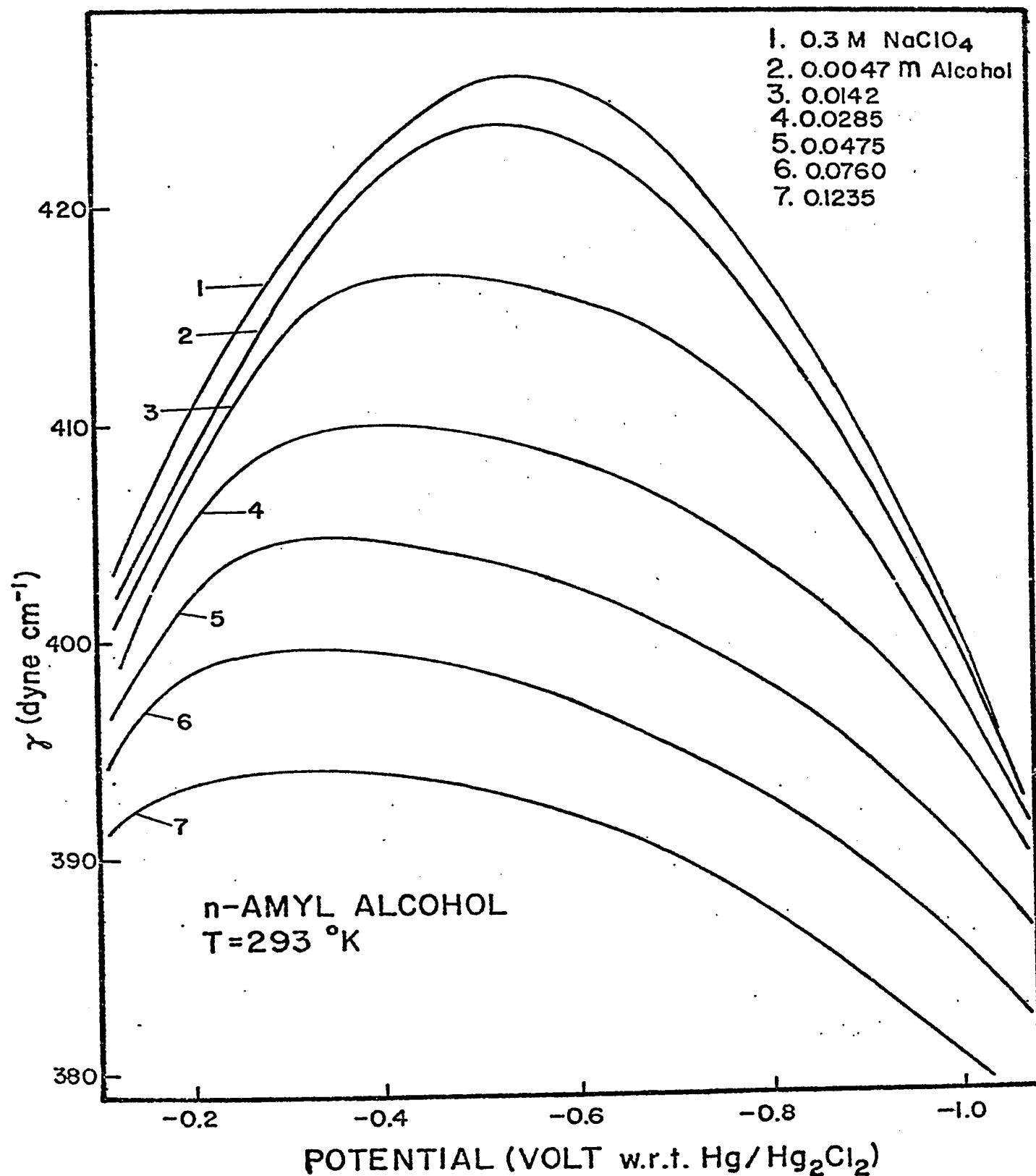


Fig. 7 Electrocapillary curves (based on γ values at 50 mV intervals) for adsorption of n-amyl alcohol from aq. 0.3 M NaClO_4 solution. $T = 293^\circ\text{K}$.

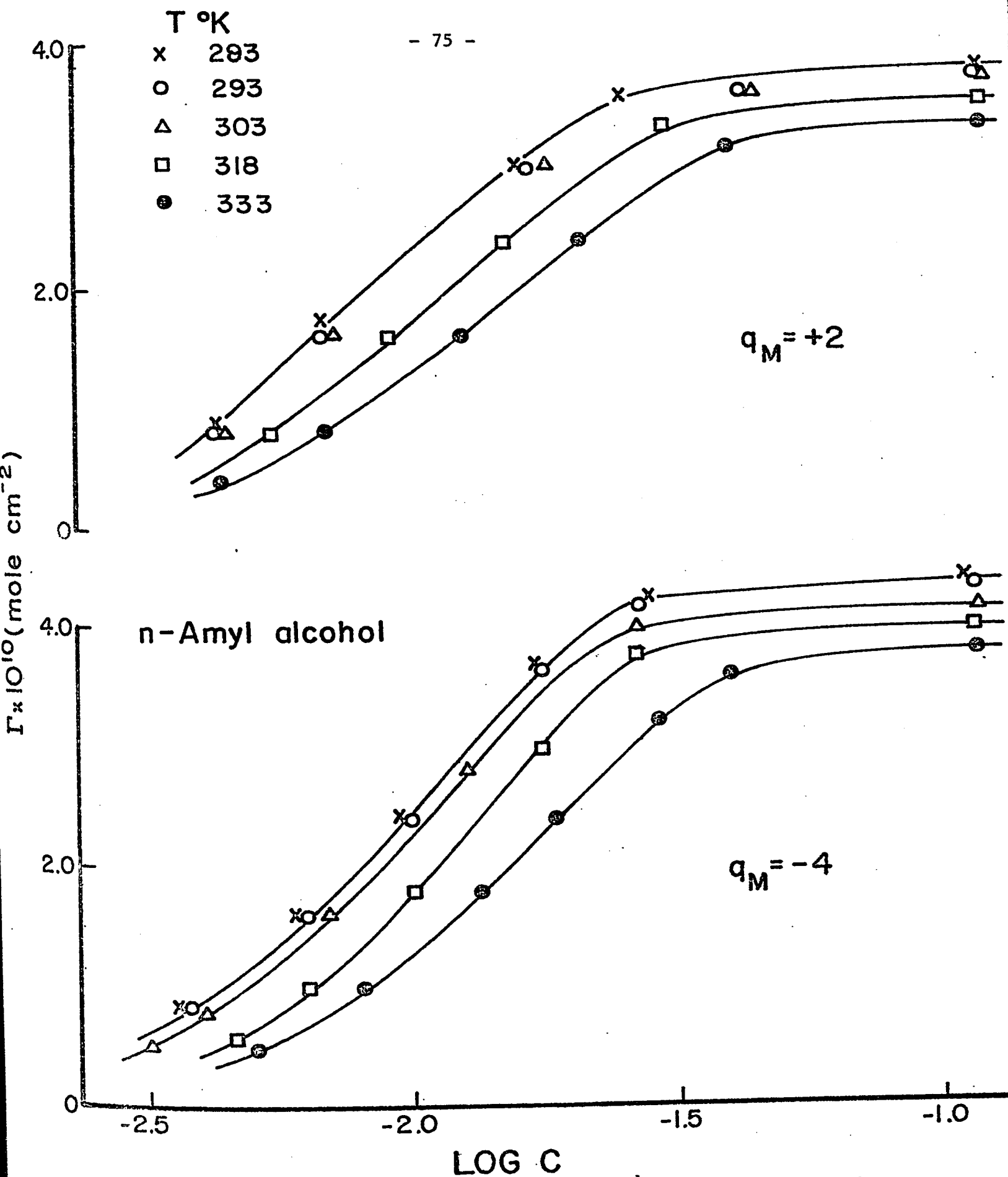


Fig. 8 Plots of Γ versus $\log C$ of n-amyl alcohol at various temperatures and two values of q_M .

n-Amyl alcohol
T = 293 °K

C
(mole l⁻¹)

- + 0.095
- 0.038
- △ 0.019
- 0.0095
- 0.0060
- x 0.0047

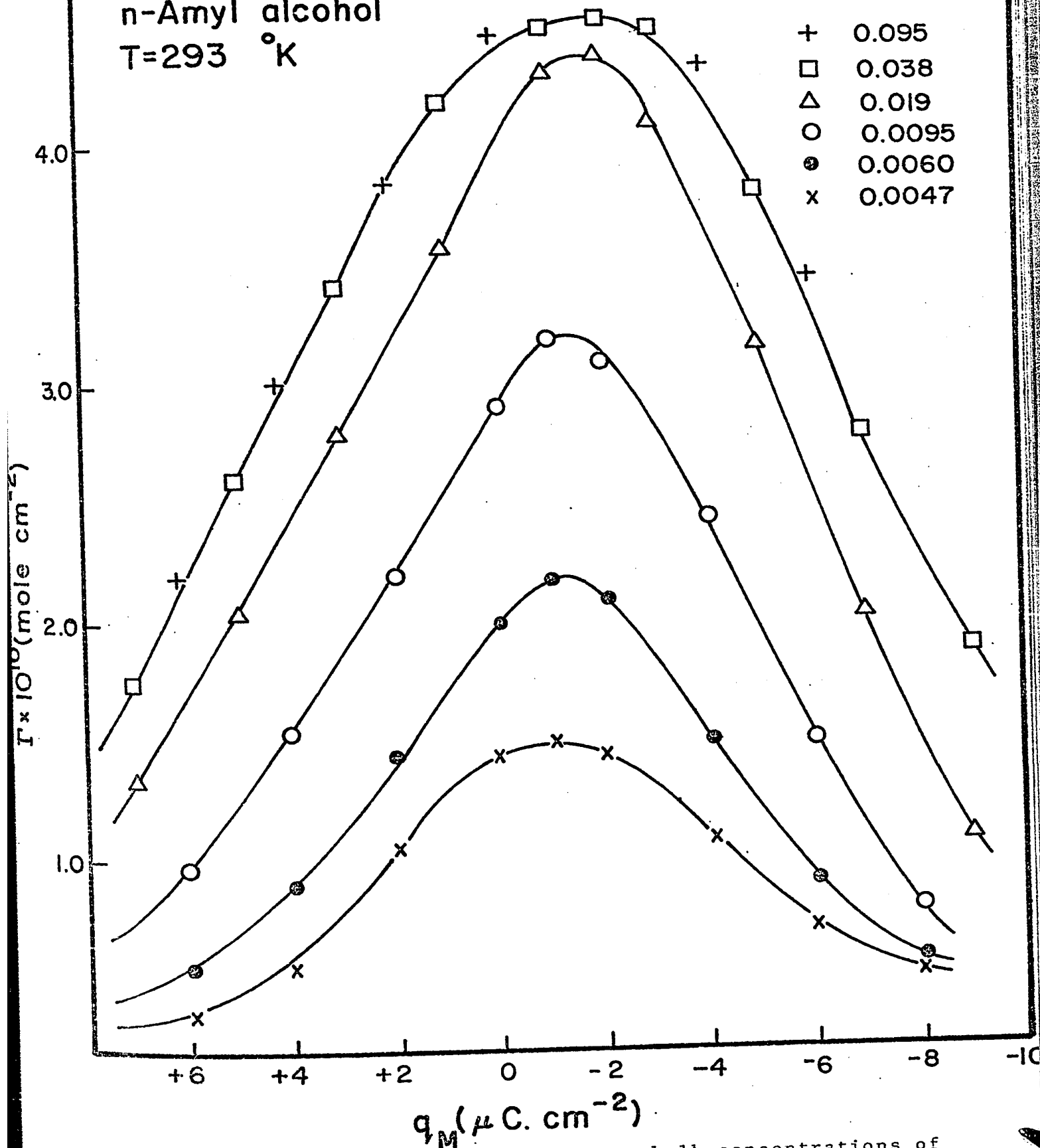


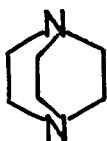
Fig. 9. Plots of Γ versus q_M for various bulk concentrations of n-amyl alcohol. $T = 293^\circ\text{K}$.

symmetrically with q_M around a charge of -1 to $-2 \mu C \text{ cm}^{-2}$, even though the molecule has a dipole moment in the -OH functional group. This indicates that the molecule probably is adsorbed in the same mean orientation at both positive and negative surface charges with the OH group orienting like neighboring H_2O molecules, "up" or "down" with changing field. The similar adsorption at positive and negative charge on the surface is probably determined mainly by the hydrophobic character of the hydrocarbon chain which displaces oriented water dipoles in a manner similar to that with pyrazine, i.e., symmetrically about $q_M = \text{ca. } -2 \mu C \text{ cm}^{-2}$ (see p.145).

5. Adsorption of 1,4-diazabicyclo-(2,2,2)octane (DBO)

DBO is a bicyclic aliphatic heterocyclic molecule with N atoms at the para positions.

DBO



The molecule is of interest in solvent substitution studies of adsorption since it is almost spherical and, overall, is non-polar. Unlike pyridine or pyrazine, the molecule is quite basic having $pK_{a,1}$ about 10 compared to 4 or 5 for pyridine and pyrazine. DBO is therefore capable of existing in two ionized as well as neutral states depending on the pH of the solution.

The adsorption of this molecule was studied from 0.3 M NaClO_4 solution. Adsorption of neutral DBO from 0.3 M NaClO_4 containing 0.01 M NaOH was not different from adsorption from 0.3 M NaClO_4 alone as judged by the shapes of the electrocapillary curves. The reference electrode consisted of a 0.3 M NaCl/calomel half-cell.

Measurements were made at a single temperature of 293°K and at the following molal concentrations: 0.003, 0.006, 0.010, 0.018, 0.030, 0.045, 0.065, 0.095, 0.140, 0.200, 0.325 and 0.500 m.

Fig. 10 shows the electrocapillary curves for several concentrations for DBO in the neutral form. Fig. 11 shows plots of Γ vs. q_M at constant solution concentrations. The curves in Fig. 10 for positive q_M values are similar to those for thiourea⁶¹, a molecule with considerable electron density on the S-atom, which could interact strongly with the metal when the latter is positively charged. The electrocapillary curves (Fig. 10) for DBO, like those for thiourea⁶¹, diverge at positive polarizations and do not coincide with the curve for the pure electrolyte. On the negative branch the curves tend to converge at a sufficiently negative potential. The above behavior suggests that different orientations of this molecule are adopted, depending on whether the electrode surface is positively or negatively charged and this gives rise to the apparently unsymmetrical behavior in adsorption for this symmetrical molecule. When q_M is positive

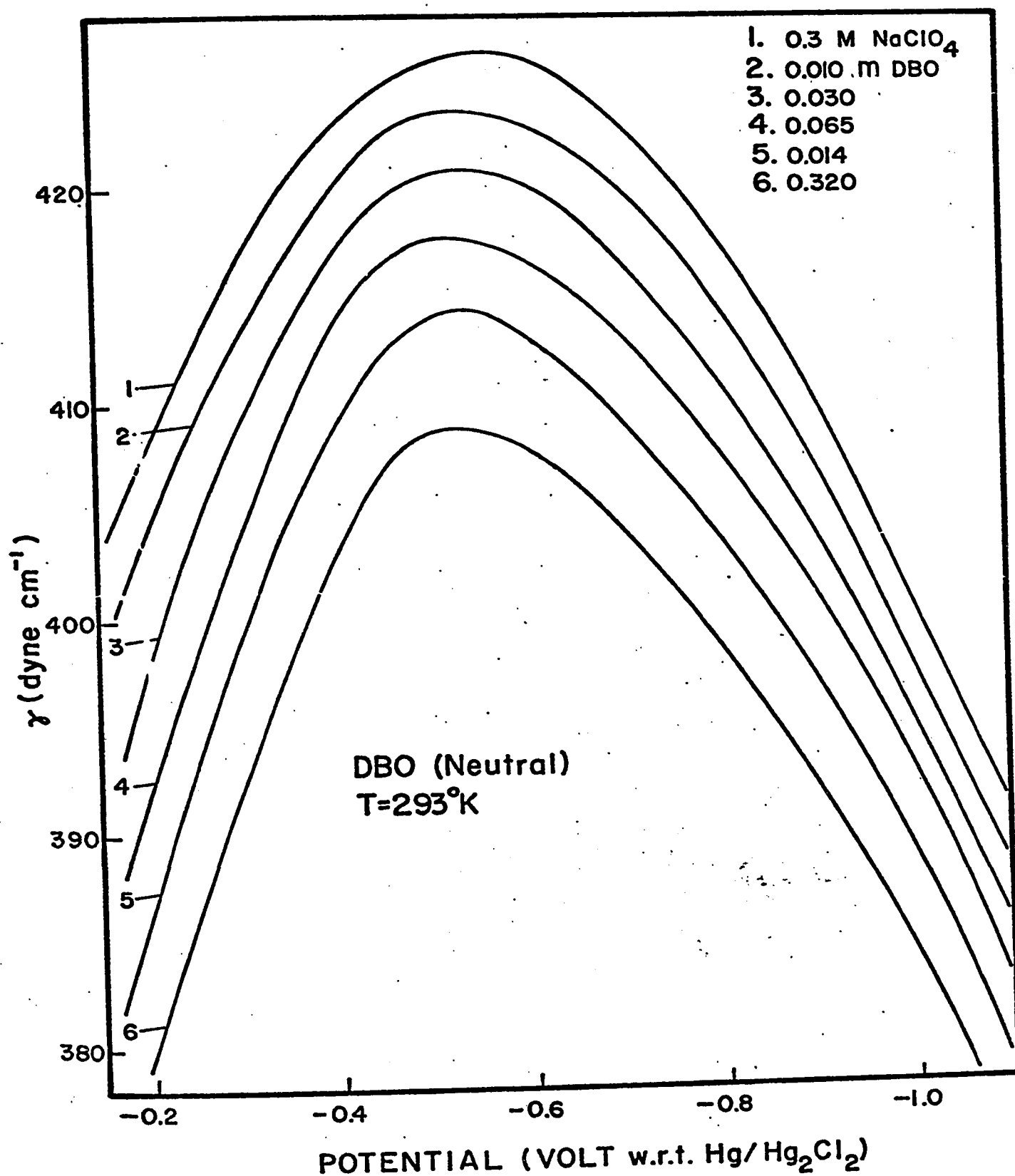


Fig. 10 Electrocapillary curves (based on γ values at 50 mV intervals) for adsorption of DBO (neutral) from aq. 0.3 M NaClO_4 solution. $T = 293^\circ\text{K}$.

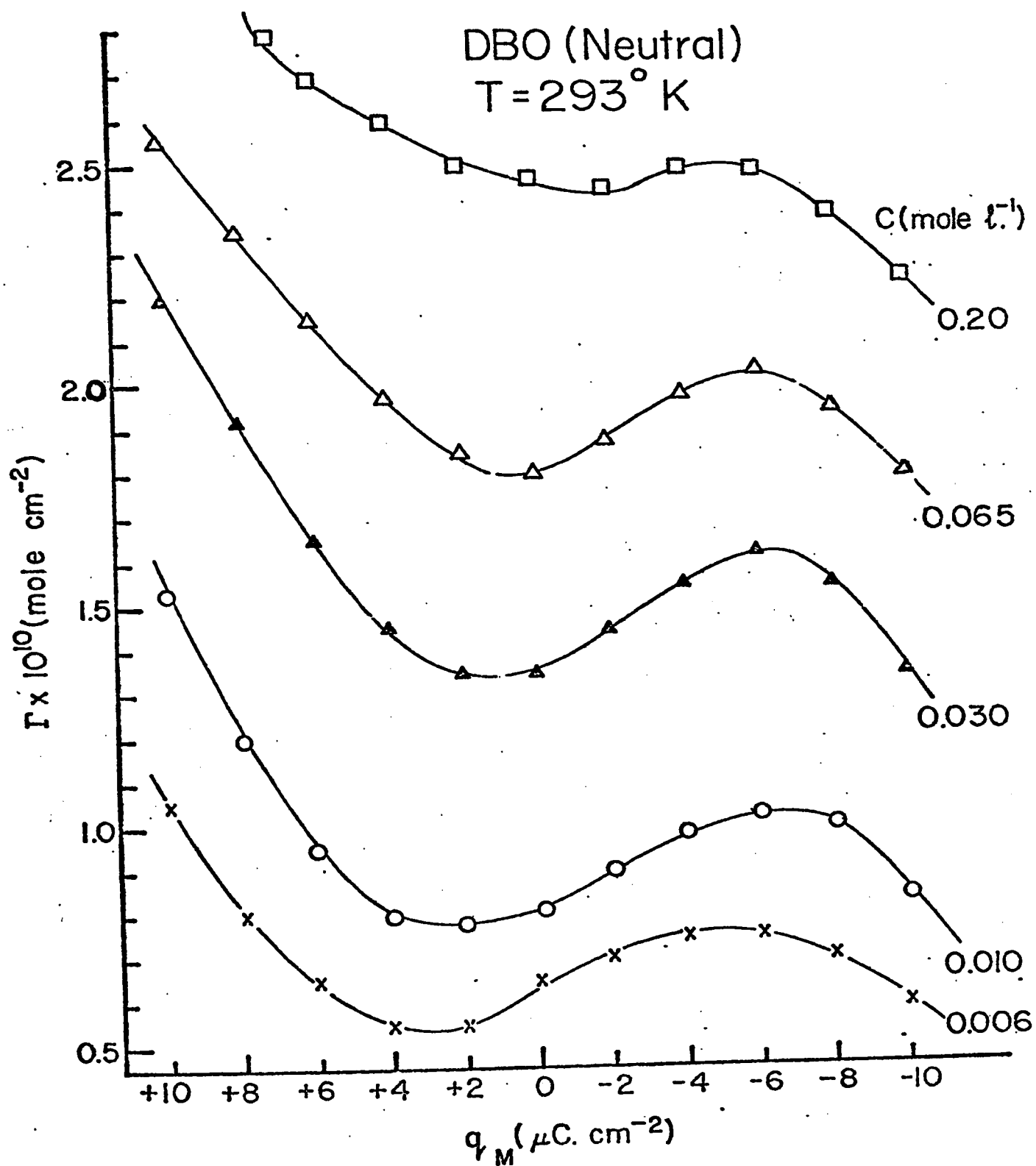


Fig. 11 Plots Γ versus q_M for various bulk concentrations of DBO (neutral). T = 293°K.

the molecule will tend to sit with one of the N atoms on the surface while around $q_M \approx -1 \mu\text{C cm}^{-2}$, the N atom will tend to move away from the surface and the hydrocarbon part (the middle section of the molecule) can more closely interact with the surface. The humps in the Γ vs. q_M curves when the electrode bears a negative charge (Fig. 11) may be interpreted in terms of replacement of oriented solvent molecules (see Section E of Chapter IV, Part I).

6. Adsorption of organic ions

(i) Adsorption of N-methyl pyridinium perchlorate

This study was carried out to provide data at sufficiently closely spaced concentrations that the nature of the interactions between adsorbed N-methyl pyridinium ions could more exactly be evaluated. Similar studies for the (protonated) pyridinium ion in HCl and HClO_4 were carried out previously in this laboratory⁸⁰ where $\Delta G_{\text{ads}}^{\circ}$ were found to vary linearly with square-root of coverage (θ) over a limited range of θ values.

N-methyl pyridinium perchlorate was adsorbed at a constant temperature of 298°K from a base solution of 1M aq. HClO_4 . A 1M NaCl/calomel half-cell was used as the reference electrode. In order that both low θ and high θ values could be reached, it was especially necessary for this molecule to be studied over a sufficiently large range of concentrations. The measurements were hence made at the following molal

concentrations: 0.001, 0.002, 0.003, 0.005, 0.008, 0.015, 0.028, 0.050, 0.080, 0.120, 0.190, 0.300, 0.500 and 0.750 m.

Several electrocapillary curves for this ion are shown in Fig. 12. Γ vs. q_M plots are shown in Fig. 13. As expected for a positive ion, the surface coverage for a given solution concentration increases with increasing negative surface charge becoming, however, more or less constant near $q_M = -6 \mu\text{C cm}^{-2}$.

(ii) Adsorption of DBO mono- and dipositive ions

Potentiometric titration of DBO with an acid showed an equivalence point around pH 4.5 when one of the two N atoms of DBO becomes fully ionized. The other equivalence point was believed to be around pH 1.5 but could not be reached by titration with dilute acid solution (0.1M). Titration with more concentrated acid gives the other equivalence point.

0.3 M aq. KH_2PO_4 solution having pH 4.5 provides an ideal buffer electrolyte for studies on the mono-positive ion. Adsorption was measured at a constant temperature of 293°K and at eleven concentrations in the range of 0.0015 to 0.290 molal. The reference electrode was a 0.3 M KCl/calomel half-cell.

Γ vs. q_M plots for the monopositive DBO ion are shown in Fig. 14.

The dipositive ion was adsorbed from 2M aq. HClO_4 solution. A 2M HCl/calomel half-cell was used as the reference

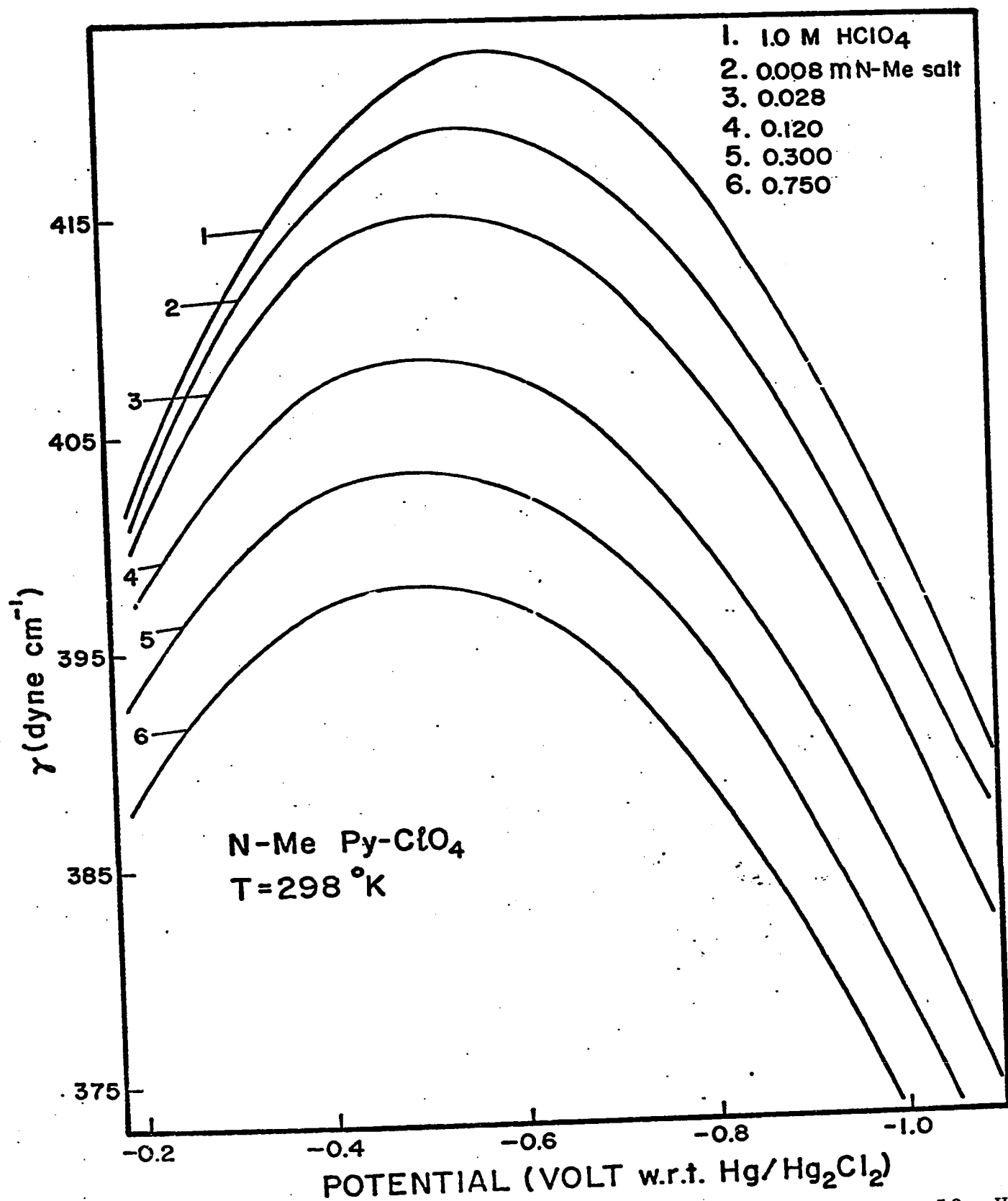


Fig. 12 Electrocapillary curves (based on γ values at 50 mV intervals) for adsorption of N-methyl pyridinium perchlorate from aq. 1.0 M HClO_4 solution.

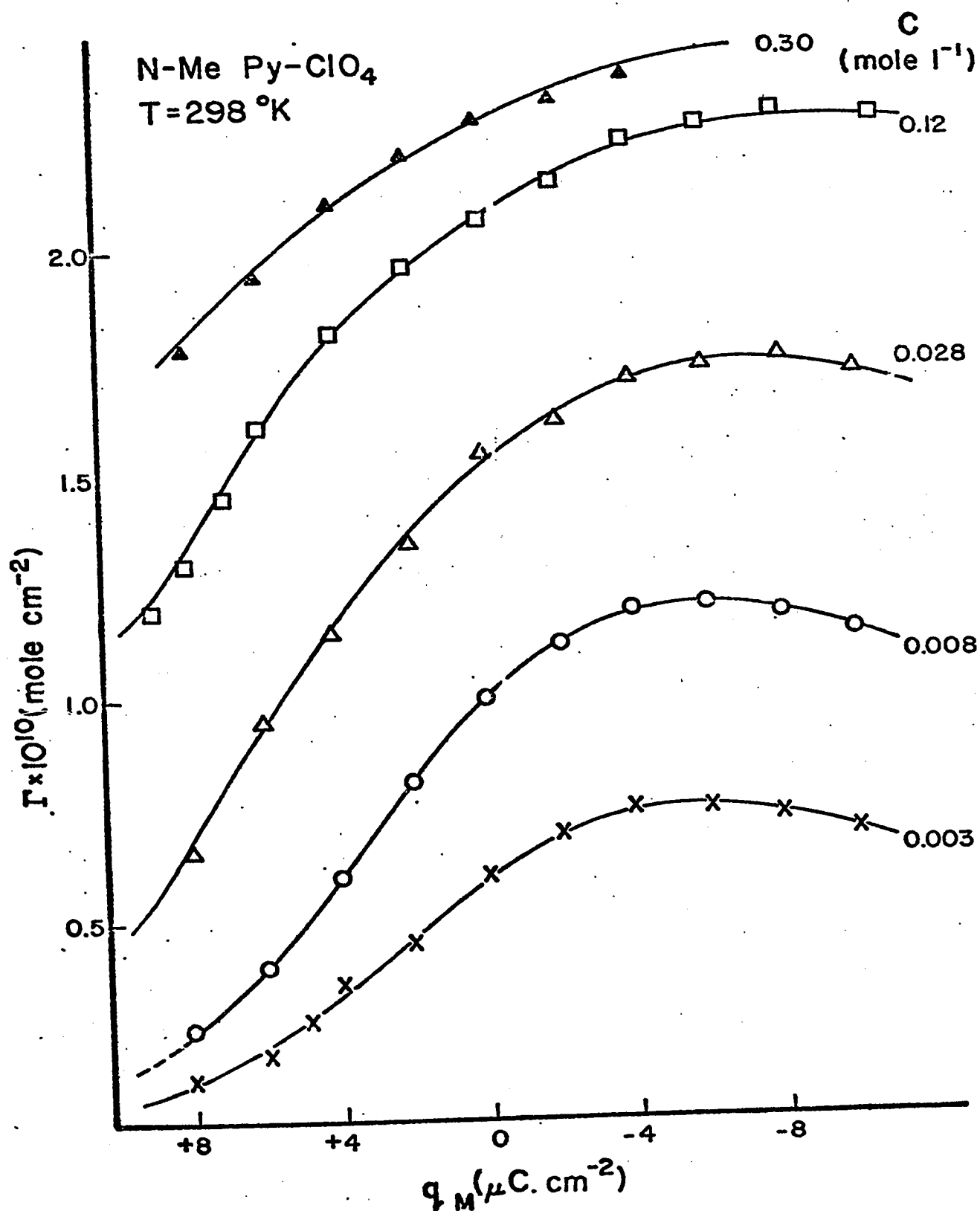


Fig. 13 Plots of Γ versus q_M for various bulk concentrations of N-Me pyridinium perchlorate. $T = 298^\circ\text{K}$.

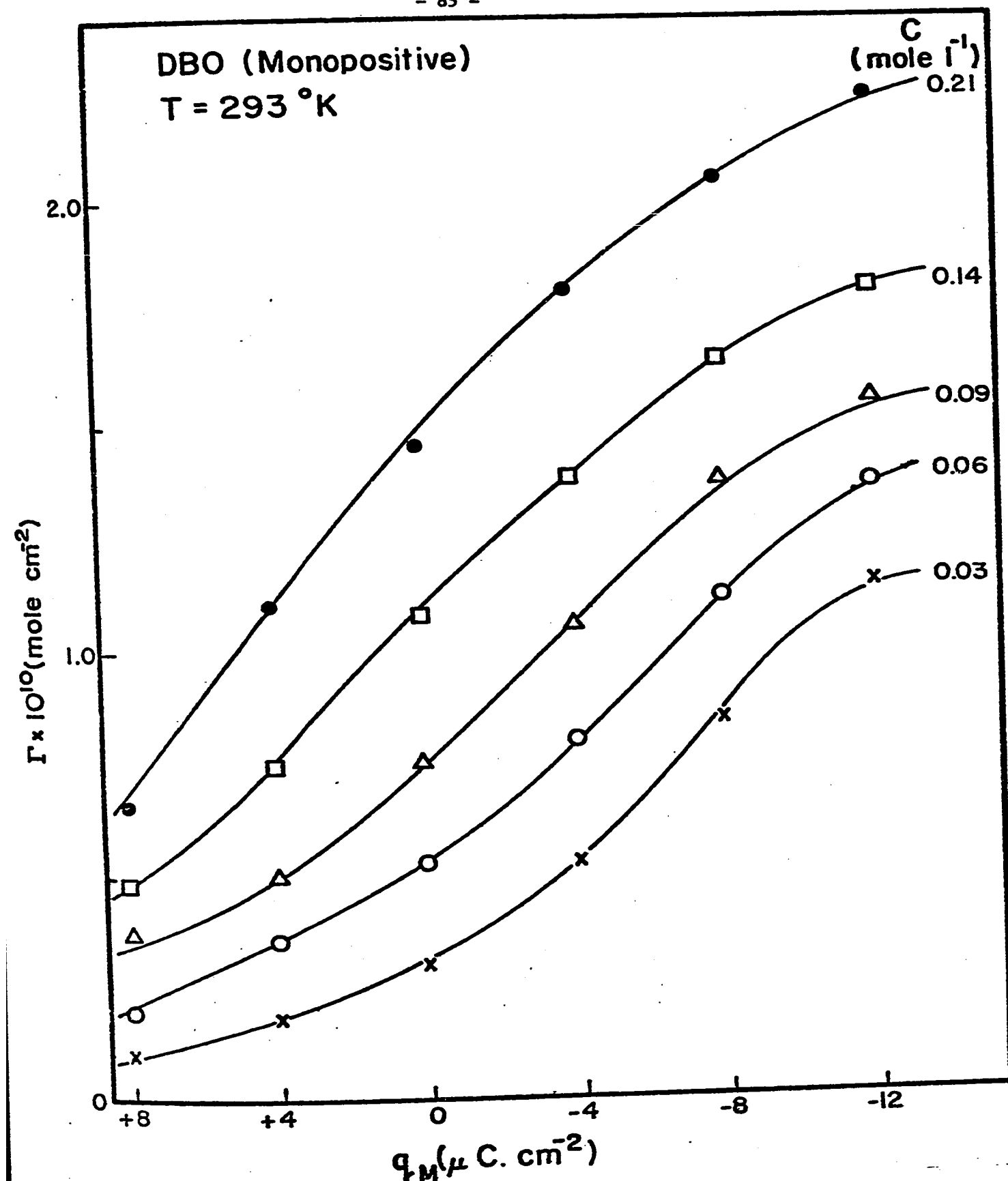


Fig. 14 Plots of Γ versus q_M for various bulk concentrations of monopositive DBO ion. T = 293°K.

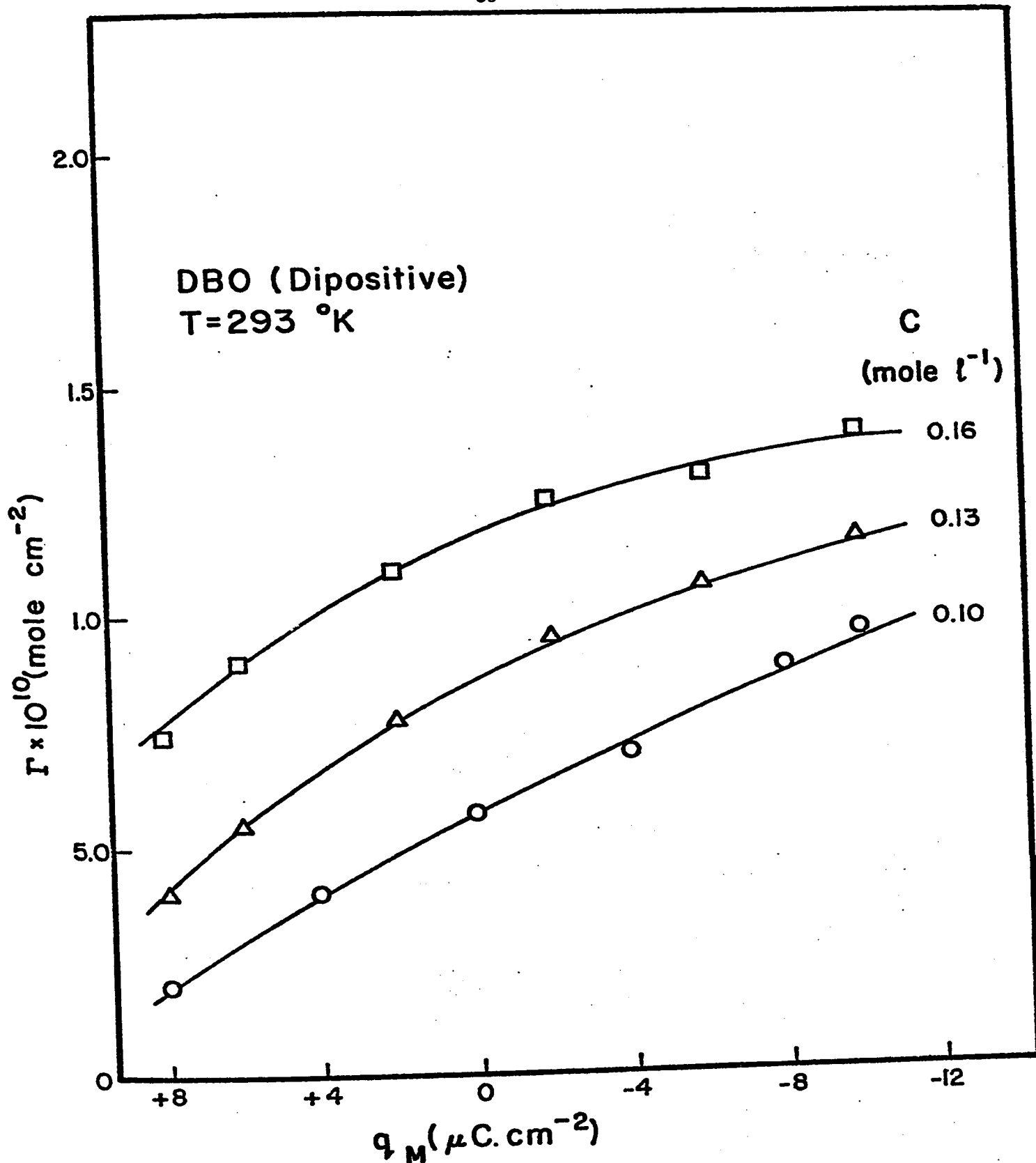


Fig. 15 Plots of Γ versus q_M for various bulk concentrations of dipositive DBO ion. T = 293°K.

electrode in this part of this work. Seven concentrations in the range 0.01 to 0.2 M were employed and the temperature was again 293°K.

Γ vs. q_M plots for the dipositive ion are shown in Fig. 15.

The monopositive ion is, as expected, more strongly adsorbed at negative surface charges and its adsorption behavior compares well with that of the N-methyl pyridinium ion (Fig. 13). In comparison with the adsorption of the monopositive ion, surface coverage by the dipositive ion is much less (at a given concentration) at both positive and negative surface charges. This reflects the smaller interaction of the dipositive ion with the metal surface due to the greater hydration of the dipositive than the monopositive ion in the double-layer.

B. Adsorption at the Air/Water Interface

1. Adsorption of pyrazine and pyridine

Experimental details of the adsorption measurements were given in Chapter II. Isotherms for pyrazine and pyridine adsorption were determined at five temperatures and, for each temperature, the number of concentrations employed was at least ten. Γ values were evaluated from γ vs. $\log C$ plots using a rectangular front-faced mirror for evaluation of the derivative of the curves at different activities. The error

in Γ in such calculations was estimated to be within $\pm 0.05 \times 10^{-10}$ mole cm^{-2} , i.e., 3%. The resulting adsorption data are shown in terms of $\Gamma - \log C$ plots in Fig. 16. For one temperature (298°K), however, activity coefficient data were available and this allowed one $\Gamma - \log a$ plot to be included in Fig. 16 (see Section D of Chapter IV, Part I, for discussion). Normal behavior of the isotherm in terms of Γ then results, i.e., the maximum in Γ for pyridine adsorption is eliminated.

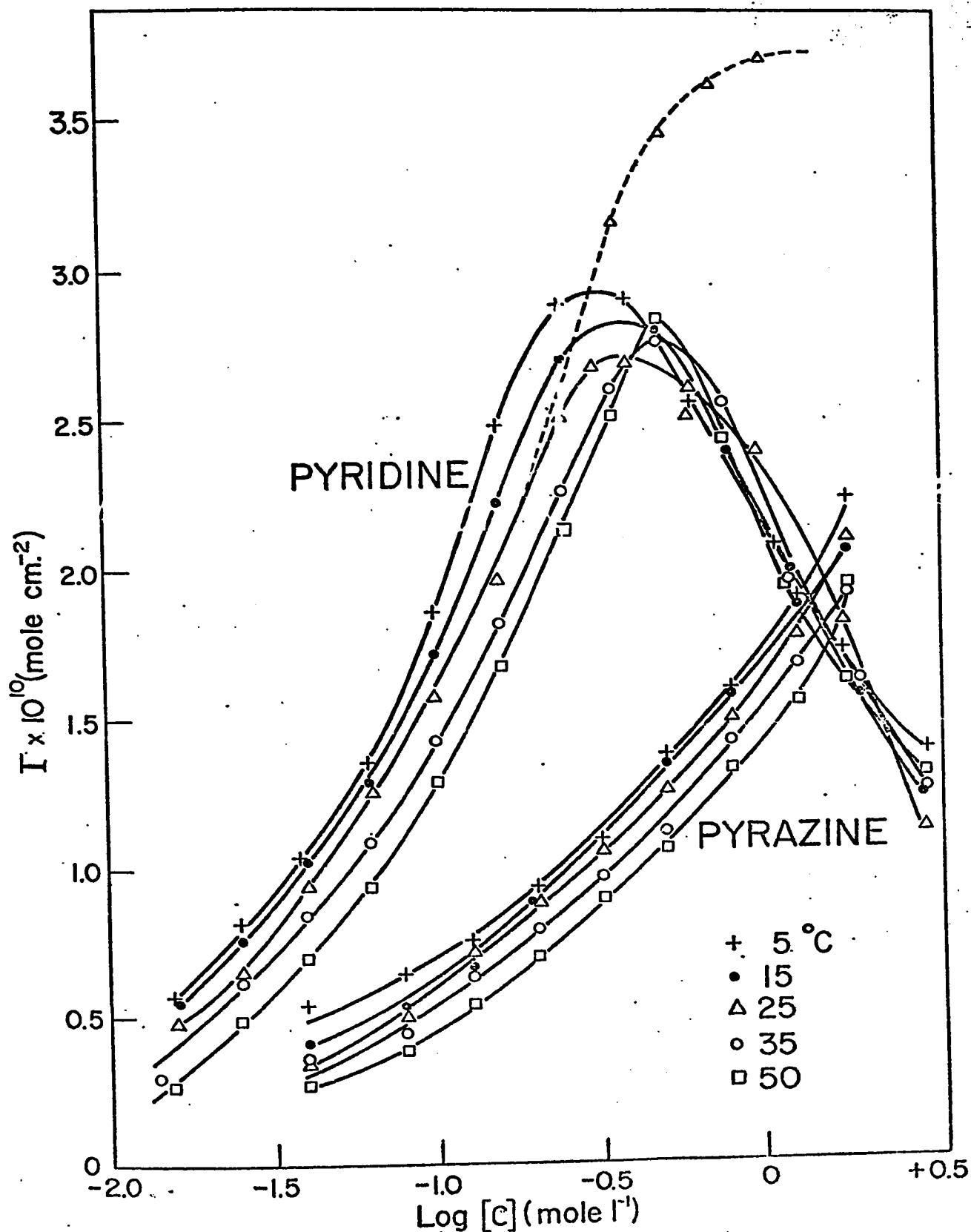


Fig. 16 Experimental isotherms for adsorption of pyridine and pyrazine at the air/water interface at various temperatures. The dashed curve shows one isotherm after activity coefficient correction for pyridine at 25°C.

CHAPTER IV

DISCUSSION

Part I: Adsorption of Neutral Molecules

A. Methods of Approach

In the discussion of the results for neutral molecules, the following aspects of the adsorption behavior will be considered: (a) the dependence of apparent standard free energy of adsorption $\Delta G_{\text{ads}}^{\circ}$ on surface charge q_M in terms of competitive adsorption involving field-oriented solvent molecules^{23,25}; (b) the dependence of $\Delta G_{\text{ads}}^{\circ}$ on coverage^{36,58,82} in relation of co-circle interaction effects (cf. co-sphere interaction effects in aqueous solutions) in the interphase; (c) orientation of solute and solvent molecules at an interface in terms of the shift of potential at which a given charge q_M arises, including $q_M = 0$, the e.c.m. condition; (d) dependence of surface pressure due to adsorbed organic molecules at a given coverage, on surface charge or metal-solution potential difference, and on orientation of the molecules; and (e) charge dependence of the isosteric³⁶ entropy and heat⁸³ of adsorption of the solute.

In examining the experimental behavior in relation to adsorption isotherms, two approaches are possible: to attempt to fit the results empirically to various kinds of

isotherms⁶⁹ which take into account, e.g. finite size of the adsorbate and/or coverage-dependent interactions between the adsorbate molecules; or to choose an appropriate configurational function (e.g. $\theta/(1-\theta)$ in the Langmuir case; see Section B) based on relevant statistical-mechanical lattice considerations and implicitly the finite size factor, and then evaluate, from the experimental results, the coverage (θ) and charge dependence of the formal equilibrium constant K_{ads} for a given value of q_M and temperature. K_{ads} can usefully be expressed in terms of the corresponding "apparent standard free energy of adsorption"^{63,82} ΔG_{ads}^0 which can vary with θ and q_M . ΔG_{ads}^0 will be dependent on θ if there are significant θ -dependent interactions^{36,63,82} involved in the interphase. Thermodynamically, any variation of ΔG_{ads}^0 with θ is equivalent to introduction of an activity coefficient $f_{\theta,q}$ in the configurational term as follows:

$$f_{\theta,q} \theta/(1-\theta) = \bar{K}_{ads} C/m_s \quad (42)$$

where $\bar{K}_{ads}$ is a true thermodynamic adsorption equilibrium constant related to the real standard free energy of adsorption $\Delta G_{o,ads}^0$ ($= -RT \ln \bar{K}_{ads}$) that would arise in the absence of interactions; C is the molar concentration (activity) of adsorbate in solution and m_s is the molar concentration of solvent (55.51 for water at 25°C). It is obvious that since $\bar{K}_{ads}/f_{\theta,q} = K_{ads}$,

$$\Delta G_{\text{ads}}^{\circ} = \Delta G_{\text{o,ads}}^{\circ} + RT \ln f_{\theta,q} \quad (43)$$

with $f_{\theta,q} \rightarrow 1$ as $\theta \rightarrow 0$. The form of the dependence of $\Delta G_{\text{ads}}^{\circ}$ with q_M at a given value of θ , and the dependence of this term upon θ , are the factors of interest^{25,58} in relation to solvent orientation and solvent structure effects in adsorption at electrodes.

Since $\Delta G_{\text{ads}}^{\circ}$ must be evaluated from an isotherm in which some configurational term ($f(\theta)$) in θ arises, we consider first some questions concerning the proper representation of $f(\theta)$ for substitutional adsorption.

B. Isotherms for Substitutional Adsorption of Molecules of Different Sizes

1. Introduction

In the electrochemical adsorption of many organic substances from water or organic solvents, e.g. CH_3OH , of small molecular size, there is usually an important difference of size between the adsorbate and solvent. Electrochemical adsorption always involves solvent displacement and the thermodynamics of the exchange of solute between the bulk phase and the interphase therefore depends on the relative size of solute and solvent since the number of solvent molecules that must be displaced depends on the size of the adsorbate. We take the projected area ratio as x . In the adsorption isotherm, x must enter in two ways: (a) in deter-

mining the standard free energy of adsorption²⁵ $\Delta G_{\text{ads}}^{\circ}$ which depends, amongst other factors, on how many (x) solvent molecules must be displaced and (b) in the form of the configurational function in surface coverage or site fraction⁸⁴ of ad-species on the adsorbent lattice. $\Delta G_{\text{ads}}^{\circ}$ will usually depend on the surface charge on the metal or local field in the Helmholtz layer since energy for solvent replacement depends^{25,37} on the energy of solvent dipoles in the electrode double-layer field.

Correct evaluation of the standard free energy of a solvent-substitution adsorption process at the charged interface from experimental coverage data cannot be made unless the configurational term in θ , or site fractions⁸⁴⁻⁸⁶ occupied by adsorbate and solvent, is properly formulated. Various forms of this term, including the Langmuir one⁸⁷, have appeared in published isotherms, in some cases without derivation or statistical-mechanical justification. It is necessary to critically examine the forms of various isotherms for adsorbates that are x times larger than the solvent molecules they replace in the interphase upon adsorption, and examine the justification of several types of isotherms that have been used previously^{32,34,63,89} for representing the adsorption of molecules of various sizes. The choice of the value of x also affects³⁷ the value of the solvent dipole interaction parameter²⁵ in the theory of substitutional adsorption involving displacement of solvent

dipoles oriented in the electrode field²⁵, which is required to account for the breadth of experimental curves of free energy of adsorption as a function of surface charge (see Section C of Chapter IV, Part I).

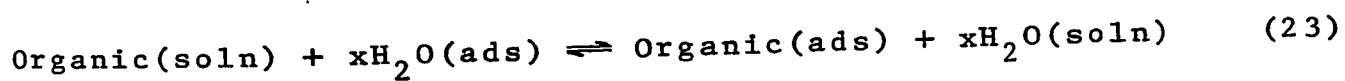
In the case of mercury, which has no specific lattice of adsorption sites, the Langmuir type isotherm and corresponding configurational term $\theta/1-\theta$ nevertheless applies for solvent substitution adsorption as shown by Frumkin⁸⁷, since the solvent lattice in the interphase is equivalent to specific solid 2-dimensional lattices in adsorption involving a solid interface. The question arises what form should the configurational term take for substitutional adsorption when adsorbate and solvent have different sizes? A factor $\theta/[x(1-\theta)^x]$, referred to as the "Flory-Huggins" term (by analogy with the results of treatments by Flory, by Huggins as well as by Orr⁸⁶ and Guggenheim⁸⁵ for polymer solutions) has occasionally been used empirically. A frequently cited reference for the derivation of an isotherm of the form

$$\frac{\theta}{x(1-\theta)^x} = \frac{C_{org}}{55.5} \exp -\Delta G_{ads}^0/RT \quad [=f(\theta)], \quad (44)$$

corresponding supposedly (see below) to the "Flory-Huggins" configurational term, is a publication of Zhukovitskii⁸⁸ who thermodynamically derived the following relation

$$b_1/b_2^x = (a_1/a_2^x) \exp f(\gamma)/RT \quad (45)$$

where b_1 and b_2 are the activities of adsorbate and solvent, respectively, in the interphase while a_1 and a_2 are the corresponding quantities in the bulk phase; γ is the surface tension of the solution. A rigorous statistical-mechanical basis for equations (44) or (45), such as exists for the Langmuir isotherm in terms of lattice statistics, does not, however, appear to have been given. Zhukovitskii's relation is, however, essentially analogous in form to the isotherm applicable to competitive (substitutional) adsorption from solution, which can be represented by the following quasi-chemical substitution process (see p.32).



2. Thermodynamic treatment of substitutional adsorption

For simplicity, the adsorbed and solution phases in process (23) will be considered ideal from the interaction point of view, so that activity coefficients can be neglected. Then the electrochemical* and chemical potential terms $\bar{\mu}$ and μ , respectively, for the organic substance (O) and water (W) in the interphase and in solution can be written:

$$\bar{\mu}_{\text{O,ads}} = \bar{\mu}_{\text{O,ads}}^{\text{O}} + RT \ln X_{\text{O}} \quad (46)$$

$$\bar{\mu}_{\text{W,ads}} = \bar{\mu}_{\text{W,ads}}^{\text{O}} + RT \ln X_{\text{W}} \quad (47)$$

* Electrochemical potentials $\bar{\mu}$ are written here since the chemical potential of dipoles is field-dependent in the double-layer.

$$\mu_{O, \text{soln}} = \mu_{O, \text{soln}}^o + RT \ln Y_O \quad (48)$$

$$\mu_{W, \text{soln}} = \mu_{W, \text{soln}}^o + RT \ln Y_W \quad (49)$$

where X_O and X_W are the site fractions of O and W in the interphase and Y_O and Y_W the mole fractions in solution corresponding to N_O and N_W mole ℓ^{-1} of organic and water. The standard states for the adsorbed species are unit site or fractional coverage (X or $\theta=1$) for the adsorbate and solvent, while the standard states for the solution phase are unit mole fractions of organic or solvent⁶³.

The condition for interphase/bulk phase equilibrium in adsorption is

$$\bar{\mu}_{O, \text{ads}} - x \bar{\mu}_{W, \text{ads}} = \mu_{O, \text{soln}} - x \mu_{W, \text{soln}} \quad (50)$$

so that the standard free energy of adsorption, using relations (46) to (49), is

$$-\Delta G_{\text{ads}}^o = RT \ln \left[\frac{(X_O) (Y_W)^x}{(X_W)^x (Y_O)} \right] \quad (51)$$

in terms of site fractions, or

$$\Delta G_{\text{ads}}^o = \left[\bar{\mu}_{O, \text{ads}}^o - \mu_{O, \text{soln}}^o \right] - x \left[\bar{\mu}_{W, \text{ads}}^o - \mu_{W, \text{soln}}^o \right] \quad (52)$$

For dilute solutions, $Y_W = 1$ and $Y_O = C_{\text{org}}/55.5$ and by definition $X_O = N_{\text{org}}/N_T$ where N_{org} is the number of solvent lattice sites on the surface occupied by organic and N_T the total number of such solvent sites. A solvent lattice

site is a position of finite area equivalent to that of a solvent molecule adsorbed, amongst other solvent molecules, with a certain coordination number and local two-dimensional structure. Then

$$N_T = N_{org} + N_W \quad (53)$$

The experimental surface excess quantities (assumed to be identical with surface concentrations at low bulk concentration) can be readily expressed in terms of the site fraction X or relative coverage; thus with

$$N_{org} = x\Gamma_{org} \quad (54)$$

$$\text{and} \quad N_W = \Gamma_W, \quad (55)$$

$$N_T = x\Gamma_{org} + \Gamma_W \quad (56)$$

where Γ is expressed here in molecules cm^{-2} . Noting that

$$\Gamma_{org} = \theta\Gamma_{org,max} \text{ (for saturation),} \quad (57)$$

$$\Gamma_W = \Gamma_{W,max} - x\Gamma_{org} \quad (58)$$

$$\text{and} \quad \Gamma_{W,max} = x\Gamma_{org,max} \quad (59)$$

it is seen that

$$\frac{x\Gamma_{org}}{x\Gamma_{org} + \Gamma_W} = N_{org}/N_T \quad (60)$$

and this is the site fraction X_0 , equivalent to θ . Correspondingly

$$X_W = 1 - \theta \quad (61)$$

Equations (60) and (61) are derived here from the Γ and N terms in order to emphasize that the fractions of sites available on the surface which are occupied by O or W , and measured by experimental Γ quantities, can always be written in terms of θ by introducing the molecular area factor x . Since the quantities in equation (51) are now fully defined, it is evident that

$$\frac{\theta}{(1-\theta)^x} = \frac{C_{org}}{55.5} \exp -\Delta G_{ads}^0 / RT \quad (62)$$

It is also evident that if the solution is regarded as a 3-dimensional lattice in which the relative size of solvent and solute is also taken as x^* , then the bulk concentration term in mole ℓ^{-1} appears as a 3-dimensional site fraction, as in the Flory-Huggins theory^{84,90}, giving

$$\frac{\theta}{(1-\theta)^x} = \frac{x C_{org}}{55.5 + x C_{org}} \exp -\Delta G_{ads}^0 / RT \quad (63)$$

which becomes at sufficiently low C_{org} ,

$$\frac{\theta}{x(1-\theta)^x} = \frac{C_{org}}{55.5} \exp -\Delta G_{ads}^0 / RT \quad (64)$$

A formal thermodynamic basis for equation (44), which has been used previously for analyzing adsorption data without

* This is, of course, not always exactly the case if electrostriction occurs in the interphase.

rigorous derivation, is thus provided. The relation between equation (64) and Zhukovitskii's equation (45) was discussed on an intuitive basis by Damaskin et al.⁹¹. Equation (44) or (64), as we show below, should not be referred to as the Flory-Huggins isotherm since the Flory-Huggins type of statistics lead, in fact, to another type of isotherm to be considered below.

3. Statistical-mechanical basis of the isotherm

The statistical-mechanical basis of the Langmuir equation for $x=1$ can be extended to consideration of adsorption of x -mers on a lattice or in substitution of x adsorbed solvent molecules by the x -mer. The treatment will be developed for flexible linear x -mers which can occupy contiguous surface sites along a "random-walk" amongst the lattice sites but a similar treatment applies⁹² for molecules of other shapes.

The adsorption of N_1 solvent molecules and N_2 x -mer molecules on a total number of sites N_0 such that $N_0 = N_1 + xN_2$ is derived from the configurational partition function

$$Q = \frac{\Omega(N_1, N_2) q_1^{N_1} q_1^{N_2}}{\Omega(N_2) \Omega(N_1)} \quad (65)$$

where $\Omega(N_1, N_2)$ is the total number of possible configurations for N_1 solvent molecules and N_2 x -mer molecules on N_0 sites, $\Omega(N_2)$ and $\Omega(N_1)$ are the numbers of arrangements amongst the

N_2 and N_1 solute and solvent molecules themselves and q_1 and q_2 are the internal partition functions of solvent and adsorbate. The calculation of the number of ways of putting a typical i'th x-mer on to the lattice, and hence the evaluation of $\Omega(N_1, N_2)$, follows standard procedures^{84,85,92} as employed by Flory and Huggins for polymer solutions⁹⁰. The essential results are

$$\begin{aligned} \ln \Omega(N_1, N_2) = & -N_2 \ln N_2 + N_2 - N_1 \ln N_1 + N_1 + N_0 \ln N_0 \\ & - N_0 + N_2(x-1) \ln \frac{(c-1)}{N_0} \end{aligned} \quad (66)$$

$$\ln \Omega(N_2) = -N_2 \ln N_2 + N_2 + xN_2 \ln xN_2 - xN_2 + N_2(x-1) \ln \frac{(c-1)}{xN_2} \quad (67)$$

where c is the coordination number for sites in the surface. From equations (65), (66) and (67), and noting that $\Omega(N_1)=1$,

$$\ln Q = -N_1 \ln \frac{N_1}{N_1+xN_2} - N_2 \ln \frac{xN_2}{N_1+xN_2} + N_1 \ln q_1 + N_2 \ln q_2 \quad (68)$$

A similar partition function is obtainable for molecules of other shapes as treated in the theory of binary mixtures⁹².

Differentiation of equation (68) with respect to N_1 and N_2 gives the respective chemical potentials of the solvent and solute on the surface. Thus

$$\left(\frac{\partial \ln Q}{\partial N_2} \right)_{N_1, T} = \frac{xN_1}{N_1+xN_2} - 1 + \frac{xN_2}{N_1+xN_2} - \ln \frac{xN_2}{N_1+xN_2} + \ln q_2 \quad (69)$$

Noting that $\frac{xN_2}{N_1+xN_2} = \theta$ and $\frac{N_1}{N_1+xN_2} = (1-\theta)$,

equation (69) can be written as

$$\left(\frac{\partial \ln Q}{\partial N_2}\right)_{N_1, T} = x(1-\theta) - 1 + \theta - \ln \theta + \ln q_2 = -\ln \left[\frac{\theta}{e^{(x-1)(1-\theta)}} \right] + \ln q_2 \quad (70)$$

$$= -\bar{\mu}_{\text{org}}/kT \quad (71)$$

From equations (70) and (71),

$$\bar{\mu}_{\text{org,ads}} = -kT \ln q_2 + kT \ln \left[\frac{\theta}{e^{(x-1)(1-\theta)}} \right] \quad (72)$$

In a similar way,

$$\left(\frac{\partial \ln Q}{\partial N_1}\right)_{N_2, T} = \frac{N_1}{N_1+xN_2} + \frac{N_2}{N_1+xN_2} - 1 - \ln \left[\frac{N_1}{N_1+xN_2} \right] + \ln q_1 \quad (73)$$

so that

$$\left(\frac{\partial \ln Q}{\partial N_1}\right)_{N_2, T} = (1-\theta) + (\theta/x) - 1 - \ln(1-\theta) + \ln q_1 = -\ln \left[\frac{(1-\theta)}{e^{(\frac{\theta}{x}-\theta)}} \right] + \ln q_1 \quad (74)$$

$$= -\bar{\mu}_{\text{W,ads}}/kT \quad (75)$$

Hence (cf.⁹³),

$$\bar{\mu}_{\text{W,ads}} = -kT \ln q_1 + \ln \left[\frac{(1-\theta)}{e^{(\frac{\theta}{x}-\theta)}} \right] \quad (76)$$

The chemical potentials in the solution phase can be written in the usual way in terms of mole fractions. Substitution of these chemical potentials into the interphase equilibrium equation (50), leads to the isotherm

$$\frac{\theta}{e^{(x-1)}(1-\theta)^x} = \frac{C_{org}}{C_W} e^{-\Delta G_{ads}^0/kT} \quad (77)$$

where $\Delta G_{ads}^0 = (-kT \ln q_2 - \mu_{org, soln}^0) - x(kT \ln q_1 - \mu_{W, soln}^0)$.

In equation (77), if ΔG_{ads}^0 is expressed per mole, then the final expression for the isotherm to be used for cases of substitutional adsorption of a species x times the area of solvent molecules would obviously involve the term $\exp -\Delta G_{ads}^0/RT$ as in equation (64) instead of $\exp -\Delta G_{ads}^0/kT$. The resulting form of equation (77) is seen to be not identical with the previously used representation (refs. 32, 34, 89 and equation (64)) of the so-called Flory-Huggins isotherm⁹⁰ nor with equation (62). If site fraction statistics were used to express bulk phase concentrations, the configurational term in equation (77) would become again a different factor

$$\frac{\theta}{x e^{(x-1)}(1-\theta)^x} \quad (78)$$

When $x=1$, this term and equation (77) become equivalent to the corresponding Langmuir case.

It is, of course, possible to combine the term $x e^{(x-1)}$ with the free energy term $\exp -\Delta G_{ads}^0/RT$, so that

$$\frac{\theta}{(1-\theta)^x} = \frac{C_{org}}{C_W} \exp -[\Delta G_{ads}^0 - RT(x-1) - RT \ln x]/RT \quad (79)$$

where the argument in square brackets can be regarded as an

effective standard free energy of adsorption that can be empirically calculated from known Γ , and hence θ values, with an x value deduced from space-filling models^{36,94}. It seems preferable, however, to use the isotherm in the form of (77) or in the form corresponding to the configurational term $\theta/\{xe^{(x-1)}(1-\theta)^x\}$ where both interphase and bulk phase concentrations are expressed in terms of site fractions. Inclusion of the term $xe^{(x-1)}$ with the $\exp(-\Delta G_{ads}^0/RT)$ factor would be equivalent to an irrational change of the standard state for the free energy change. It is evident that equation (77), or the form with the configurational term (78), should properly be referred to as the "Flory-Huggins" isotherm, and not equations (44) or (64).

4. Properties of the isotherm relation (77)

It is of interest to compare the values of the configurational $f(\theta)$ for various θ values taking selected values of x likely to be encountered with small adsorbate molecules. Figs. 17, 18 and 19 show $f(\theta)$ for various x values for the three principal forms of the configurational term in θ . These will determine the values of ΔG_{ads}^0 derived from experimental data on coverages in equilibrium with various bulk solution concentrations. Fig. 20 shows how the values of standard free energy of adsorption, that might be calculated from a series of experimental results interpreted on the basis of the Langmuir (L) isotherm for a range of θ values arising at

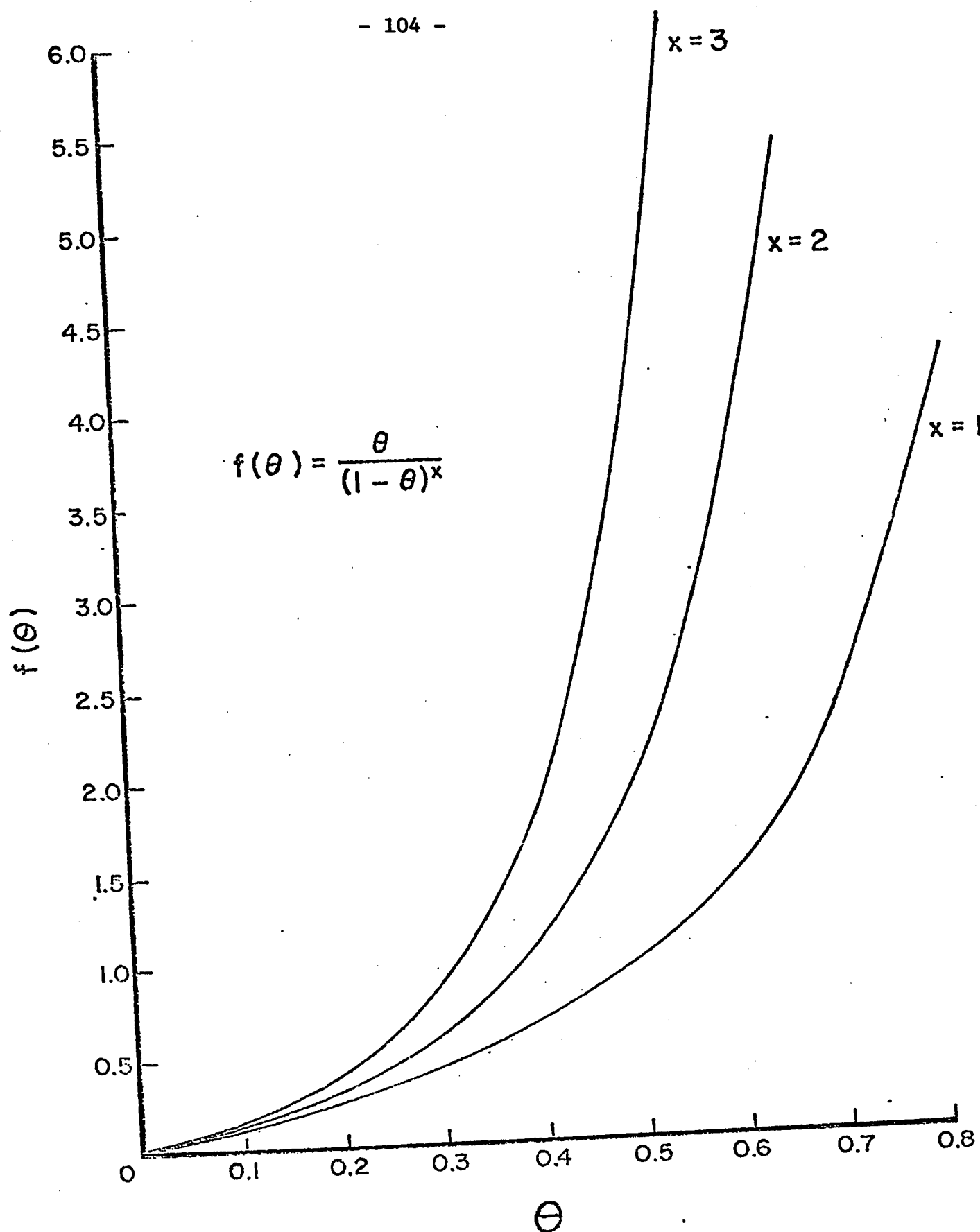


Fig. 17 Plot of the configurational $f(\theta) = \theta/(1-\theta)^x$ for various θ and x values.

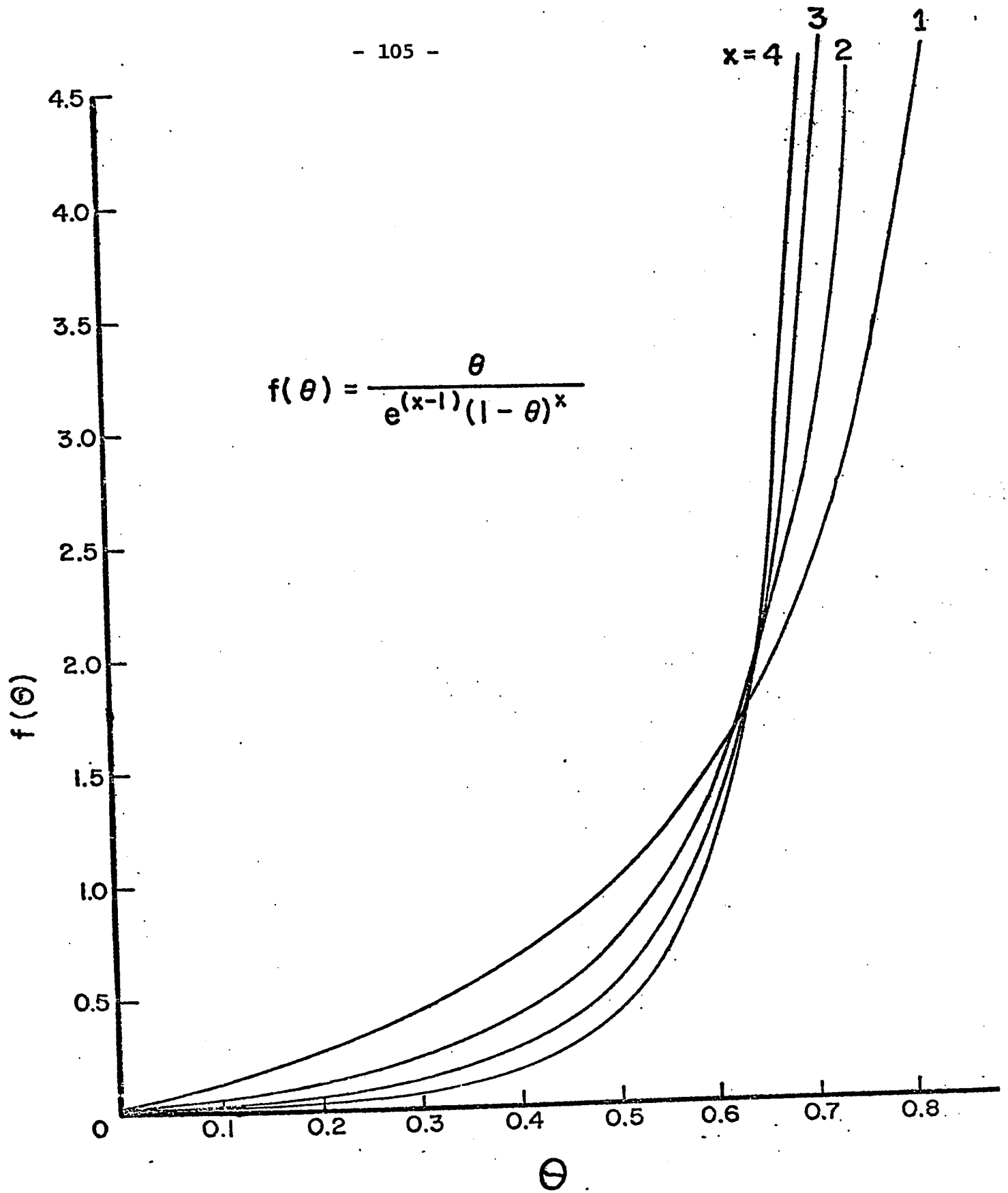


Fig. 18 Plot of the configurational $f(\theta) = \theta/e^{x-1}(1-\theta)^x$ for various θ and x values.

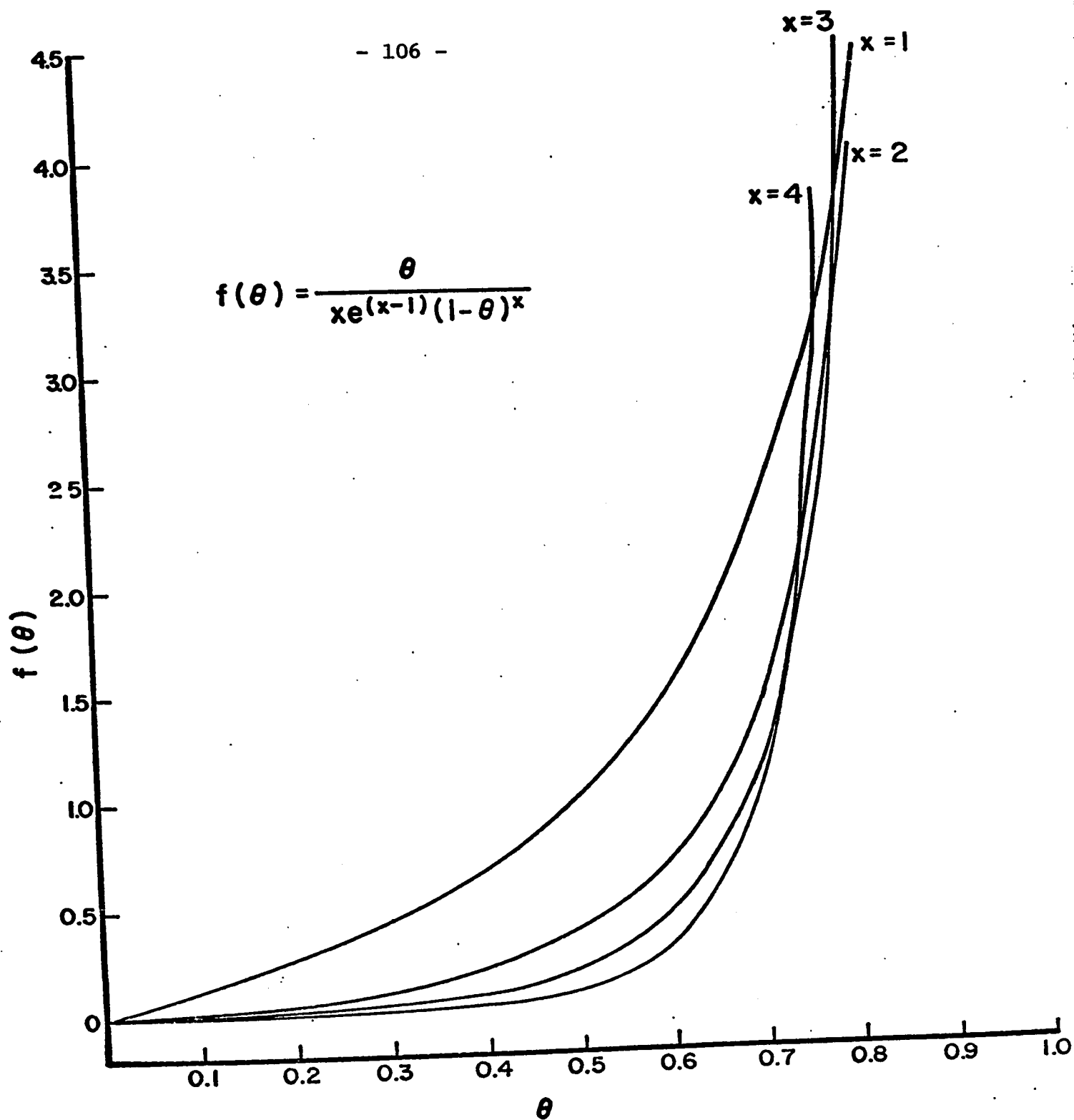


Fig. 19 Plot of the configurational $f(\theta) = \theta / x e^{x-1} (1-\theta)^x$ for various θ and x values.

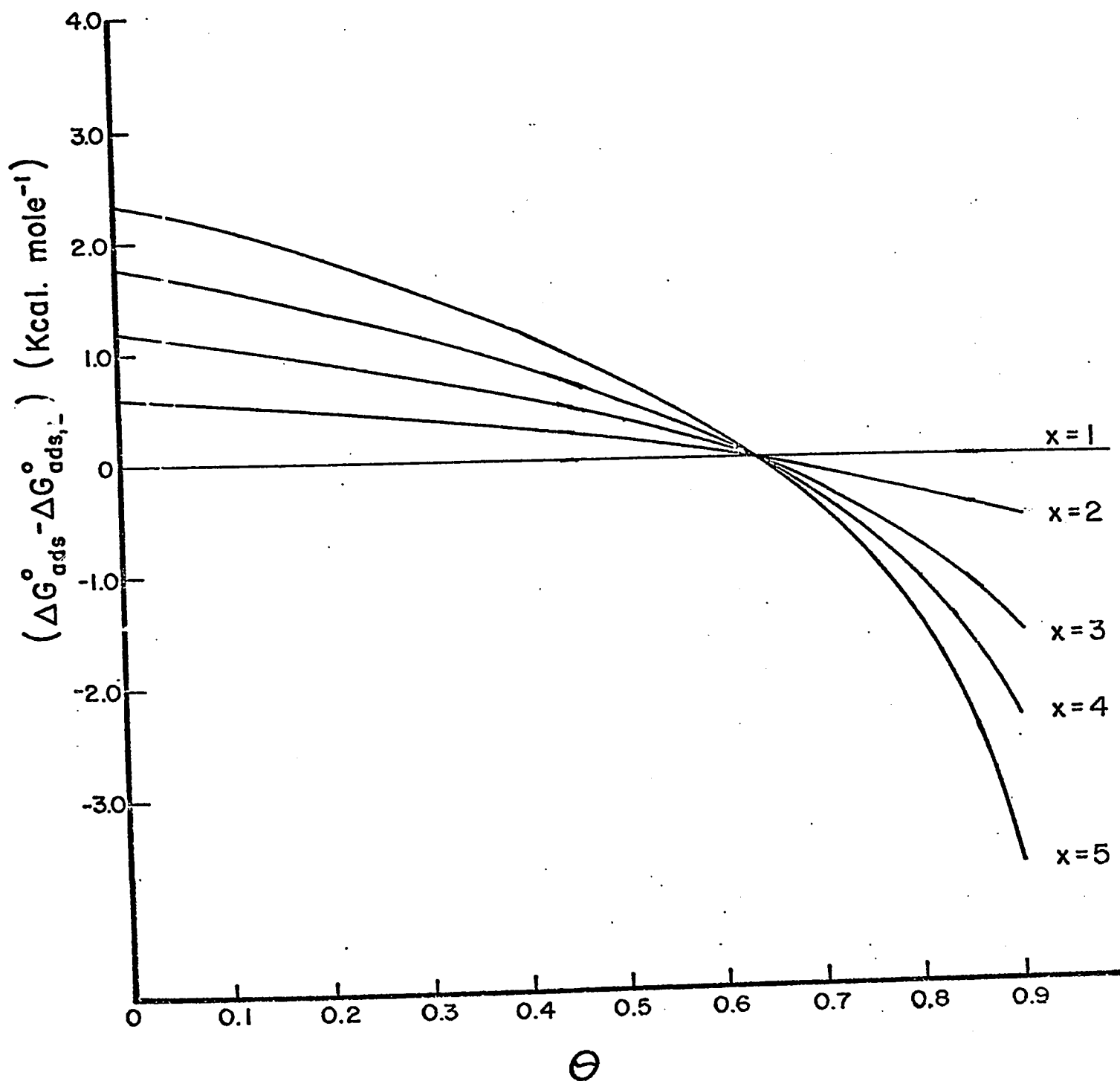


Fig. 20 Plot of the difference between $\Delta G_{\text{ads}}^{\circ}$ values calculated from equation (77) and from the Langmuir (L) isotherms for a given arbitrary solution concentration and various θ values.

equilibrium for various ΔG_{ads}^0 for a given solution concentration, would differ from those calculated for the same θ values and solution concentration on the basis of the configurational term $\theta/e^{(x-1)}(1-\theta)^x$. This difference, as a function of θ , may be expressed as

$$\frac{1}{RT} (\Delta G_{ads}^0 - \Delta G_{ads,L}^0) = (x-1) + (x-1) \ln (1-\theta) \quad (80)$$

for any given solution concentration (which does not enter into the determination of the difference of calculated ΔG_{ads}^0 values given by equation (80)). Especially when $\theta > \text{ca. } 0.3$, the ΔG_{ads}^0 derived from a series of experimental results will evidently depend quite appreciably on choice of the configurational $f(\theta)$ and the particular x value. It is evident that the lines of Fig. 20 will cross at an identical point for all x values when $\ln(1-\theta) = -1$, i.e., when $\theta = 0.63$ as seen from the Figure.

5. Remarks on the isotherm of Bockris and Swinkells and of Schuhmann

On the basis of the mass-action law applied to the quasi-chemical adsorption equilibrium process (23), Bockris and Swinkells^{64,94} derived the following isotherm

$$\frac{\theta}{(1-\theta)^x} \cdot \frac{[\theta + x(1-\theta)]^{(x-1)}}{x^x} = \frac{C_{org}}{C_W} \exp -\Delta G_{ads}^0 / RT \quad (81)$$

which differs from the other forms of isotherm considered earlier in this thesis. They wrote the mass-action equilibrium

constant in terms of an activity quotient expressed in terms of mole fractions in the interphase and bulk phase. Mole fractions were then subsequently converted to site fractions, i.e. θ terms, by means of the relations

$$n = \frac{\theta}{x - (x-1)\theta} = \frac{\theta}{\theta + (1-\theta)x} \quad (82)$$

or

$$\theta = nx / (1 - n + xn) \quad (83)$$

where n is the mole fraction of the organic adsorbate in the interphase. For molecules of solvent and adsorbate in the interphase, it does not seem appropriate to express the chemical potentials of species of different size in the interphase in terms of mole fractions and then derive a standard free energy of adsorption in terms of a mole fraction mass-action quotients.* As in the theory of polymer solutions, the thermodynamics of the system must be expressed ab initio in terms of site fraction (or volume fraction⁹⁰) statistics at the stage of expressing the relation for μ terms and hence ΔG_{ads}^0 for the substitutional adsorption process (23); that is, the mass-action quotient

$$\frac{(n_{org,ads}) (n_{W,soln})^x}{(n_{org,soln}) (n_{W,ads})^x}$$

used by Bockris and Swinkells to represent an equilibrium adsorption such as (23) is not appropriate when $x > 1$. Hence, equation (81) does not seem consistent with the lattice

* This may be readily demonstrated, for example, by calculating the chemical potential μ_p of polymer in a polymer solution in terms of mole fractions and then converting it to a corresponding value expressed in terms of site fractions. The result is incorrect and completely different from that derived by partial differentiation of the polymer partition function derived by means of site-fraction statistics (Flory-Huggins theory).

statistics required to deal with the problem of adsorption of a substance by substitution of a number of smaller, initially adsorbed solvent molecules. Alternatively, if mole fractions are used in equations such as (46), (47) or (51), a size-factor activity coefficient must be introduced, as in the treatment⁹⁶ of ionic solutions for the case where solute ions and solvent molecules differ significantly in size.

Equation (77), or the corresponding one with the configurational term (78), is therefore to be recommended in adsorption thermodynamic calculations for electrode interfaces. Of course, ΔG_{ads}^0 is normally a function of surface charge q_M and may also be dependent itself on coverage, reflecting significant interaction or solvent-structure³⁶ terms (co-sphere interactions) equivalent to the introduction of an activity coefficient for the adsorbate in the interphase^{37,97}. In these cases, equation (77) or an analagous one based on (78) would include the usual coverage-dependent interaction term^{38,82,98} $\exp(-g\theta^m)$ on the right hand side, depending on the force field of the interaction determined by m and the strength of the interaction determined⁸² by the proportionality factor g (or a in Frumkin's equation³⁸).

6. Significance of surface coverage terms in isotherms

The significance of differences between Γ and θ values can become important under certain conditions, especially when $x > 1$, and lead to errors in evaluation of free energy of adsorption.

The experimental quantity normally obtained from electrochemical adsorption measurements, based on capacitance or surface tension determinations, is the surface excess Γ . As is well known, this differs from the surface concentration by the quantity δC_0 of molecules that would, in any case, be in the interphase of thickness δ ⁹⁹, when the bulk concentration is C_0 . In adsorption from strong solutions or in weak adsorption from dilute solutions, δC_0 may be appreciable, e.g., 10-20% of Γ . The question then arises what quantity is to be used for θ in the configurational term of isotherms? Particularly when $x \gg 1$, the difference δC_0 can introduce an appreciable error in evaluations of ΔG_{ads}^0 using an isotherm of the form of (77), if θ is identified with Γ/Γ_{max} . Since all the particles in the interphase layer of thickness δ (we assume here for simplicity that δ corresponds to the thickness of a single molecular layer, e.g. as in short-range, specific adsorption in the compact double-layer, thus excluding diffuse-layer effects) are in contact with the surface, it might be supposed that θ should be taken equal to $\Gamma + \delta C_0$ divided by the saturation surface concentration. Such a proposition seems logical since once the $\Gamma + \delta C_0$ molecules are at the surface, it is impossible to distinguish between the Γ mole cm^{-2} that accumulate in the interphase because of the interaction with the surface and the δC_0 mole cm^{-2} that are in the interphase anyway. Thus, the surface forces are not "switched on" for only those molecules in the interphase of thickness δ

which correspond to the quantity Γ ; the accumulation corresponding to adsorption is, of course, a statistical effect. The total number of molecules per cm^{-2} , it seems, is what must constitute θ in the configurational term $\theta/(1-\theta)$ of the isotherm. A contradiction appears to arise, however, since only Γ mole cm^{-2} get attracted to the surface by the adsorption forces. If θ is defined as $\Gamma + \delta C_o$ then evaluations of ΔG_{ads}^o for adsorption from relatively concentrated solutions must take into account the δC_o term. The δC_o molecules in the interphase do not, however, have to displace solvent from the lamina at the surface but they will tend to interact with the metal surface like the Γ moles cm^{-2} of adsorbate.

Some clarification of which representation is correct may be given by examining the question in terms of chemical (or electrochemical, in the case of an electrode interphase) potentials; thus, the equilibrium of an adsorbate i between the interphase and the bulk phase is determined by the condition $\mu_{i,s} = \mu_{i,b}$ where s and b signify the surface and bulk phases, respectively. In the simplest case, $\mu_{i,s}$ can be expressed in terms of the surface mole fraction $X_{i,s}$, i.e.

$$\mu_{i,s} = \mu_{i,s}^o + RT \ln \frac{n_{i,s}}{n_{i,s} + n_{j,s}} = \mu_{i,b}^o + RT \ln a_{i,b} \quad (84)$$

where $n_{i,s}$ and $n_{j,s}$ are defined as the actual numbers of moles per cm^2 of adsorbate i and solvent j in the interphase

lamina s. The bulk activity $a_{i,b}$ can also be expressed in terms of mole fraction of i in a lamina of bulk solution of the same thickness δ , redefining $\mu_{i,b}$ as

$$\mu_{i,b}^{\circ'} + RT \ln \frac{n_{i,b}}{n_{i,b} + n_{j,b}}$$

Then, for isomegethic ($x = 1$) molecules of solvent and adsorbate, and in the absence of striction in the interphase, $n_{i,s} + n_{j,s} = n_{i,b} + n_{j,b}$, so that the following simple distribution relation results:

$$n_{i,s} = n_{i,b} \exp(-\Delta\mu_{ads}^{\circ}/RT) \quad (85)$$

The surface excess Γ is then given by the difference

$$n_{i,s} - n_{i,b} = n_{i,b} (\exp(-\Delta\mu_{ads}^{\circ}/RT) - 1) = \Gamma \quad (86)$$

from which it is readily seen that Γ is not expressible directly by the distribution equation (85), relating interphase and bulk phase concentrations (Henry's Law isotherm) through $\exp(-\Delta\mu_{ads}^{\circ}/RT)$. Only in the case of a small standard free energy adsorption ($\Delta\mu_{ads}^{\circ}/RT \ll 1$) can we directly relate Γ to $\Delta\mu_{ads}^{\circ}/RT$ and $n_{i,b}$, viz.

$$\Gamma = n_{i,s} - n_{i,b} = -n_{i,b} \frac{\Delta\mu_{ads}^{\circ}}{RT} \quad (87)$$

The above discussion demonstrates that θ in the isotherm must be based on the total surface concentration,

rather than net surface excess in cases where solution concentrations of adsorbate molecules are appreciable.

A problem of a different kind arises when an isotherm of the Frumkin type³⁸ is involved which takes into account long-range lateral interaction effects. For such a case, the isotherm, in a general form, is

$$\frac{\theta}{1-\theta} = (K' \exp -g\theta) C_o = KC_o \quad (88)$$

i.e. where the adsorption equilibrium constant K is a function of θ . K usually decreases with increasing θ in many adsorption processes, where repulsion forces^{36,82,97} or solvent structure changes³⁶ in the interphase are significant. The question then arises what " θ " is to be used in the interaction term $\exp -g\theta$? θ certainly cannot be taken simply as $\Gamma/\Gamma_{\max}$ since the lateral interactions to be considered in the isotherm must certainly involve all the molecules in the interphase, i.e. $\Gamma + \delta C_o$, irrespective of those which have become accumulated there (the Γ quantity) on account of the surface forces. Again, the total surface concentration is to be used.

The question finally arises what will be the magnitude of errors resulting from neglect of the correction term $C_o \delta$ in the surface coverage factor? For relatively weak adsorption, the correction term could amount to, say, 50% of the measured Γ and thus change θ by a factor, say, of 2 at the worst. While the error in any calculation of ΔG_{ads}^o would still be relatively

small ($< \text{ca. } 0.4 \text{ kcal mole}^{-1}$) in the Langmuir case, it could become more serious for adsorption of molecules, e.g., pyridine^{36,37} or phenol where¹⁰⁰ x is appreciable (3-4).

7. Standard states in isotherms

The question of the choice of standard states in isotherms is somewhat arbitrary. A variety of standard states can be chosen depending on how the experimental results are to be treated. However, the standard states have to be specified at the stage of derivation of the isotherm. For adsorption of a gas on a solid surface, the Langmuir isotherm is simply derived by equating the rate of adsorption to the rate of desorption of the gas. In such a derivation, no standard states for the system are explicitly defined. In the statistical derivation, standard states for the Langmuir isotherm are unit pressure in the gas phase and half coverage in the adsorbed layer (see e.g. ref.¹⁰¹).

For the Langmuir isotherm, applicable⁶³ to adsorption from solution (of equal sized molecules), convenient standard states are unit site fractions of both the adsorbate and the solvent in the surface phase, and unit mole fractions in solution. Similar standard states have been assumed in the derivations of the isotherm functions (62) and (77).

One can also assume standard states of unit molar concentrations for both adsorbate and solvent in the solution phase, together with unit coverages in the surface phase.

Standard states of unit mole fraction in the surface phase were assumed by Bockris and Swinkells⁶⁴ in deriving the isotherm constituting equation (81). Surface concentrations for unequal sized molecules when expressed in mole fraction units differ significantly from the corresponding quantities expressed in site fractions. In the case of large molecules, surface coverage may approach saturation even though the mole fraction of the molecules on the surface remains relatively low, e.g. molecules three times as big as water molecules may occupy half of a surface (i.e. $\theta = \frac{1}{2}$), though the mole fraction would be only $\frac{1}{4}$. Thus, it appears unsatisfactory to express surface concentrations of adsorbed solute and solvent in terms of mole fractions when molecules differ appreciably in size.

C. Adsorption of Pyrazine and Pyridine at the Hg Electrode

1. Free energy of adsorption

(i) Evaluation of ΔG_{ads}° for pyrazine and pyridine

The surface excess data for pyrazine and pyridine were employed in a Langmuir isotherm ($x = 1$, see below) and in the isotherm relation (64) which takes into account the relative size of the adsorbate and solvent molecules. The apparent standard free energies of adsorption, ΔG_{ads}° , were evaluated at various surface charge densities q_M . The ΔG_{ads}° corresponding to the true Flory-Huggins relation (77) could be obtained by

subtracting $RT[\ln x - (x-1)]$ from the values calculated from relation (64). $x=3$ was taken as the most probable size ratio for pyrazine (or pyridine) and water based on Courtauld space-filling models⁹⁴. Plots of ΔG_{ads}^0 as function q_M are shown for pyrazine at various θ values in Fig. 21. Results for pyridine adsorption from the thesis of Gordon⁶⁰ are shown for comparison at one comparable coverage. Fig. 22 shows adsorption results for pyridine, obtained by the present author.

It is of importance to note, from the theoretical point of view (see below), that the ΔG_{ads}^0 curves for pyrazine should be symmetrical in shape with respect to $\pm q_M$ values around the zero charge value ($q_M=0$) (Fig. 21). The minima are actually at $q_M = -2 \mu\text{C cm}^{-2}$. Very few molecules that are sufficiently soluble in water for experiments to be conducted are electrically neutral in the sense of having zero net dipole moment. Dioxane approaches this category but is not flat and may exhibit a dipole moment in a field⁶⁵ corresponding to the boat conformation. For a molecule that is electrically and chemically symmetrical, the electrostatic theory of competitive adsorption between solute and solvent at the Hg electrode predicts a symmetrical variation of free energy of adsorption with changing field or surface charge around the zero-charge potential. For the case of pyridine^{36,59}, it is seen (Fig. 22), as expected, that the molecule is adsorbed much more strongly on the negatively charged electrode than on the positive one. This is due⁵⁹ to the more favorable interaction of the N-end of

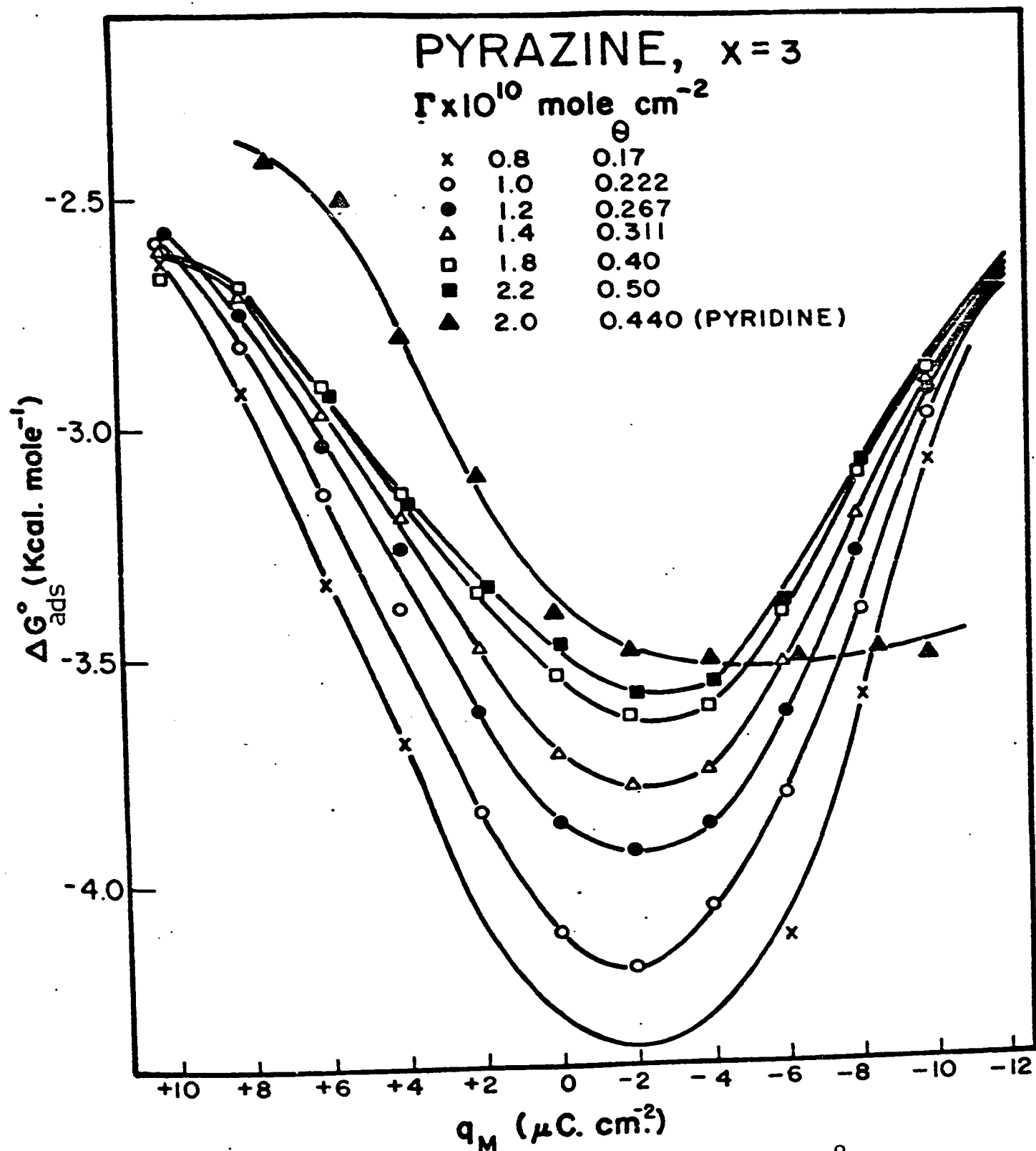


Fig. 21 Variation of $\Delta G^{\circ}_{\text{ads}}$ of pyrazine at 20° as a function of q_M at various θ values (data for one coverage by pyridine⁶⁰ is included for comparison).

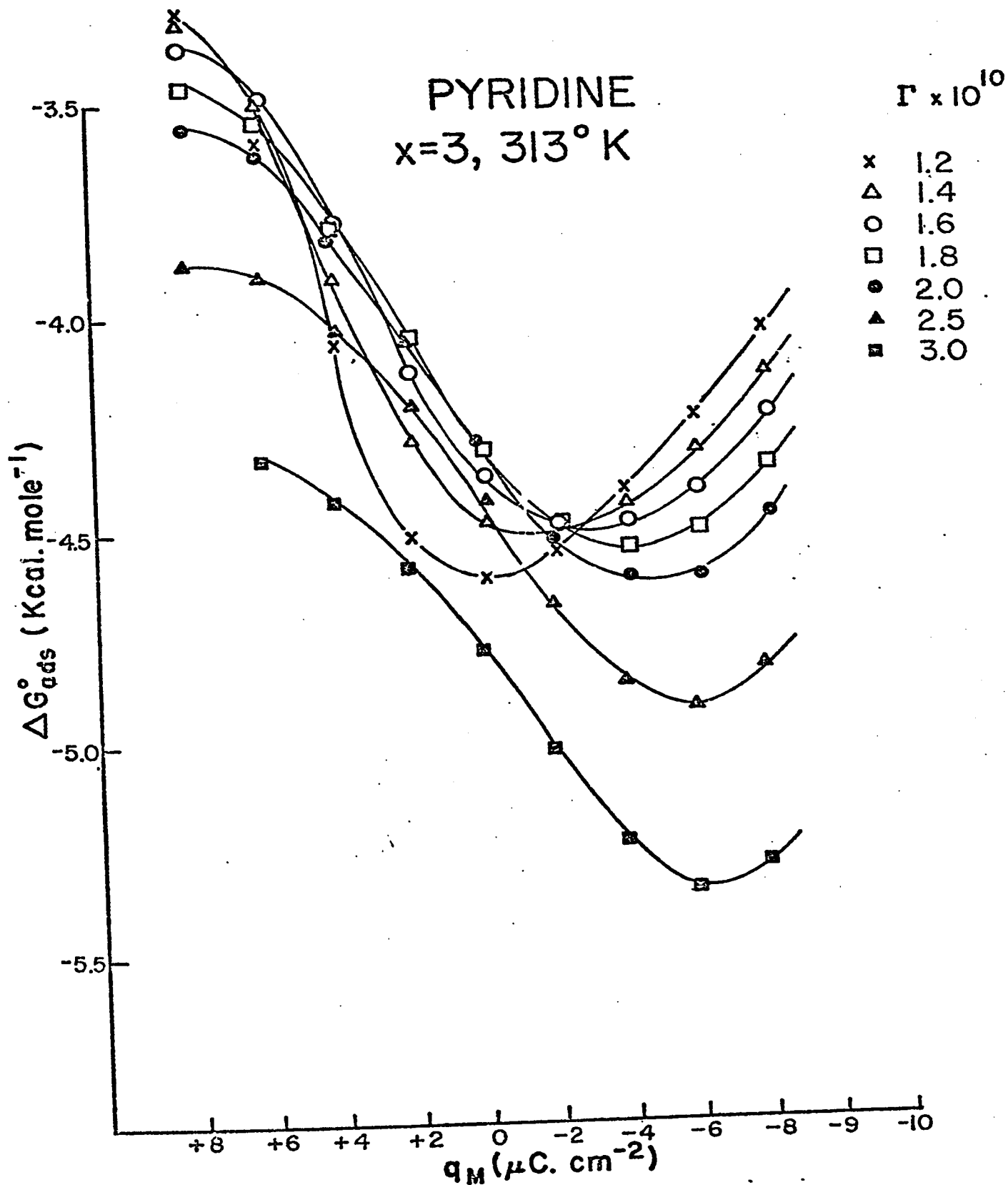


Fig. 22 Apparent standard free energy of adsorption ΔG_{ads}° of pyridine at Hg/H₂O interface at 40°C as function of q_M and coverage (calculated for $x = 3$).

the adsorbed oriented molecule with the water solvent when the molecule is oriented with the N atom away from the Hg surface when the latter is negatively charged than when it is positively charged; under the latter conditions, the molecule is oriented in the opposite direction or, more probably (see below), flat in the interphase. The symmetrical nature of the $\Delta G_{\text{ads}}^{\circ}$ vs q_M curves for pyrazine provides strong support for this interpretation of pyridine adsorption (if the pyridine was oriented flat on the Hg surface at all potentials, this asymmetry in comparison with the pyrazine behavior would not arise).

(ii) Comparison of theoretical and experimental
 $\Delta G_{\text{ads}}^{\circ}$ for pyrazine

Because of the symmetry and rigidity of the pyrazine molecule, the form of the $\Delta G_{\text{ads}}^{\circ}$ vs q_M relations in Fig. 21 provides a particularly useful case for comparison with theoretical predictions that may be made for interacting and non-interacting oriented water dipoles according to Bockris, Devanathan and Müller's development²⁵ of the treatment of Mott and Watts-Tobin^{47,48} for orientation of water molecules at an electrode surface.

For an adsorbate which displaces x water dipoles, it has been shown in Section B of this Chapter that the isotherm is^{25*} (cf. equations (21) and (77)).

*In the original paper²⁵, no x factor was included in the configurational term $\theta/(1-\theta)$ although x was correctly introduced in the expression for ΔG° .

$$\frac{\theta}{e^{(x-1)}(1-\theta)^x} = \frac{C_{org}}{55.5} \exp -\Delta G_{chem}^0/RT \cdot \exp \{-xB(\mu F - BUc)/kT\} \quad (89)$$

where ΔG_{chem}^0 is the maximum free energy of adsorption when there is no net water orientation, other terms being as defined before. The argument of the exp term in B represents the variation of net free energy of adsorption with field and is analogous to the earlier Butler term⁴⁰ for the difference in the polarization of adsorbate and solvent.

Fig. 23 shows how the function $\exp\{-xB(\mu F - BUc)/kT\}$ depends on the surface charge $\pm q_M$ (this function is symmetrical in q_M about the axis $q_M=0$) for $Uc/kT = 0, 3$ or 6 and for $x = 1$ or 3 , the latter figure being the most reasonable for pyrazine as indicated by space-filling models. Corresponding values of B as a function of $\pm q_M$ are also shown and represent the changing solvent orientation corresponding to the variation of free energy of adsorption of the solute with the field. For a given value of x, the breadth of the curve of $\exp f(B, F)$ in terms of $\pm q_M$ or μF at half its height (cf.¹⁰²) should give a basis for the estimation of the solvent dipole interaction parameter, Uc/kT , in terms of the following analysis.

For any conditions, the standard molar free energy of adsorption ΔG_{ads}^0 in equation (77) is given through equation (89) as

$$\exp -\Delta G_{ads}^0/RT = \exp -\Delta G_{chem}^0/RT \cdot \exp \{-xB(\mu F - BUc)/kT\} \quad (90)$$

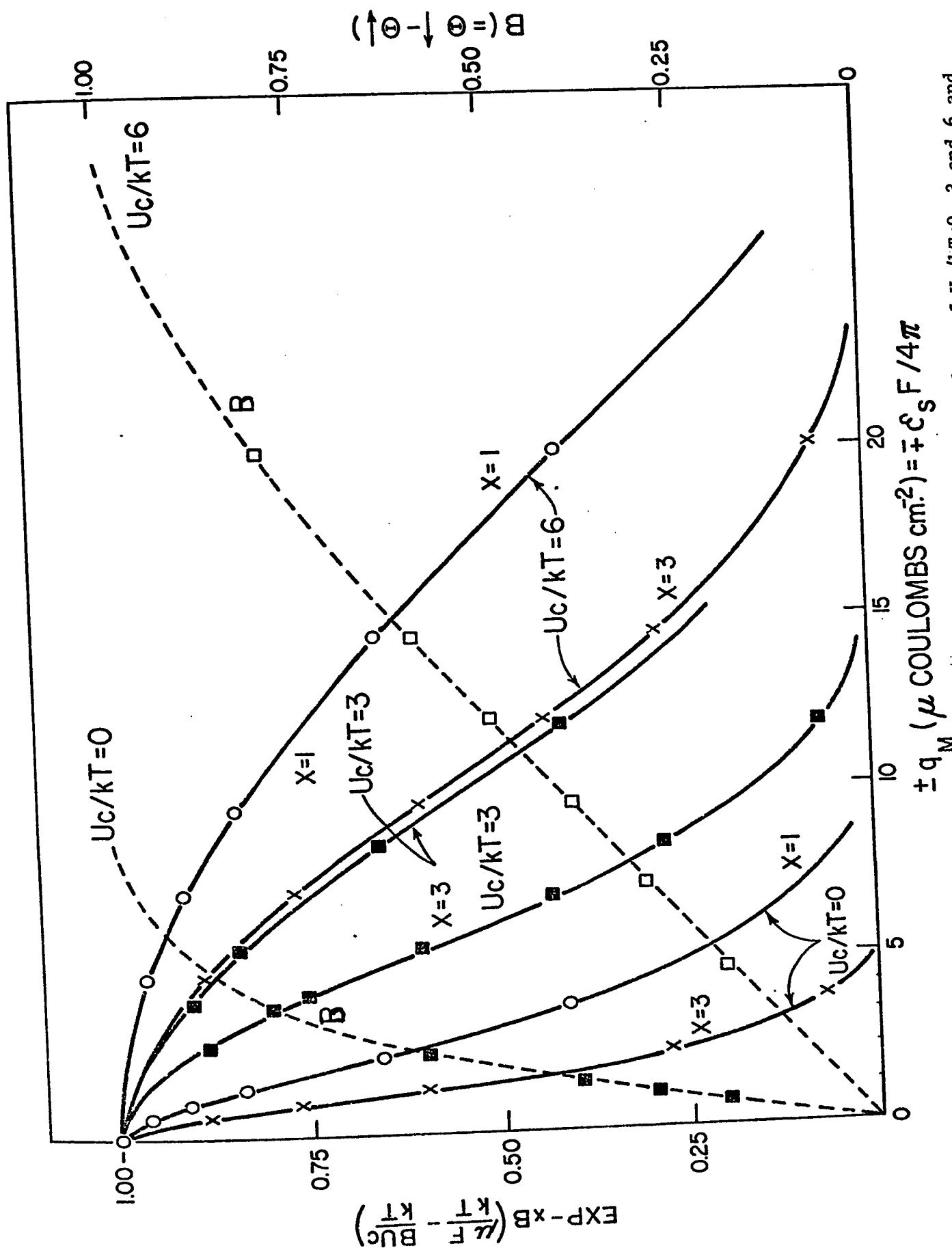


Fig. 23 Variation of the function $\exp -B(\mu F - BU_C)/kT$ with $\pm q_M$ for values of $U_C/kT=0, 3$ and 6 and for $x=1$ or 3 (calculated for $T=298^\circ K$). Values of the orientation function B are also shown as $f(q_M)$.

or ,

$$\exp -xB(\mu F - BUc)/kT = \exp(\Delta G_{\text{chem}}^{\circ} - \Delta G_{\text{ads}}^{\circ})/RT = f(B, F) \quad (91)$$

The right-hand side of equation (91) can be calculated as $f(q_M)$ from the experimental values of free energy of adsorption ($\Delta G_{\text{ads}}^{\circ}$) and the maximum (negative) free energy of adsorption ($\Delta G_{\text{chem}}^{\circ}$) which arises at $q_M = -2 \mu C \text{ cm}^{-2}$. Such plots at various θ values are shown in Fig. 24 for adsorption of pyrazine. Comparison of Figs. 23 and 24 shows that when $\theta = 0.22$ the interaction parameter, Uc/kT , for the water dipoles may be estimated as 2. From equation (90), it is now possible to estimate $\Delta G_{\text{ads}}^{\circ}$ from the value of $\Delta G_{\text{chem}}^{\circ}$ and the water orientation contribution to the free energy, $f(B, F)$, when $Uc/kT = 2$, and compare it with the experimental values of $\Delta G_{\text{ads}}^{\circ}$. Such a comparison is shown in Fig. 25. The agreement is very good over the whole curve. It is surprising to find that the variation of $\Delta G_{\text{ads}}^{\circ}$ with q_M is fitted well for a value of Uc of only $2kT$. This is much less than the maximum lateral interaction of two oriented water dipoles (ca. $9kT$) and suggests that orientation of water at charged interfaces, over the accessible range of q_M values, is rather less than that corresponding to the limiting $\uparrow$ or $\downarrow$ states considered by Bockris, Devanathan and Müller²⁵. Presumably there is a cooperative effect amongst groups of solvent molecules in the interphase (cf. correlation effects in dielectric theory) involving only partial orientation of individual molecules.

PYRAZINE

$x=3, T=293^{\circ}\text{K}$

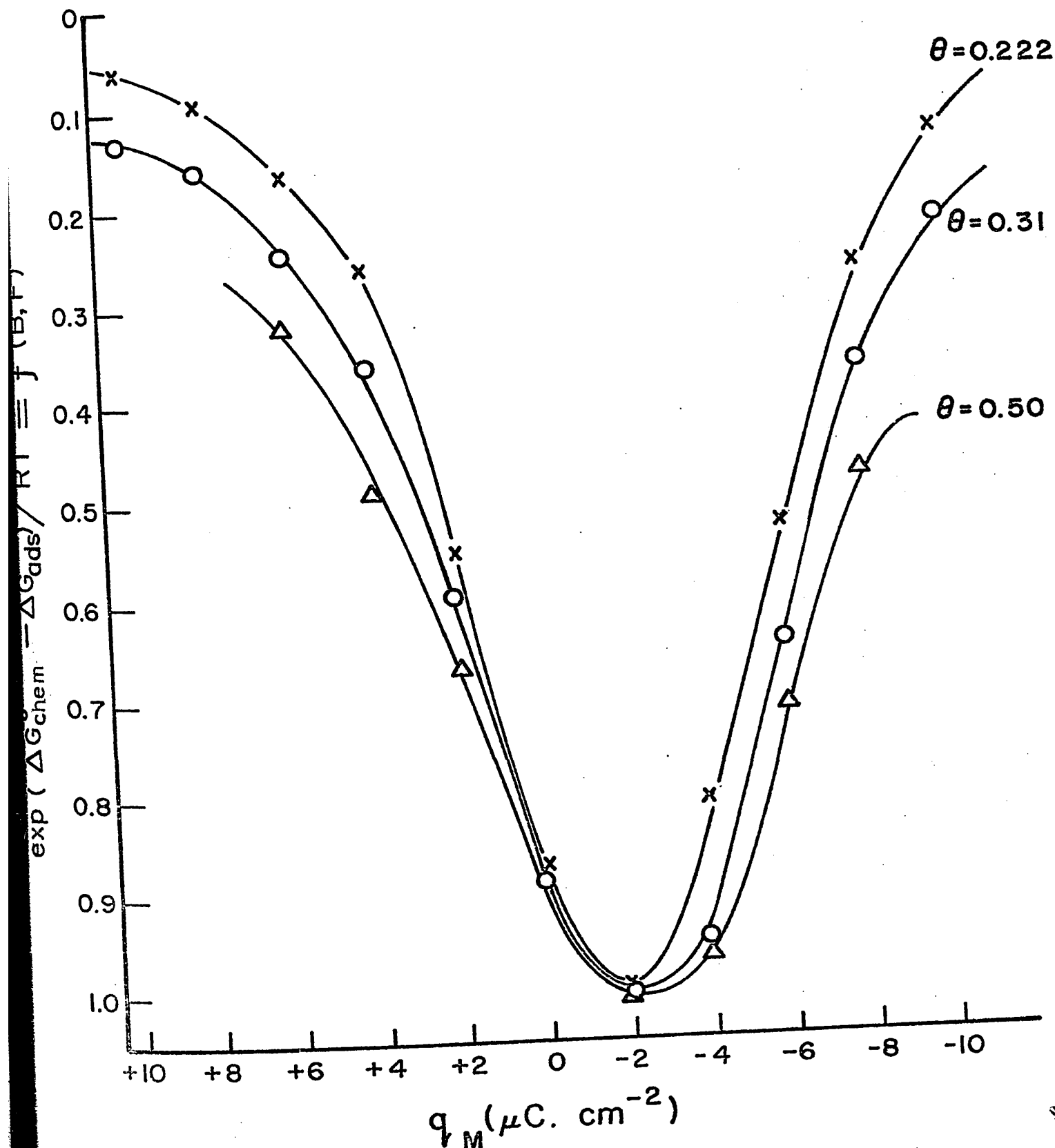


Fig. 24 Plot of $\exp(\Delta G_{\text{chem}}^{\circ} - \Delta G_{\text{ads}}^{\circ})$ as $f(q_M)$ and θ for pyrazine ($x=3$, $T=293^{\circ}$).

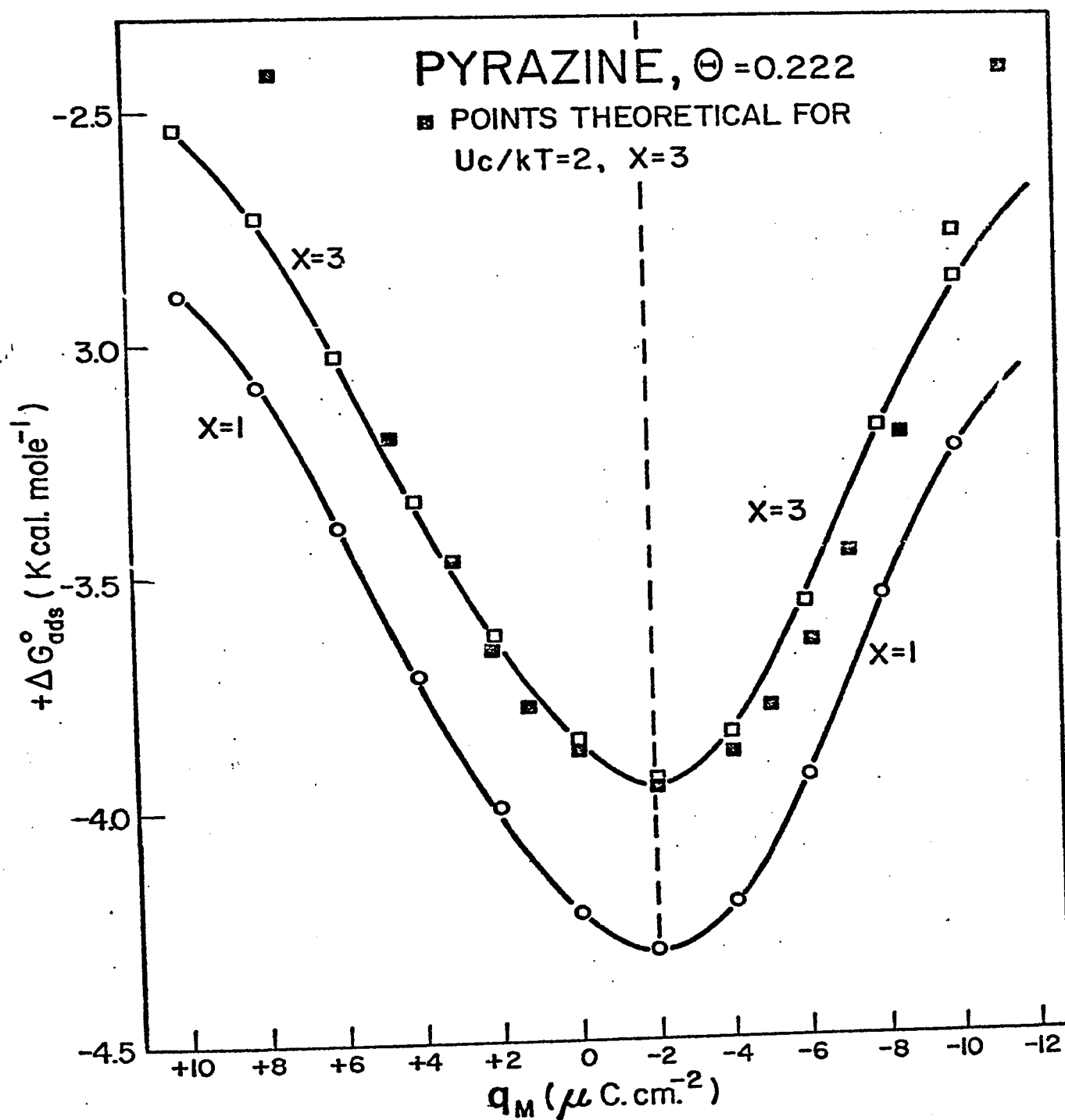


Fig. 25 Fit to the variation of $\Delta G_{\text{ads}}^{\circ}$ for pyrazine adsorption with q_M for $U_c/kT = 2, x = 3$, using equation (90); data for 308°K.

This is consistent with Mott and Watts-Tobin's view⁴⁷ that only a component of the water dipole is oriented in the field.

A further conclusion of general importance from Figs. 23 and 25 is that when a realistic value of x is taken into consideration in equation (89), i.e. $x > 1$, then the breadth of the curve representing variation of free energy of adsorption with q_M (Fig. 23) becomes narrower for a given value of Uc/kT as $x > 1$. Thus, the adsorption becomes more sensitive to solvent orientation, through q_M , as the number of solvent molecules x which must be displaced becomes larger, as may be expected. Correspondingly, a smaller value of Uc/kT is required to account for experimental results when a realistic value of x (>1) is employed in equations (89) or (90).

Comparisons of the results in Figs. 21 and 22 for pyrazine and pyridine in relation to the conclusions made above regarding the role of water orientation in accounting for the experimental variation of ΔG_{ads}^0 with q_M (Figs. 21 and 25), indicate that the variation of ΔG_{ads}^0 with q_M for pyridine on the positive branch ($q_M = +ve$) can be mainly accounted for by solvent orientation rather than pyridine-field interaction, i.e. pyridine, like pyrazine, probably lies flat in the interphase when q_M is positive. Elsewhere (see Section C.3.), we show that the similar Esin and Markov effects which are observed for pyridine and pyrazine when q_M is positive, give support for this conclusion about pyridine orientation.

Also, comparing pyrazine with pyridine, the symmetry of the curves of $\Delta G_{\text{ads}}^{\circ}$ as a $f(q_M)$ means that the "chemical" component of the free energy of adsorption, $\Delta G_{\text{chem}}^{\circ}$ (equation²⁵ (89)) is independent of q_M and the change of free energy arises by displacement of solvent whose orientation and interaction with the field is a $f(q_M)$. However, with pyridine there is real change of $\Delta G_{\text{chem}}^{\circ}$ with q_M due to orientation of the pyridine molecule itself.

(iii) Dependence of $\Delta G_{\text{ads}}^{\circ}$ on coverage θ

The $\Delta G_{\text{ads}}^{\circ}$ vs q_M curves for pyrazine (Fig. 21) lie at progressively larger (less negative) values of $\Delta G_{\text{ads}}^{\circ}$ as θ increases. This behavior is found for $x = 1, 2$ or 3 ($x = 3$ is the geometrically justified value for pyrazine and pyridine). If the data were calculated for $x > 3$, e.g. 4 or 6, the $\Delta G_{\text{ads}}^{\circ}$ vs q_M curves do not present themselves in a sensible order with increasing θ , so that the data for $x = 3$ are to be preferred. Extrapolations (cf. ref.¹⁰³) to obtain $\Delta G_{\text{o,ads}}^{\circ}$ (equation (43)) were not attempted, owing to the difficulty of obtaining data of sufficient accuracy in Γ below $\theta = 0.15$.

In the pyrazine case, there is an appreciable variation of $\Delta G_{\text{ads}}^{\circ}$ with coverage (Figs. 26 and 21) not only at finite q_M but also at the potential of zero charge. This cannot be attributed to long-range dipole repulsion⁵⁹ within a layer of oriented pyrazine molecules since, with pyrazine, the

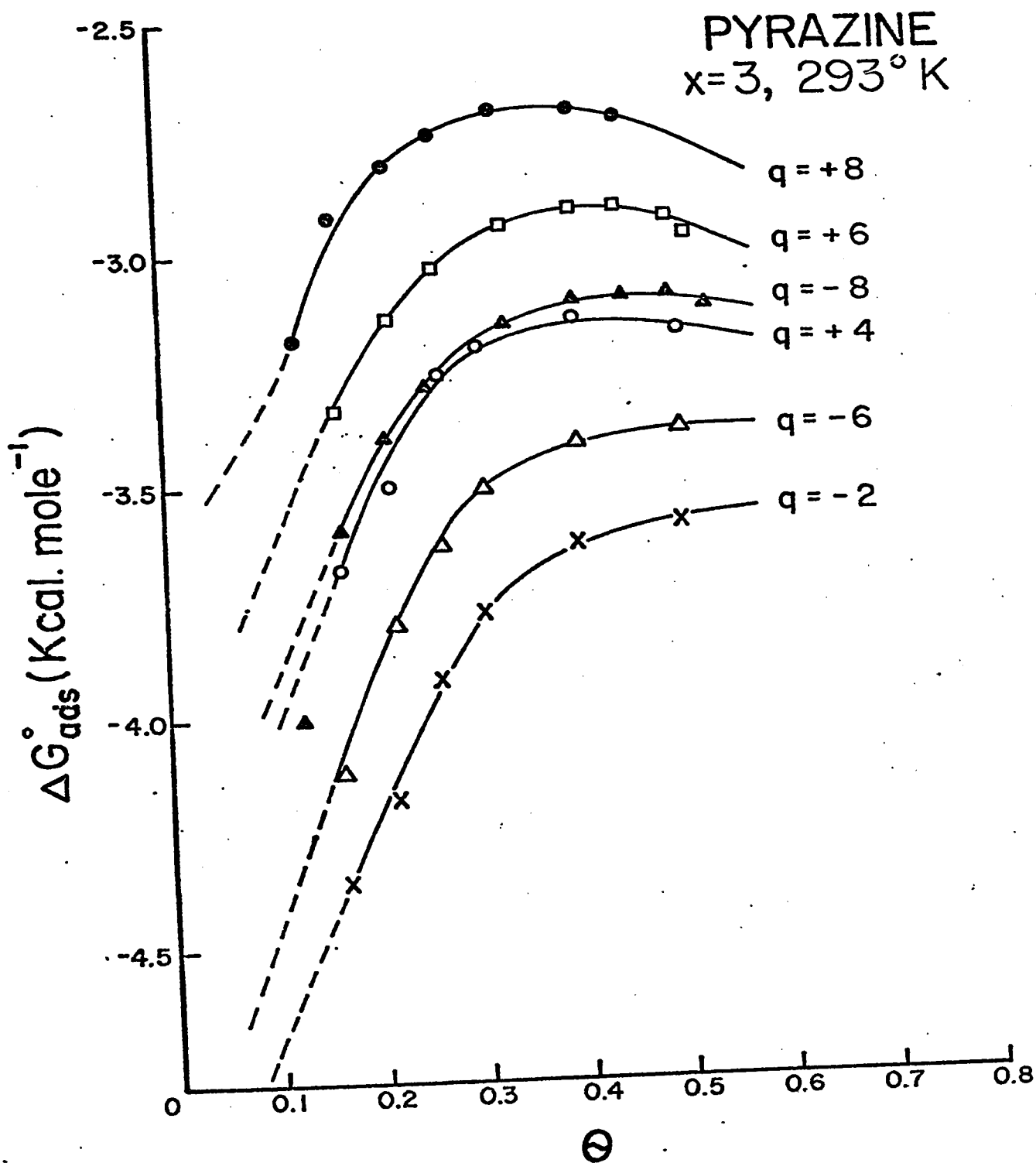
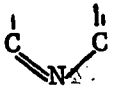


Fig. 26 Variation of $\Delta G^{\circ}_{\text{ads}}$ with θ by pyrazine for several values of q_M at Hg at 293°K .

net dipole orientation tendency will be virtually absent in comparison with the case of pyridine (although effects of field heterogeneity on the local  in pyrazine may be significant).

An important conclusion from Figs. 21 and 26 is hence that the variation of $\Delta G_{\text{ads}}^{\circ}$ with θ at a given q_M is probably due more to changing energy of solvent replacement (see below) with increasing coverage by pyrazine than it is to simple electrostatic effects. Such a variation of solvent replacement energy presumably arises from effects in 2-dimensions analogous to the co-sphere hydration interactions familiar in 3-dimensional solutions of organic ions and molecules¹⁰⁴. Such effects are supported by the entropy/enthalpy compensation effects discussed below and the variation of heat of adsorption with coverage which is much larger than the variation of $\Delta G_{\text{ads}}^{\circ}$ with coverage.

As the coverage by pyrazine increases towards $\theta = 0.5$, the depth of the bell-shaped curves diminishes (Fig. 21), and the interaction between water dipoles increases (cf. Figs. 23 and 24), e.g., as θ for pyrazine increases from 0.2 to 0.5, the interaction parameter U_c/kT for water dipoles increases from 2 to 3. This effect is, presumably, related to water-pyrazine interactions on the surface. At higher coverage, interactions between solvated pyrazine molecules are expected to become greater while any two-dimensional structure of water previously in the interphase will become changed.

Fig. 27 shows $\Delta G_{\text{ads}}^{\circ}$ vs θ plots for pyridine. Comparison of Figs. 26 and 27 for pyrazine and pyridine reveals that at lower coverages and for positive q_M , the adsorption behavior of pyrazine is similar to that of pyridine and both show apparent repulsive interaction amongst the molecules on the surface (i.e. $\Delta G_{\text{ads}}^{\circ}$ increases with θ). At higher coverages and for negative q_M the pyridine molecule become oriented* and its adsorption then becomes more favored as is evident from the decreasing $\Delta G_{\text{ads}}^{\circ}$ values with increasing θ (Fig. 27).

2. Entropy and enthalpy of adsorption of pyrazine and pyridine at the Hg surface

From the adsorption measurements at various temperatures, isosteric entropies and heats of adsorption were evaluated at fixed q_M values for various coverages. The various types of heats of adsorption that may be evaluated have been referred to in a previous publication³⁶, following the definitions of Everett⁸³. Here, the heat of adsorption evaluated is equivalent to Everett's $\bar{H}_a - \bar{H}_s$ where $\bar{H}_s$ is the partial molar heat content of the adsorbate in solution and $\bar{H}_a$ that in the adsorbed phase; $\bar{H}_a$ is defined as $(\partial H_a / \partial n_a)_{T,P,A}$ where H_a is the enthalpy of the adsorbed phase, n_a the number of moles of adsorbate in that phase and A is the area per

* More conclusive evidence for this statement is given by the Esin and Markov results and surface pressure behavior to be discussed in Section E of this Chapter.

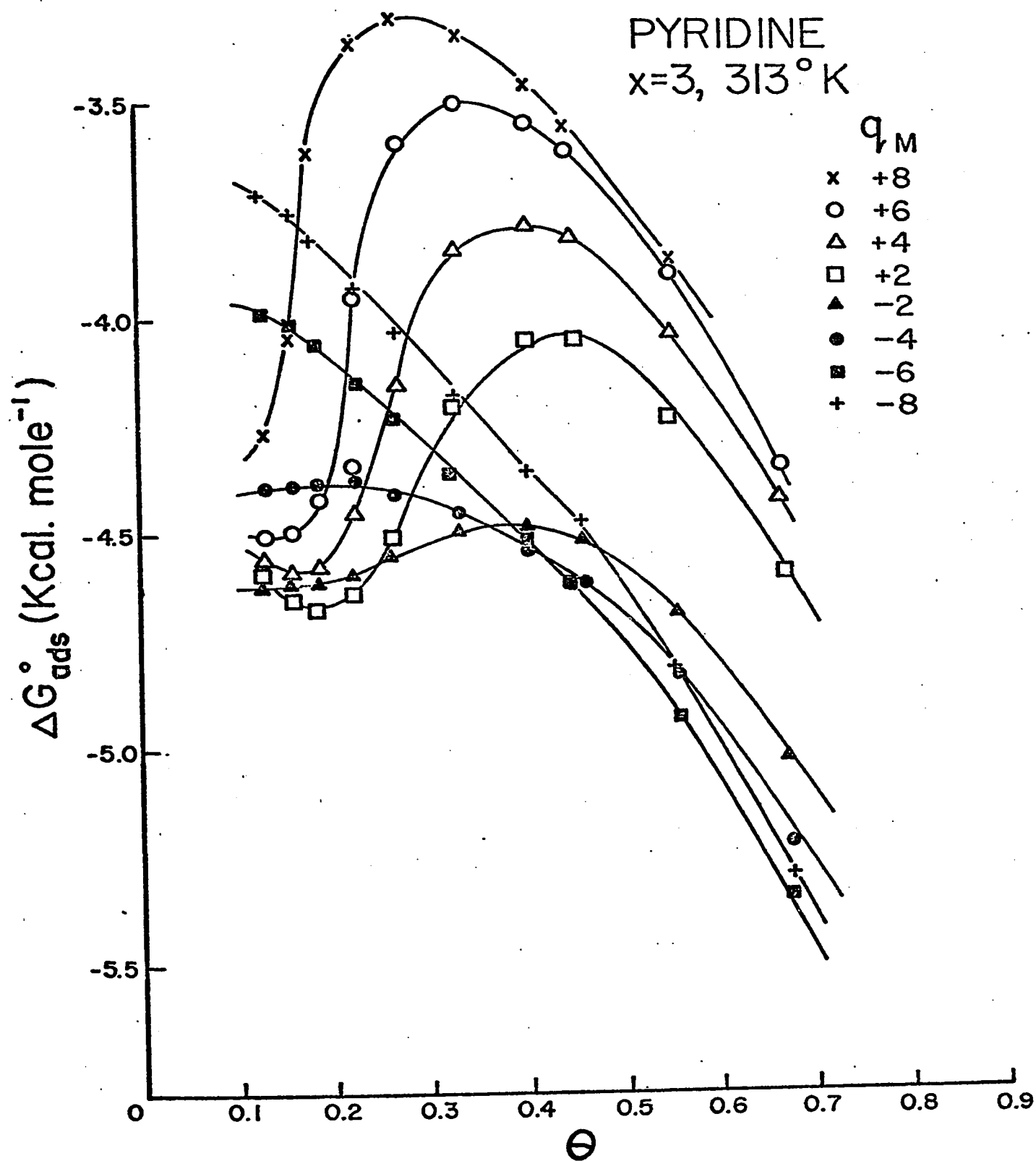


Fig. 27 Variation of $\Delta G^{\circ}_{\text{ads}}$ with θ by pyridine for several values of q_M at Hg at 313°K .

molecule. In addition, under the present electrochemical adsorption conditions, it is necessary¹⁰⁵ to add another restriction in the partial differential, viz. that of constant q_M .

With the ΔG_{ads}^0 values at several temperatures, the standard entropies of adsorption ΔS_{ads}^0 can be evaluated from the thermodynamic relation, $\Delta G = \Delta H - T\Delta S$, for the same standard conditions as those defining ΔG_{ads}^0 . Plots of ΔG_{ads}^0 vs T , in most cases, gave straight lines. Where a straight line relationship was not obtained, mean ΔS_{ads}^0 values were calculated from the best straight line that could be drawn through the data.

The course of the ΔS_{ads}^0 and ΔH_{ads}^0 functions with q_M are shown in Figs. 28 and 29, respectively, for pyrazine at various θ values. ΔS_{ads}^0 has a minimum negative value at the lowest coverage. Negative values of ΔS_{ads}^0 indicate that adsorption is relatively unfavorable at higher temperatures, i.e. in terms of the molecular picture for the adsorption, it becomes more difficult to displace water molecules from the surface. At a fixed coverage, ΔS_{ads}^0 become more positive with increasing orientation of water dipoles as $\pm q_M$ increases. This can arise because, when oriented water is substituted by pyrazine, negative entropy associated with the orientation is released so that a positive entropy contribution to the entropy of adsorption arises. This effect is also reflected in the fact that at higher temperatures the extent of water orientation

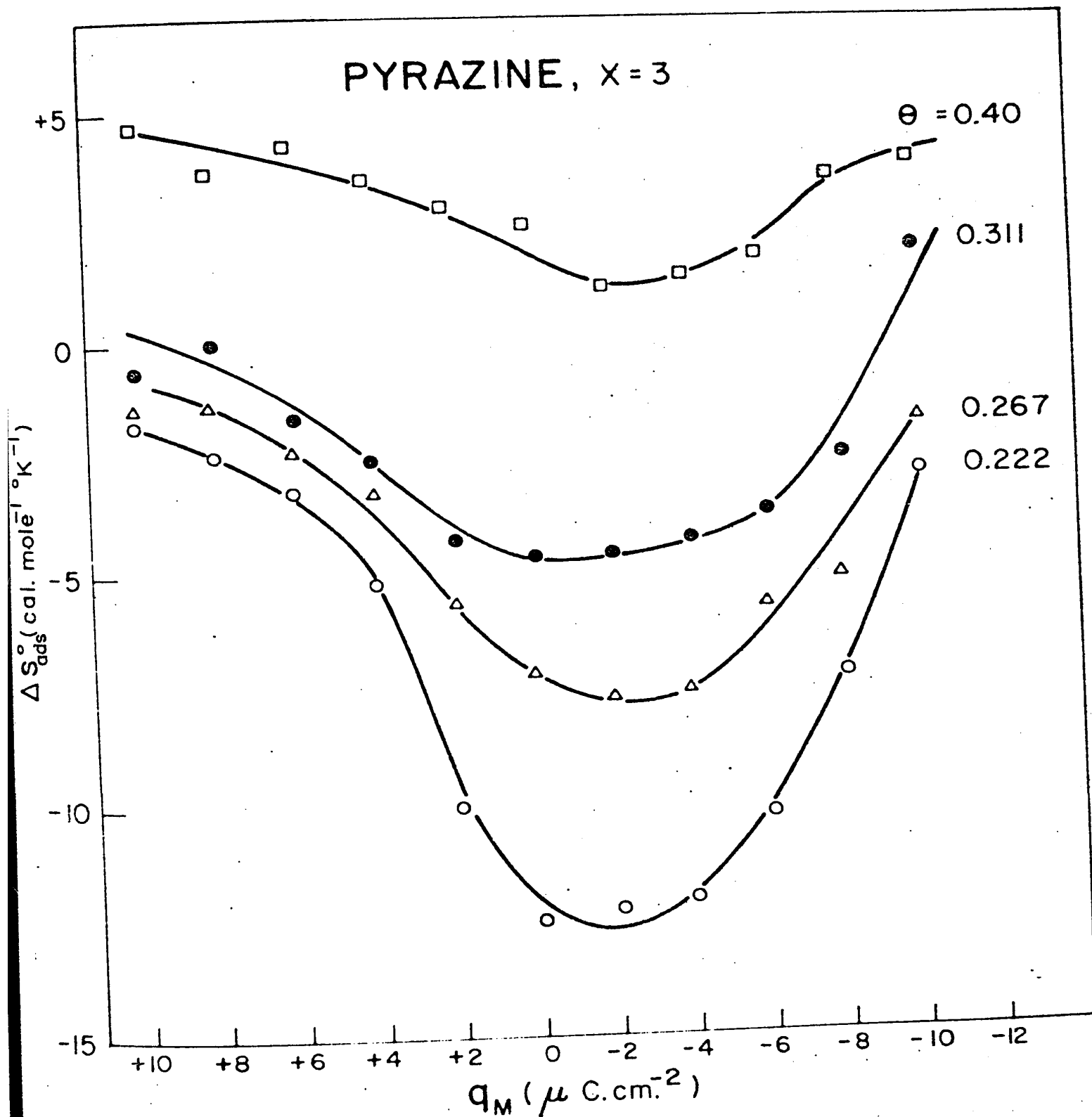


Fig. 28 $\Delta S_{\text{ads}}^{\circ}$ for pyrazine at the Hg electrode as a function of q_M for various values of θ .

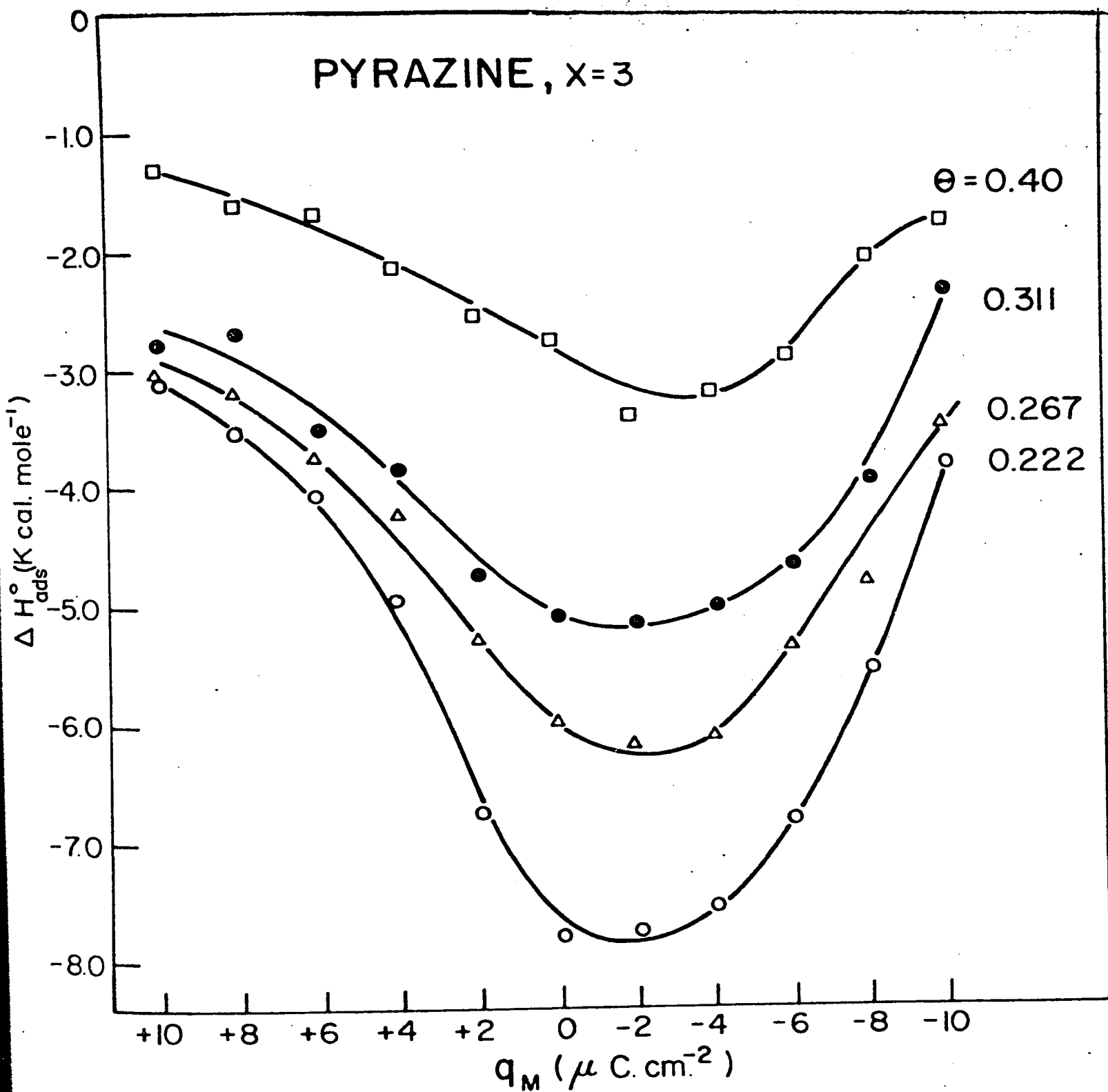


Fig. 29 $\Delta H_{\text{ads}}^{\circ}$ for pyrazine at the Hg electrode as a function of q_M for various values of θ .

at a given q_M will normally be less than at lower temperatures (see p.158), so that substitution by pyrazine will involve a more negative free energy change.

Fig. 30 shows that there is a substantial compensation between ΔH_{ads}° and ΔS_{ads}° , typical¹⁰⁶ of solvent-structure effects in solvation associated with the aqueous medium. As can be seen, at different q_M values, the ΔH_{ads}° vs ΔS_{ads}° plots are linear and have the same slope of 292°K. A slope of 298°K at 25°C corresponds to complete compensation.

It seems that an optimum heat of adsorption of pyrazine arises (Fig. 29) when water is least oriented allowing optimum lateral H-bonding interactions between water and pyrazine N atoms lying in the interphase. This would also correspond to minimum entropy of the adsorbed pyrazine. Similar effects arise at the air-water interface (see Section D of Chapter IV, Part I).

When there is complete compensation between ΔS_{ads}° and ΔH_{ads}° , the following analysis of Fig. 30 is useful. The experimental ΔG_{ads}° can be written as (cf. equation (90))

$$\Delta G_{ads}^{\circ} = \Delta G_{chem}^{\circ} + xB\left(\frac{\mu F}{kT} - \frac{BUc}{kT}\right) RT \quad (92)$$

Also,

$$\Delta G_{ads}^{\circ} = \Delta H_{ads}^{\circ} - T\Delta S_{ads}^{\circ} \quad (93)$$

From Fig. 30, ΔH_{ads}° at different q_M can be expressed as

$$\Delta H_{ads}^{\circ} = C(q_M) + T\Delta S_{ads}^{\circ} \quad (94)$$

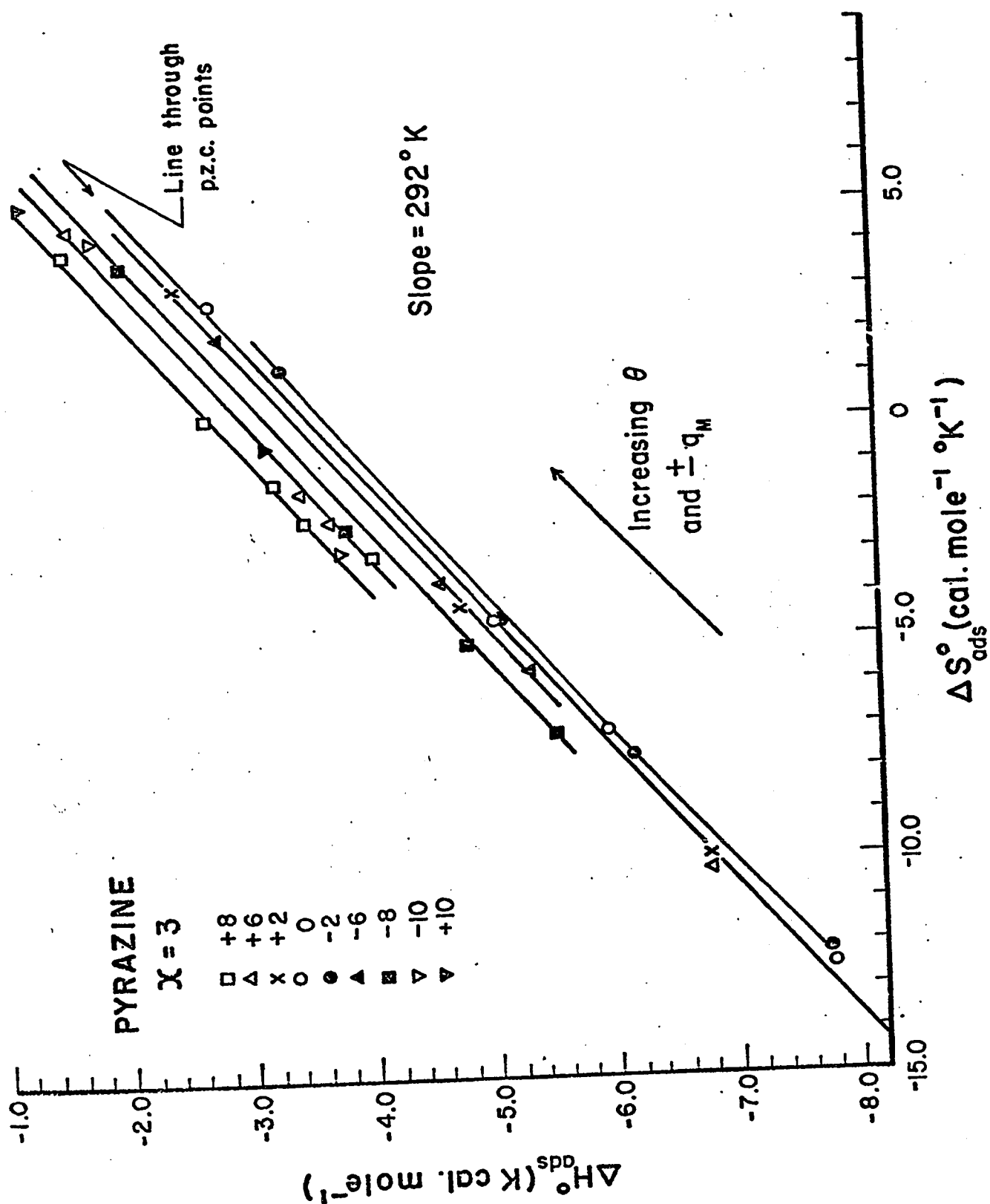


Fig. 30 Compensation effect between ΔH_{ads}° and ΔS_{ads}° for various values of θ and q_M in pyrazine adsorption at Hg.

where $C(q_M)$ is the intercept of the $\Delta H_{ads}^{\circ} - \Delta S_{ads}^{\circ}$ straight lines at $\Delta S_{ads}^{\circ} = 0$. From equations (92), (93) and (94),

$$C(q_M) = \Delta G_{chem}^{\circ} + xB\left(\frac{\mu F}{kT} - \frac{B\mu c}{kT}\right) RT \quad (95)$$

so that the intercepts $[C(q_M)]$'s are actually the standard electrochemical free energies of adsorption at a certain coverage (depending on q_M) when $\Delta S_{ads}^{\circ} = 0$.

For pyridine, ΔS_{ads}° vs q_M curves are shown in Fig. 31. These plots are not obviously symmetrical like those for pyrazine (Fig. 28), and are not easy to interpret. For positive q_M and at low θ for pyridine (up to ca. $\Gamma = 2.2 \times 10^{-10}$ mole cm^{-2}), interpretations applicable to pyrazine seem to apply. However, with increasing θ and negative q_M , the pyridine molecule itself orients from the flat to the upright position. By virtue of the dipole in pyridine, interaction of the molecule with the double-layer field is possible and the behavior of ΔS_{ads}° with respect to q_M and Γ is quite different from that found for pyrazine.

The ΔH_{ads}° vs q_M plots for pyridine are shown in Fig. 32. The ΔH_{ads}° vs ΔS_{ads}° plots are shown in Fig. 33. There is substantial compensation between ΔH_{ads}° and ΔS_{ads}° when q_M is positive and for low θ (at $35^{\circ}C$ a slope of $308^{\circ}K$ is expected). When q_M is negative and for larger θ , a linear relation between ΔH_{ads}° and ΔS_{ads}° is not observed, which perhaps reflects interactions of pyridine itself with the field at the Hg surface.

In the case of n-amyl alcohol, ΔH_{ads}° and ΔS_{ads}° are both much less dependent on q_M or θ than in the case of

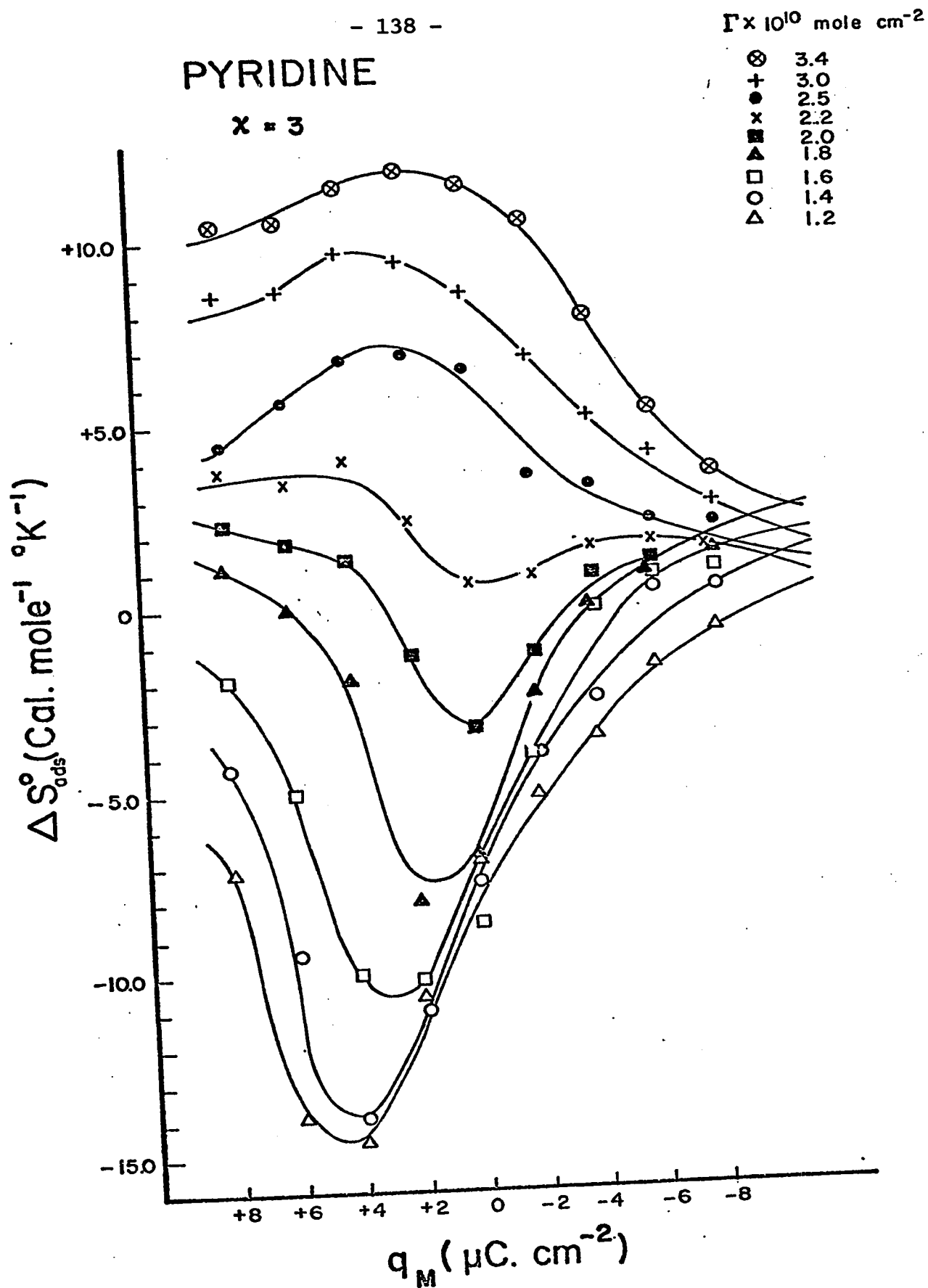


Fig. 31 $\Delta S_{\text{ads}}^{\circ}$ for pyridine at the Hg electrode as a function of q_M for various Γ (or θ) values.

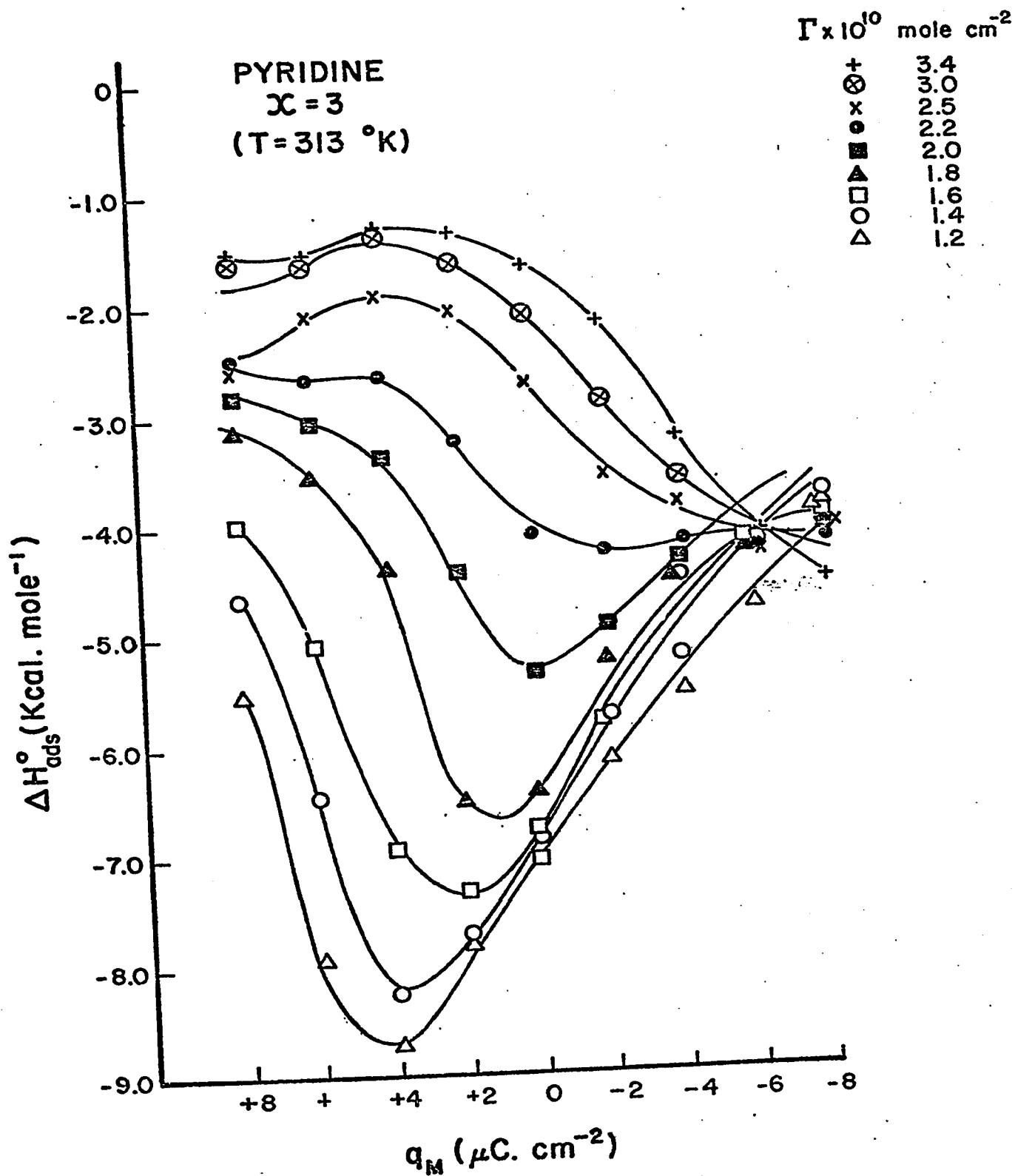


Fig. 32 $\Delta H_{\text{ads}}^\circ$ for pyridine at the Hg electrode as a function of q_M for various Γ (or θ) values.

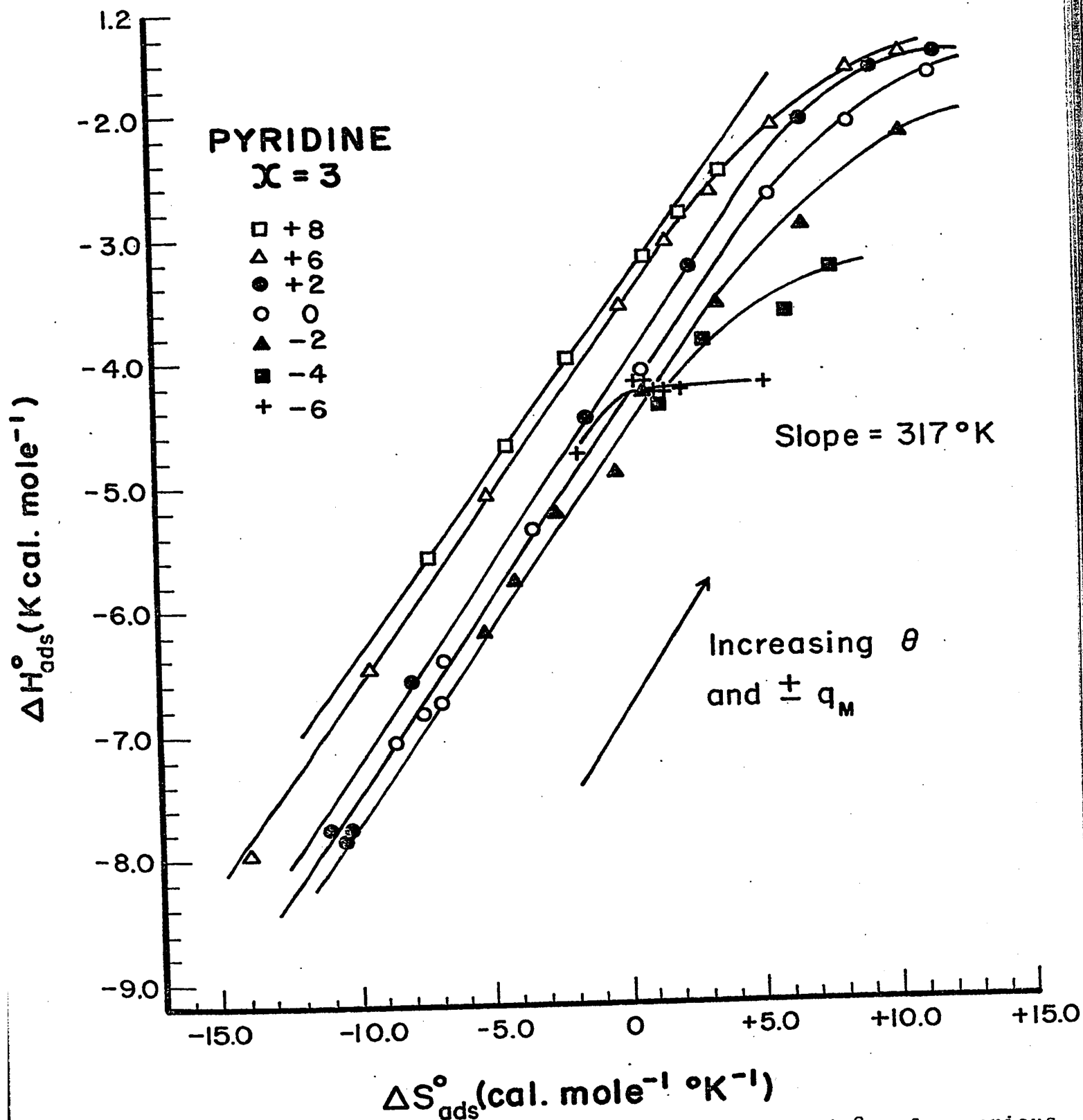


Fig. 33 Compensation effect between ΔH_{ads}° and ΔS_{ads}° for various of θ and q_M in pyridine adsorption at Hg.

pyridine or pyrazine. Hence evaluation of compensation effects is of little interest. However, both ΔH_{ads}^0 and ΔS_{ads}^0 are positive, indicating displacement of oriented and/or structured water in the interphase, depending on q_M .

3. Esin and Markov effects

(i) Solvent and adsorbate orientation

Information on orientation of adsorbate dipoles has previously been considered⁶⁵ in terms of the Esin and Markov (EM) effects (shift of potential of zero charge) related to the dipole p.d., χ , established according to the Helmholtz relation.

$$\chi = 4\pi N\bar{\mu}/\epsilon_s \quad (96)$$

for N dipoles of moment $\bar{\mu}$ normal to the surface in an interphase of dielectric constant ϵ_s (note that ϵ_s is itself expected limitingly to be a $f(\chi)$ and $\bar{\mu}$ can be a $f(N)$).

The previous treatments of effects due to χ have not taken into account contributions due to solvent orientation. That this is a significant, if not major, factor is indicated from Fig. 34 which shows a substantial EM effect for adsorption of the non-polar molecule naphthalene⁶⁰ from a methanolic 1 N H_2SO_4 solution at $q_M=0$. The EM effect can also be evaluated for q_M values other than zero and hence provides a means of evaluating not only the qualitative role of solvent orientation, but quantitatively the solvent dipole orientation contribution in $\Delta\chi$ which determines the experimental change of potential ΔE_q for a given q_M value as the extent of solute adsorption increases.

Results for $\Delta E_q (= E_{q, \text{base solution}} - E_{q, \text{adsorbate}})$

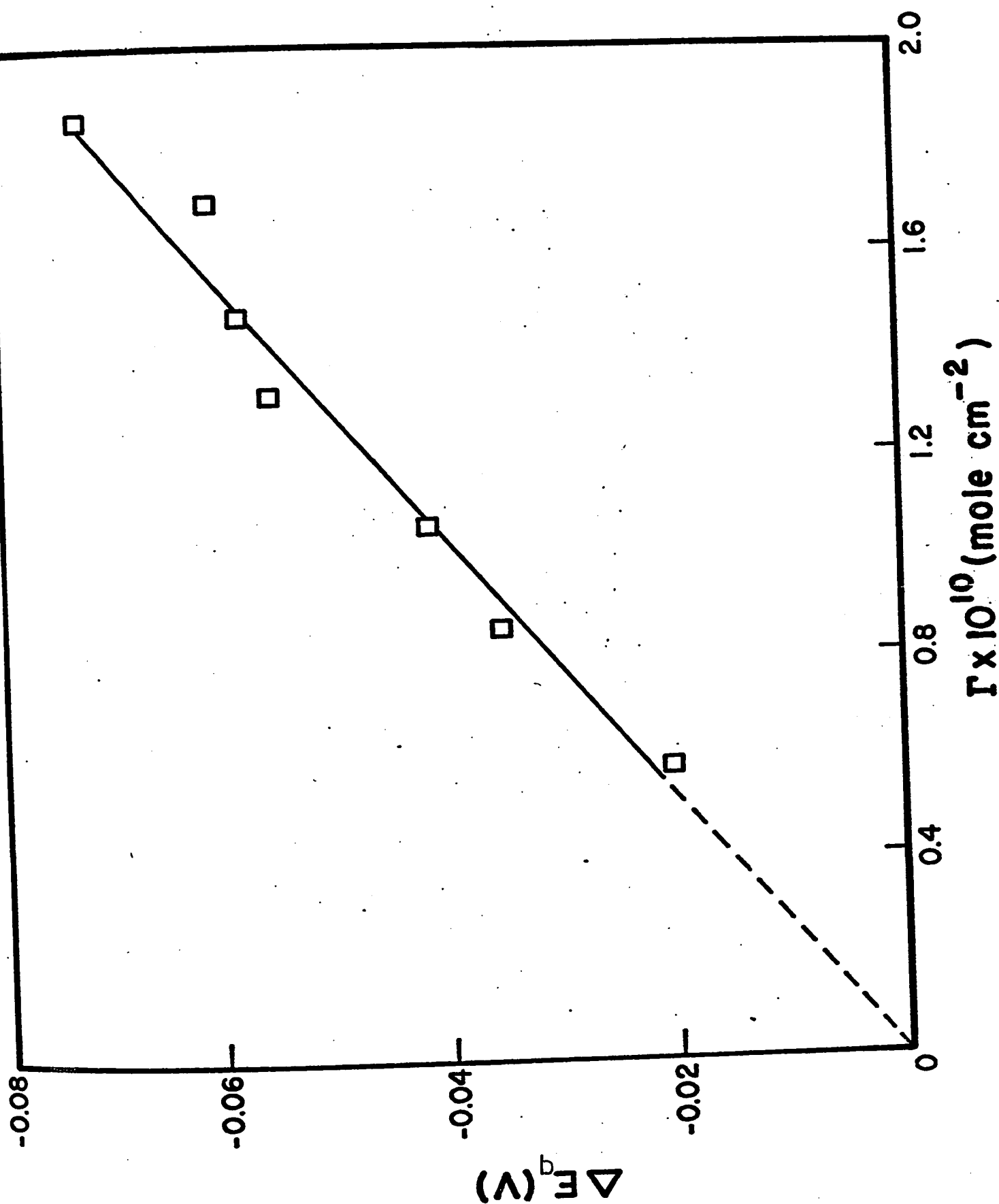


Fig. 34 Esin and Markov effect for adsorption of naphthalene at Hg from methanolic Na_2SO_4 solution at 25°C at the potential of zero charge.

for a given electrode surface charge are shown in Fig. 35 for pyrazine adsorption at several temperatures from solutions in 0.03 M aq. NaClO_4 . ΔE_q shows a linear change with Γ with a slope depending on q_M . At $q_M = 0$, there is an appreciable dependence of ΔE_q on Γ as in the case of naphthalene. Pyrazine is a flat molecule (like naphthalene) with zero (net) dipole moment and will not itself tend to be oriented in the double-layer field. Hence the substantial effects in Fig. 35 must be attributed to charge dependent, water dipole orientation.

Such effects arise because adsorption of pyrazine must occur by displacement²⁵ of solvent molecules already adsorbed and oriented in the interphase, to an extent determined by q_M or the corresponding outer field. It is of interest that zero ΔE_q as $f(\Gamma)$ arises not at $q_M = 0$ but at $-2 \mu\text{C cm}^{-2}$ which indicates intrinsic orientation of water at the p.z.c. From the sign of ΔE_q , the orientation must be with the O atom towards the Hg surface, a direction consistent with greater image energy²⁵. This is also consistent with the increasingly negative ΔE_q for more positive q_M where relatively greater extents of H_2O dipole orientation will arise, also with the negative ends of the dipoles disposed towards the positive Hg surface. Fig. 35 shows that the EM effect is symmetrical about $q_M = -2$ for various other q_M values.

This behavior is consistent with the results presented in Section C.1 where the standard free energy of adsorption of the specially selected molecule pyrazine was

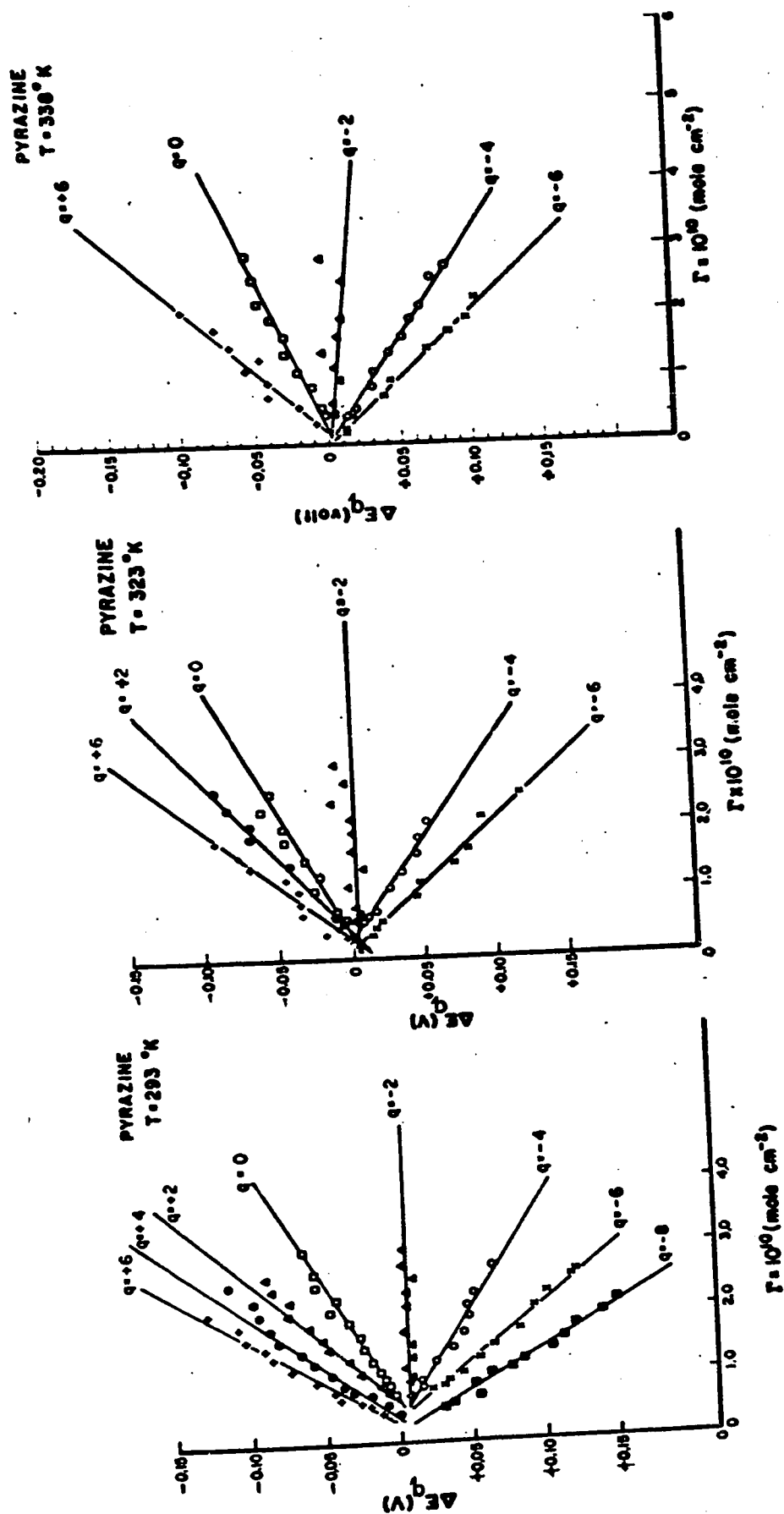


Fig. 35 Esin and Markov plots for pyrazine adsorption at Hg as a function of Γ at various q_M values in 0.03 M aq. NaClO_4 . a) 293°K; b) 323°K; c) 338°K.

also shown to be a symmetrical function of q_M about $q_M = -2 \mu C \text{ cm}^{-2}$ (Fig. 21), thus providing an ideal basis for examining the theory of adsorption by solvent displacement.

(ii) Changes of χ potential due to replacement of oriented solvent dipoles

(a) Pyrazine

Let the experimental slope of an EM effect relation be $m = d(\Delta E_q)/d\Gamma = \delta(\Delta E_q)\delta\Gamma$ where δ represents a finite change of ΔE or Γ with increasing coverage by the adsorbate, itself remaining unoriented. The number of oriented solvent dipoles can be represented²⁵ as $(N\uparrow - N\downarrow)_{q_M} \text{ cm}^{-2}$ at a given q_M and will be $f(q_M)$. At a given q_M , each pyrazine molecule replaces x adsorbed water molecules ($x = 3^{37}$). Hence for $\Gamma \text{ mole cm}^{-2}$ of adsorbed pyrazine, $x\Gamma \text{ mole cm}^{-2}$ water oriented in the ratio $N\uparrow/N_T$ and $N\downarrow/N_T$ are replaced. Therefore a degree of net solvent orientation in the double-layer has been eliminated by displacement equivalent to $x\Gamma(N\uparrow - N\downarrow)/N_T$ where $N_T = N\uparrow + N\downarrow$. This change of extent of solvent dipole orientation per cm^{-2} gives rise to

$$\Delta E_q = \frac{x\Gamma (N\uparrow - N\downarrow)}{N_T} 4\pi\bar{\mu}/\epsilon_s \quad (97)$$

The experimental slope m of the integral $\Delta E_q - \Gamma$ relation is hence

$$m = d\Delta E_q/d\Gamma = \delta\Delta E_q/\delta\Gamma = \frac{x(N\uparrow - N\downarrow)}{N_T} 4\pi\bar{\mu}/\epsilon_s \quad (98)$$

Now^{25,47} (see p.29)

$$\frac{N_{\uparrow} - N_{\downarrow}}{N_T} = \tanh \left[\frac{\mu F}{kT} - \frac{U_c}{kT} \left(\frac{N_{\uparrow} - N_{\downarrow}}{N_T} \right) \right] \quad (18)$$

which enables $\frac{N_{\uparrow} - N_{\downarrow}}{N_T}$ to be estimated for various values of the quantity U_c/kT (p. 30).

Fig. 36 shows how $\frac{N_{\uparrow} - N_{\downarrow}}{N_T}$ evaluated from the experimental results of Fig. 35 compares with that calculated from equation (18) taking $U_c/kT = 2, 3, 3.5$ or 4 , μ for water 1.8 D and $\epsilon_s = 6$ ^{25,46}. The experimental relation for pyrazine is consistent with a theoretical curve having U_c/kT between 2 and 3 . This agrees quite well with the value of 2 derived earlier for this interaction parameter from the ΔG_{ads}^0 values (see Fig. 25). The experimental line is displaced from the theoretical line by $2 \mu C \text{ cm}^{-2}$ since the maximum adsorption occurs at $-2 \mu C \text{ cm}^{-2}$ rather than at zero, as mentioned earlier.

Damaskin et al.⁹¹, have remarked that EM effects as large as 0.5 V cannot be explained in terms of solvent orientation since the maximum χ given by the theory of Bockris, Devanathan and Müller is 0.1 V. This conclusion is, however, incorrect since the correct maximum value of χ is, in fact, ca. 1.2 V and its actual value, e.g. at $q_M = \pm 15 \mu C \text{ cm}^{-2}$, depends on the value of U_c/kT and the value of N_T for the water layer, as shown by Conway, MacKinnon and Tilak¹⁰⁷. It is seen from ref.¹⁰⁷ that a change of χ of the magnitude demonstrated in the present work can easily arise from dis-

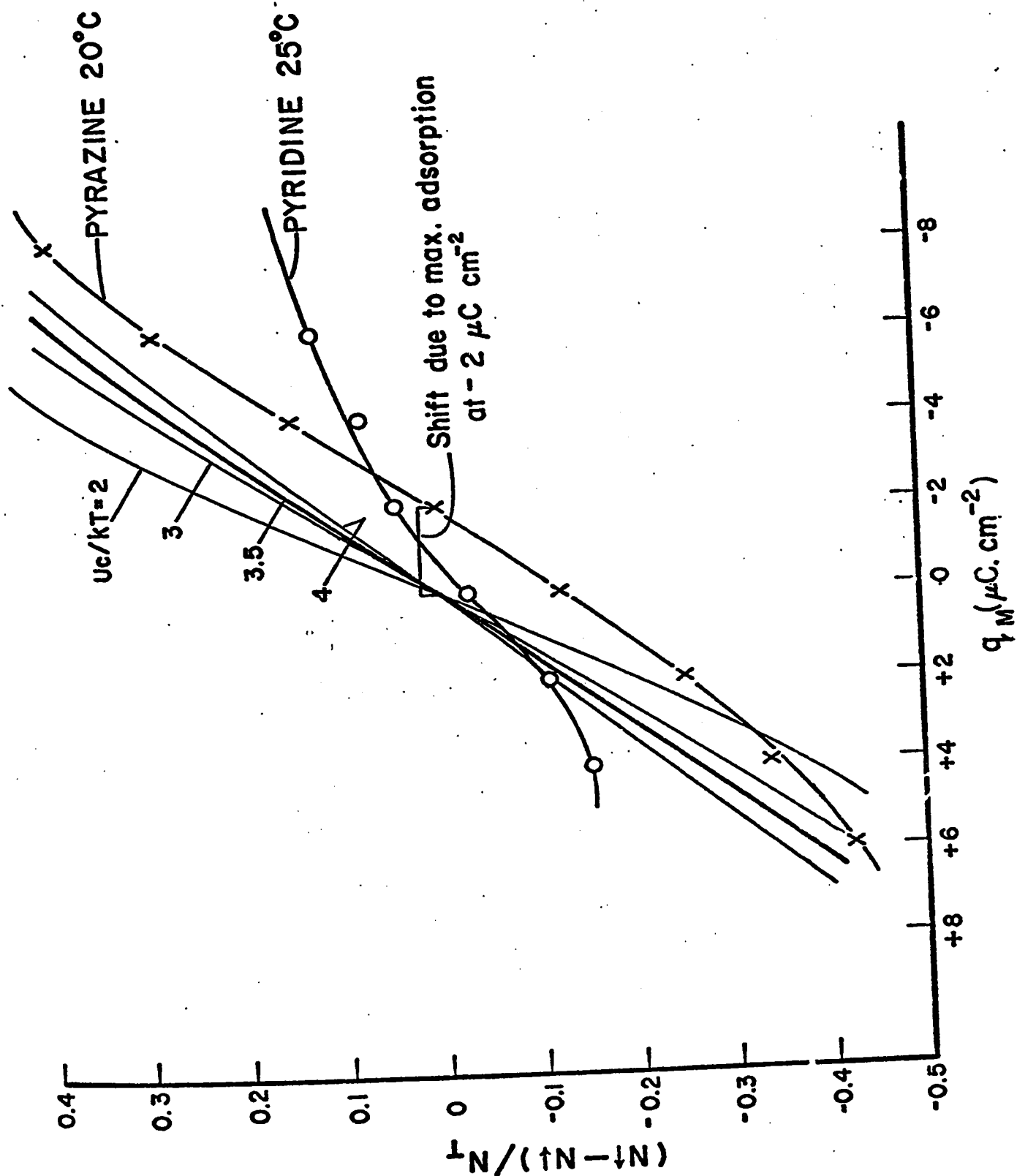


Fig. 36 Evaluation of the solvent orientation distribution function $(N^+ - N^-)/(N^+ + N^-)$ from data of Fig. 35a in relation to values calculated from equation (18) with various U_c/kT values. The distribution function from pyridine adsorption data of Fig. 37b is also shown.

placement of oriented solvent dipoles if $U_c/kT = 2$ to 6 and if $x = 3$ to 4 , values which it has been shown here are also consistent with the dependence of standard free energy of adsorption on q_M (Fig. 21).

(b) Pyridine

The results for ΔE_q as $f(\Gamma)$ for various q_M in the case of pyridine (Fig. 37) are strikingly different from those for pyrazine (Fig. 35): beyond a given value of Γ , dependent on q_M , the $\Delta E_q - \Gamma$ relations suddenly change slope to lines having approximately the same slopes independent of q_M . This effect is evidently related to the changes of slope with increasing Γ also seen in the $\phi_q - \Gamma$ plots to be discussed below. Qualitatively, these sudden changes of slope of the EM plots are probably the result of orientation of the pyridine molecules themselves, as indicated in other ways in previous thermodynamic work^{65,108}.

If a sudden and complete change of orientation of adsorbed pyridine occurred at a critical Γ , with continuing further orientation at higher Γ , an EM relation would result having the form of Fig. 38a which is not similar to the experimental behavior (Fig. 38c). A progressive effect involving two parallel orientation processes 1, 2, as in Fig. 38b, is required to account for the experimental results (Fig. 37) with pyridine. Process 2 originates at a critical value of Γ (which experimentally depends on q_M). The behavior

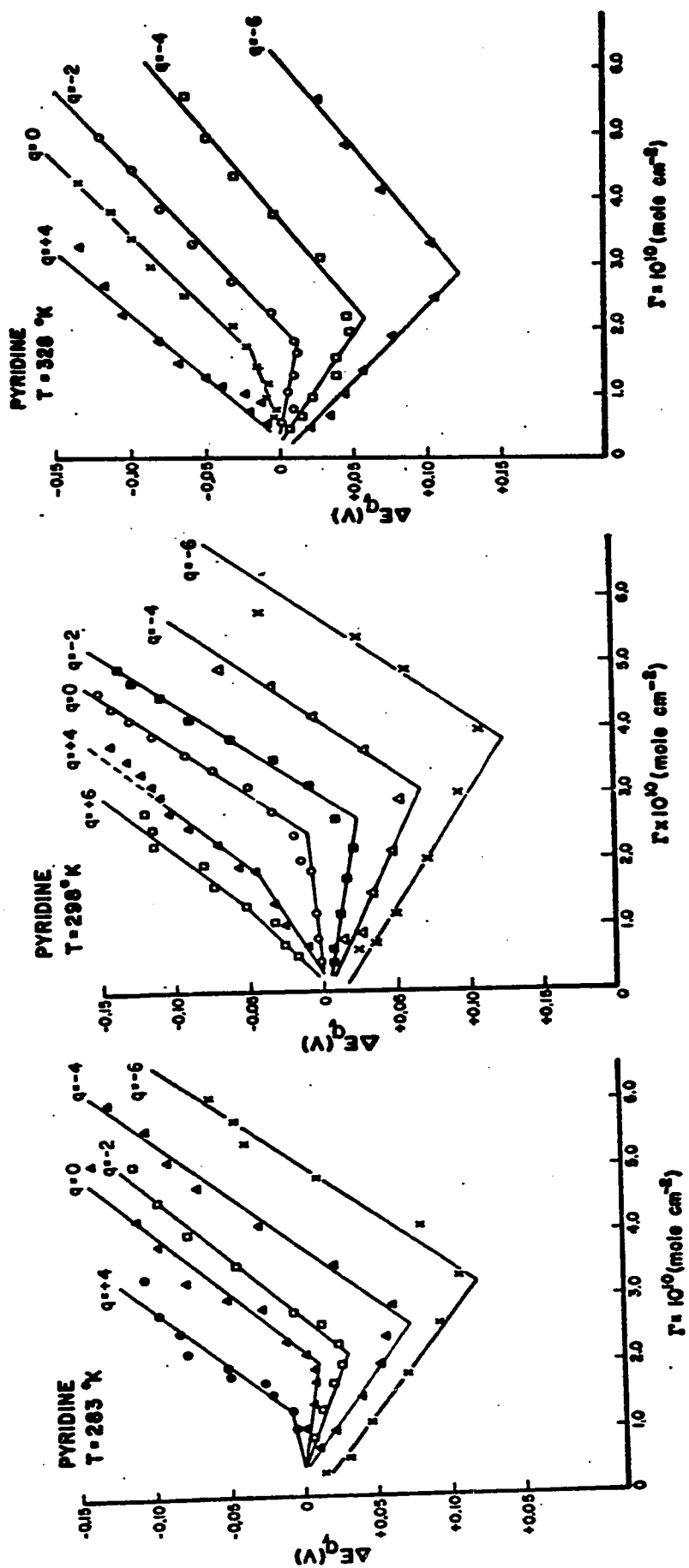


Fig. 37 Esin and Markov plots for pyridine adsorption at Hg as a function of Γ at various q_M values in 0.03 M aq. NaClO₄. a) 283°K; b) 298°K; c) 328°K.

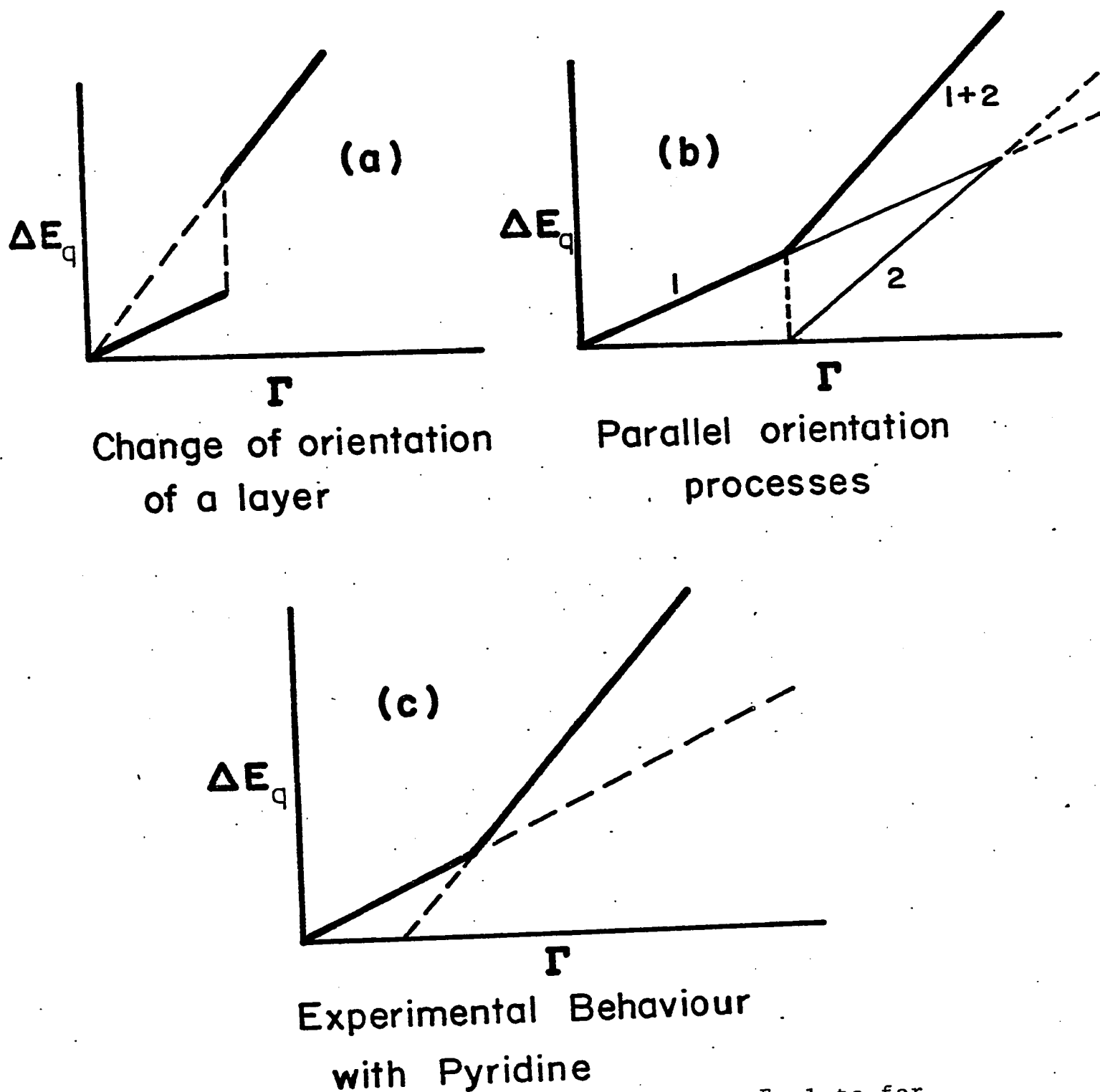


Fig. 38 Schematic representation of $\Delta E_q - \Gamma$ plots for (a) sudden change of orientation of a layer of dipoles; (b) a parallel orientation process and (c) typical experimental behavior with pyridine at negative q_M values.

exhibited in Fig. 37 can now be understood in relation to that of Figs. 34 and 35 and equations (97) and (18) in the following way.

At low positive, and all negative q_M values, adsorption of pyridine appears to behave like that of pyrazine where the molecule probably lies flat in the interphase producing $\Delta\chi$ change only by displacement of previously oriented solvent dipoles. Thus, the initial regions of the EM relations of Fig. 37 for various temperatures are similar to the whole series of lines of Fig. 35 for pyrazine and correspond to progressive replacement of $\uparrow$ and $\downarrow$ dipoles distributed according to the value of q_M , the surface charge.

Beyond a critical coverage, and dependent on q_M , a fraction of pyridine molecules reorients from a flat to an upright position and then contributes a relatively large ΔE_q having a dependence on Γ characterized by a slope m' which varies with q_M (see below). The direction of change of ΔE_q is consistent with the assumed orientation of pyridine at negative q_M , i.e. when the positive end of the pyridine dipole is oriented towards the surface a negative ΔE_q results (note that ΔE_q changes in the positive direction when water dipoles oriented with the positive) H-ends towards the Hg surface are replaced). Thus, the total ΔE_q will then be related* to q_M and by a "free" solute dipole

* Damaskin et al. (p.132 in ref.⁹¹) considered 2-position adsorption and treated the contributions from flat and oriented adsorbate molecules to the adsorption potential difference in relation to the dependence of free energy of adsorption on coverage using a model of the double-layer involving 2 or 3 parallel condenser components.

orientation term plus a term similar to that in equation (97) for pyrazine.

The total EM effect for oriented dipoles in substitutional adsorption will then be

$$\Delta E_q = 4\pi\Gamma\bar{\mu}_{py}/\epsilon_s + \frac{x\Gamma(N\uparrow - N\downarrow)}{N_T} 4\pi\bar{\mu}_s/\epsilon_s \quad (99)$$

where $\bar{\mu}_{py}$ is the effective normal moment* of pyridine and $\bar{\mu}_s$ that of the solvent, water. The slope m' of the EM line will now be

$$m' = \delta\Delta E_q/\delta\Gamma = \frac{4\pi}{\epsilon_s} \left\{ \bar{\mu}_{py} + \frac{x(N\uparrow - N\downarrow)}{N_T} \bar{\mu}_s \right\} \quad (100)$$

The progressive change of slopes of the lines in Fig. 37 for the EM effect with pyridine is accounted for by the two terms of eqn. (99). With increasing $-q_M$, orientation of water with H atoms nearest to the Hg surface increases gives an increasingly positive change of ΔE_q due to solvent replacement in the interphase while pyridine itself becomes increasingly oriented. If the two effects were independent, the difference of slopes of the two regions would give the contribution due to pyridine orientation. This is shown in Fig. 38A as a function of q_M , together with the initial solvent orientation effect. It is clear that at $+6 \mu C \text{ cm}^{-2}$ pyridine orientation, while significant beyond $\Gamma = 1.3 \times 10^{-10}$

* For free dipole orientation $\bar{\mu}_{py}$ can be $f(q_M)$, as in low field dielectric theory. However, in the double-layer, for $q_M > \text{ca. } 2 \mu C \text{ cm}^{-2}$ high field conditions obtain. Also, previous experimental results^{65,108} indicate that the onset of orientation of pyridine at the Hg electrode is rather sharp.

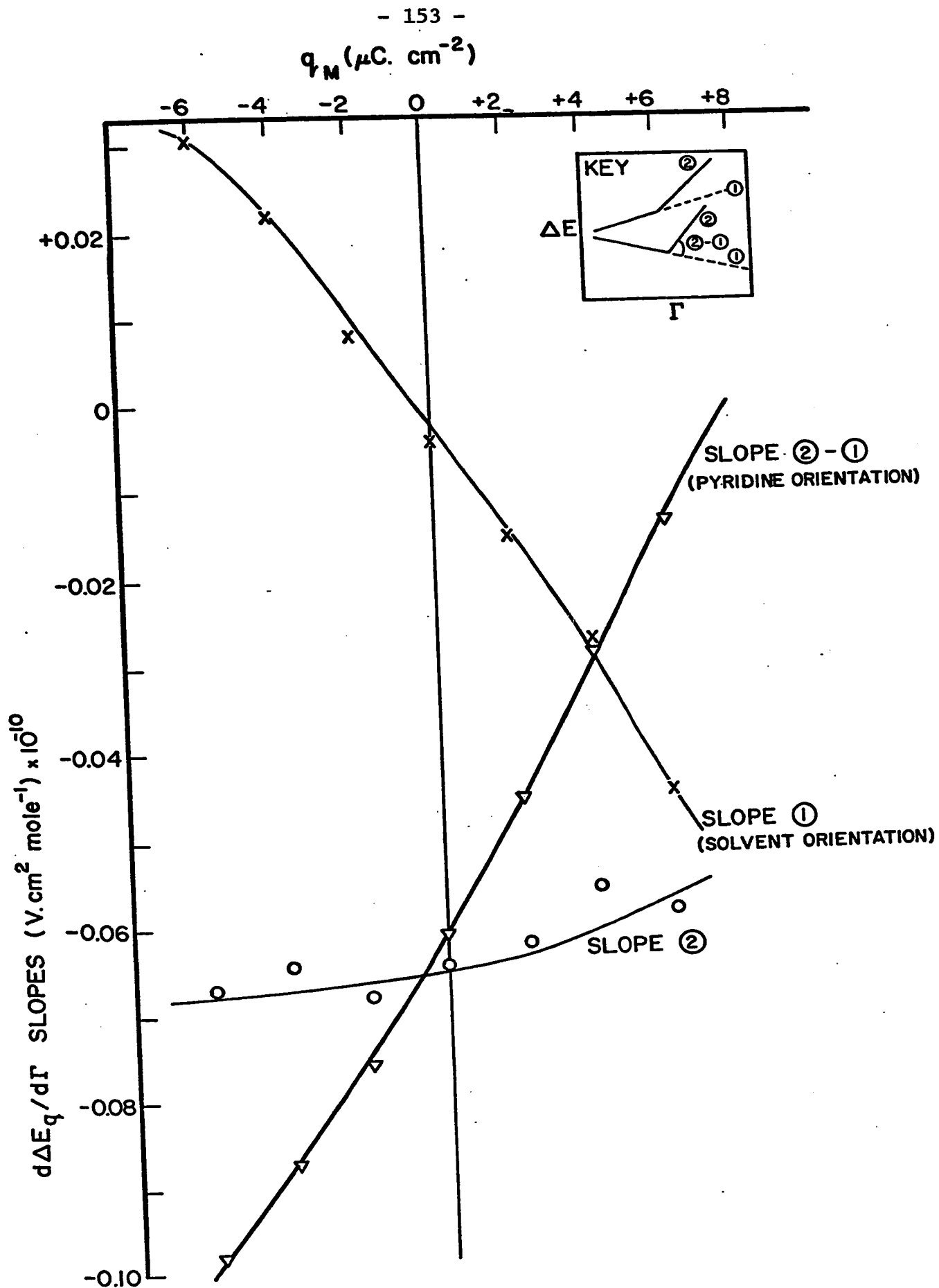


Fig. 38A Resolution of slope components in the Esin and Markov plots of Fig. 37, based on water and pyridine orientation contributions.
 $T = 298^\circ K$

mole cm^{-2} , is quite small as indicated by the slope difference in Figs. 38A and 37. However, as q_M becomes more negative, pyridine orientation increases and the effect is almost linear in q_M . Since the changes of slopes arise suddenly at critical Γ values, dependent on q_M (Fig. 37), it seems that a certain fraction of pyridine molecules in the surface must become more or less completely oriented and this fraction increases with more negative q_M ; a sudden transition of the type shown by the EM plots could hardly arise if all pyridine molecules at a given Γ were oriented to some mean but smaller extent, dependent on q_M .

The above interpretation suggests that pyridine orientation is associated with a two-phase equilibrium in the interphase between unoriented and oriented, possibly associated, pyridine molecules, with the relative quantities of the two species depending on Γ and q_M . This is consistent with previously expressed views that pyridine orientation is a cooperative phenomenon involving a 2-dimensional phase transition.

(c) n-Amyl alcohol

In comparison with pyridine and pyrazine, n-amyl alcohol is a flexible molecule that can accumulate hydrophobically at the Hg surface with its OH group oriented toward or away from the metal, depending on q_M . The EM plots for this substance are shown in Fig. 39. For various q_M values, the $\Delta E_q - \Gamma$ lines are almost symmetrical again about $q_M = -2$

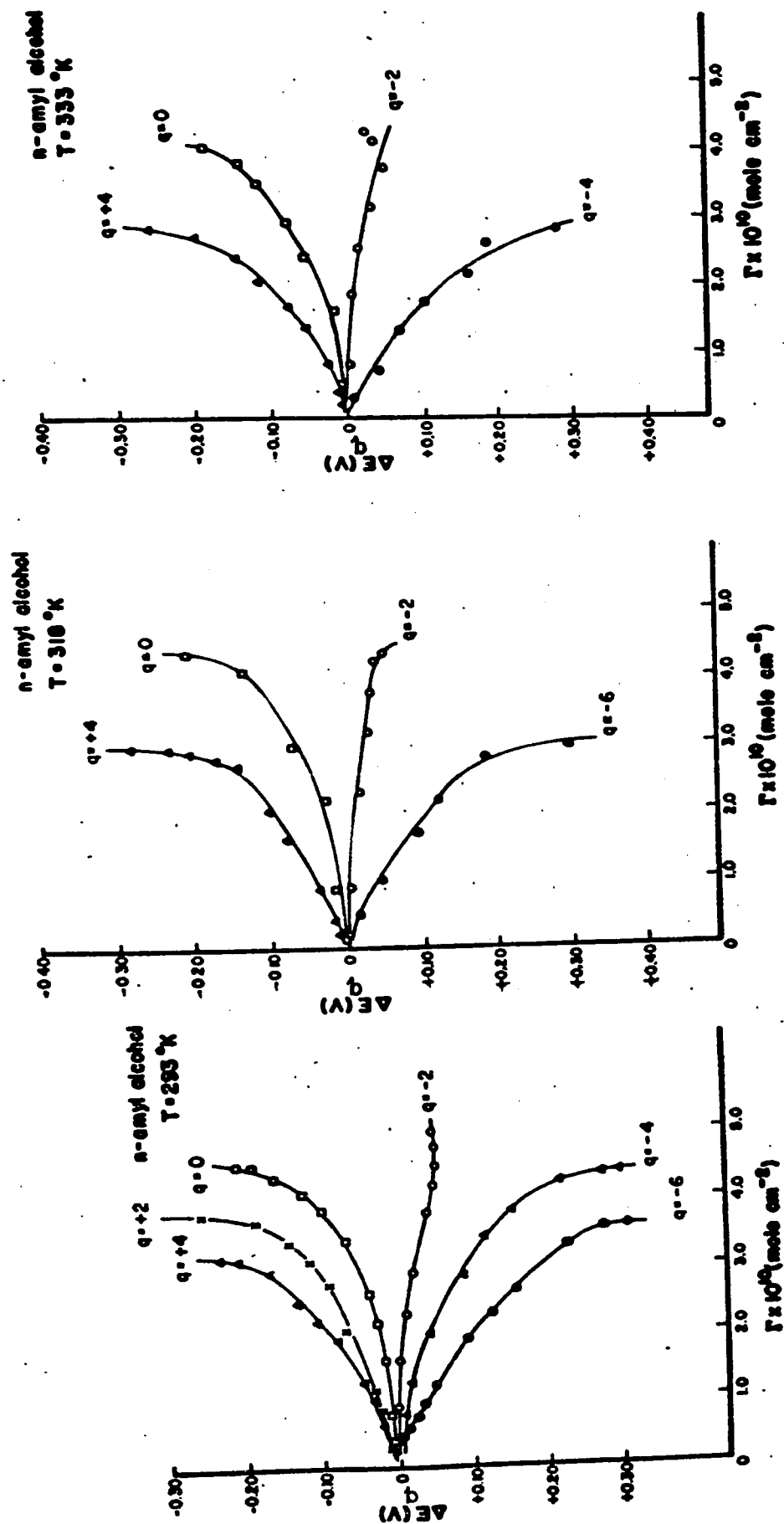


Fig. 39 Esin and Markov plots for n-amyl alcohol adsorption at Hg at various q_M values in 0.3 M aq. NaClO_4 . a) 293°K ; b) 318°K ; c) 333°K .

$\mu\text{C cm}^{-2}$ which, $\pm 0.5 \mu\text{C cm}^{-2}$, is probably to be regarded as the charge for zero net solvent orientation. Apart from the ΔE_q changes which arise towards the limit of saturation of the surface layer, the magnitudes of ΔE_q as Γ increases are similar to those for pyrazine (Fig. 35). There is no evidence for independent orientation of the dipolar OH group as there is for the pyridine dipoles; presumably the OH group resides amongst solvent water molecules and behaves simply as part of the assembly of H-bonded water OH groups. The rather rapid changes of ΔE_q towards the highest Γ values are of interest and may be due to isolation of the last H_2O molecules at the interface amongst C_5H_{11} -chains giving rise to relatively stronger orientation of these H_2O molecules by the field arising from charge q_M . Their final replacement then occurs with a larger ΔE_q as $\theta \rightarrow 1$ for n-amyl alcohol. This mechanism is supported by the fact (Fig. 39) that the effects referred to arise at both positive and negative q_M , symmetrically about $q_M = -2 \mu\text{C cm}^{-2}$.

(iii) Relation to evaluation of $(N_{\uparrow} - N_{\downarrow})/N_T$ and Uc/kT from free energy of adsorption

In addition to evaluation of $(N_{\uparrow} - N_{\downarrow})/N_T$ from the EM effects, it is possible to calculate this quantity from the experimental values of $\Delta G_{\text{ads}}^{\circ}$ and $\Delta G_{\text{chem}}^{\circ}$ of pyrazine and pyridine. Thus, the water orientation term B ($= (N_{\uparrow} - N_{\downarrow})/N_T$)

and the lateral-interaction parameter Uc/kT at various q_M (and hence F) values can be calculated using the following equations

$$B = \frac{N_{\uparrow} - N_{\downarrow}}{N_T} = \tanh \left(\frac{\mu F}{kT} - \frac{BUc}{kT} \right) \quad (18)$$

$$\Delta G_{ads}^{\circ} = \Delta G_{chem}^{\circ} + xB \left(\frac{\mu F}{kT} - \frac{BUc}{kT} \right) RT \quad (92)$$

Table I shows not only that B varies with q_M (as expected) but also Uc/kT is dependent on q_M . Thus, it is evident that Uc is not a constant* (cf.²⁵) but increases with q_M . This

Table I

Values of $B (= \frac{N_{\uparrow} - N_{\downarrow}}{N_T})$ and Uc/kT as a function of q_M

calculated from data for pyrazine and pyridine adsorption

293°K q_M	Pyrazine		Pyridine	
	B	Uc/kT	B	Uc/kT
+8	-0.655	3.2	-0.595	3.65
+6	-0.595	3.2	-0.53	3.25
+4	-0.50	2.38	-0.39	3.5
+2	-0.380	1.97	-0.235	2.0
0	-0.235	1.45	-0.14	3.1
-2	0	0	0	0
-6	+0.324	0.80	**	
-8	+0.47	1.35	**	
-10	+0.59	1.8	**	

** From $q_M < -2 \mu C \text{ cm}^{-2}$, appreciable orientation of pyridine itself occurs.

* In the theoretical evaluation of ΔG_{ads}° values as $f(q_M)$, Uc has been empirically assumed constant (see p.123).

result is perhaps not unexpected since it is, in fact, unlikely (a) that the water dipole orientation will be limitingly $\uparrow$ or $\downarrow$ (a distribution of angular orientations may be expected, depending on temperature and F , as shown elsewhere¹⁰⁹) and (b) c may increase with q_M due to electrostriction⁴³ in the double-layer.

It is encouraging to find that the B values computed from both the pyrazine and pyridine adsorption results are similar at the same q_M . This supports the interpretation given to the initial regions of the EM plots for pyridine (Fig. 37) in relation to the EM lines for pyrazine (Fig. 35). The B values cannot be expected to be exactly equal to those derived from the EM plots by the method exemplified in Fig. 36 since the treatment involved in that case empirically assumed constant U_c values, independent of q_M , as in ref. 25.

(iv) Temperature coefficient of surface dipole potentials

Generally, increase of temperature will tend to diminish dipole orientation as it does orientation dielectric polarization in a field. For pyrazine adsorption, this is borne out by the general trend of the results in Fig. 40a for pyrazine where the tendency is for the slopes $d\Delta E_q/dT$ which are positive or negative, depending on q_M and the sign of $N\uparrow - N\downarrow$, to diminish with increasing T . Of course, for either orientation, N_T will tend to diminish somewhat with T owing to the thermal expansion of the interphase water. The

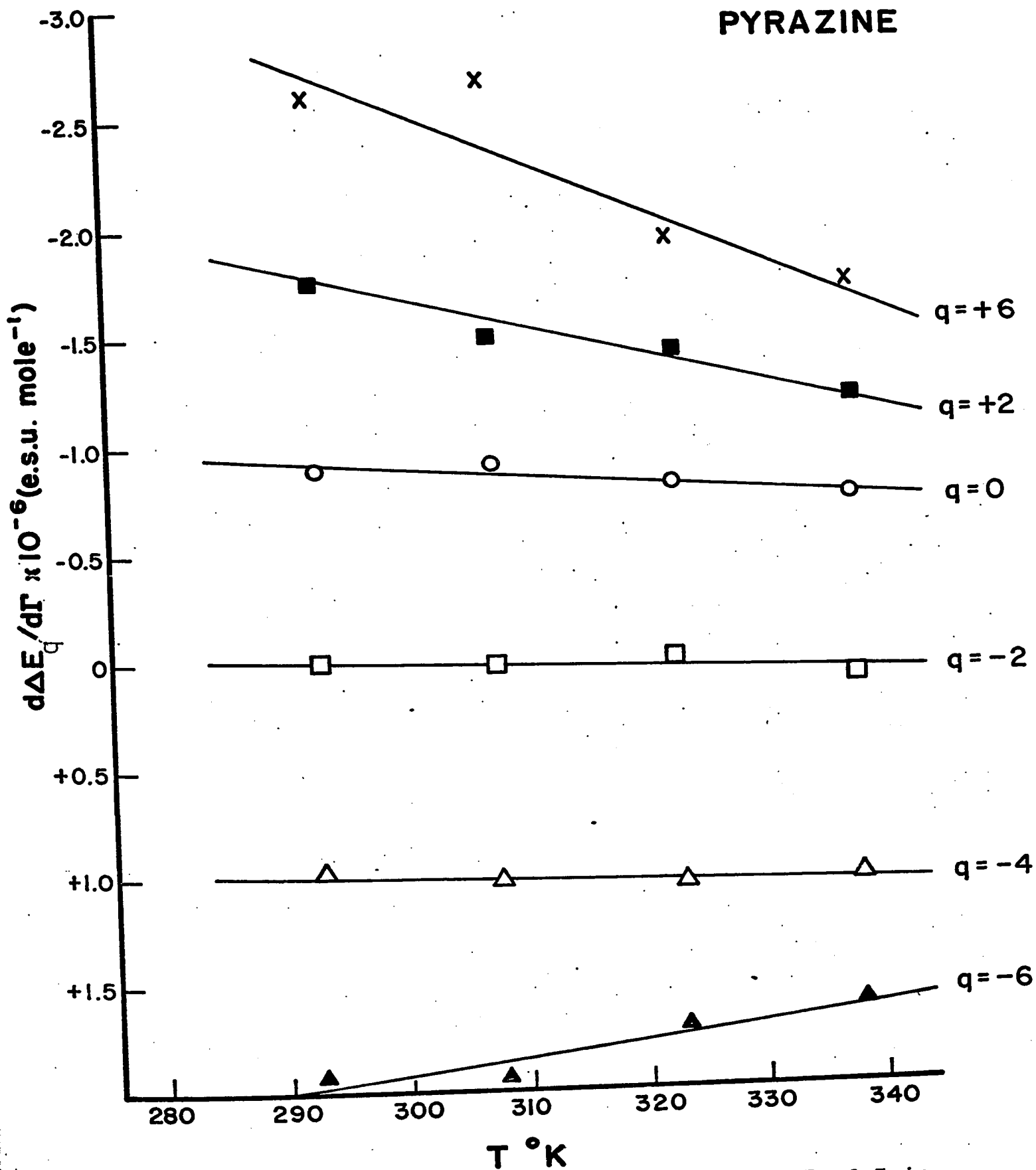


Fig. 40a Temperature dependence of slopes $d\Delta E/dT$ of Esin and Markov plots for pyrazine adsorption.

temperature dependence of χ will depend on the magnitude of U_c , and for higher values of U_c/kT the sign of the temperature dependence of χ and hence $d\Delta E_q/d\Gamma$ can become changed¹⁰⁷, e.g. as seems to be the case for the pyridine results in Fig. 40b, in comparison with those for pyrazine in Fig. 40a. For the sections of the EM plots for pyridine at high Γ values beyond the inflection points in Fig. 37, $d\Delta E_q/d\Gamma$ decreases appreciably with T as expected if this region of the EM plots corresponds to pyridine molecule orientation. Also, in Fig. 40a, the fact that $d\Delta E_q/d\Gamma$ is almost independent of T at $q_M = -2$ to $-4 \mu C \text{ cm}^{-2}$ but is not zero at $q_M = 0 \mu C \text{ cm}^{-2}$ confirms the view that zero net water dipole orientation obtains at ca. $-2 \mu C \text{ cm}^{-2}$ but not at $q_M = 0$.

4. Surface pressure relations for pyrazine and pyridine

Further indications of the relative orientation of pyrazine and pyridine as $f(q_M)$ can be obtained from examination of the surface pressure ϕ_q as $f(q_M)$ and Γ . Surface pressures were calculated from the surface tension values at various q_M 's by the method described earlier (Section A.1 of Chapter III).

Figs. 41 and 42 show the relation of ϕ_q to Γ at various surface charges for pyrazine and pyridine, respectively. It is clear that the $\phi_q - \Gamma$ relations are almost independent of q_M for pyrazine while they are quite dependent on q_M for pyridine. This suggests that changes of surface charge cause

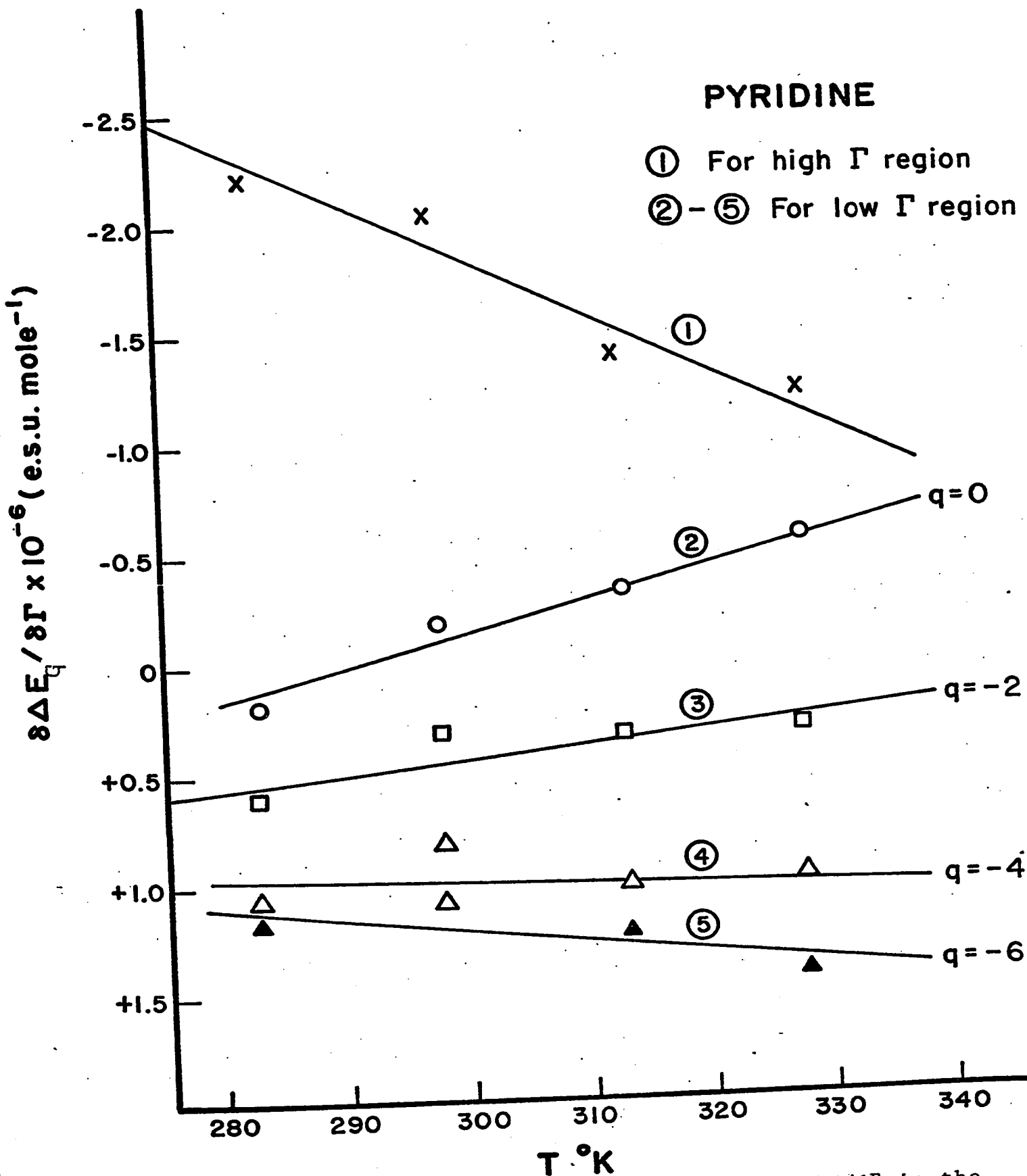


Fig. 40b Temperature dependence of slopes $d\Delta E/d\Gamma$ in the two regions of the Esin and Markov plots of Fig. 37 for pyridine adsorption.

PYRAZINE
T = 283 °K

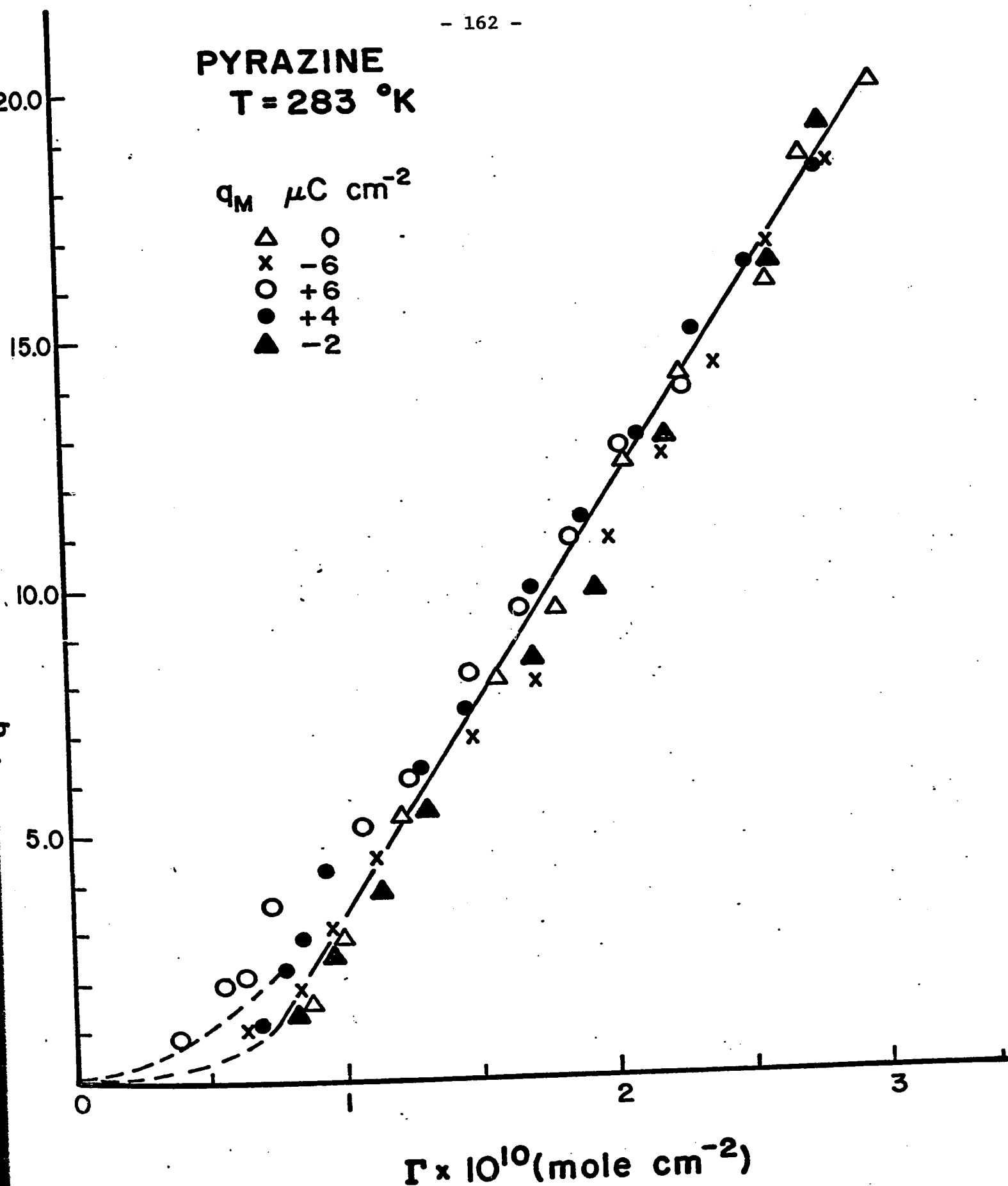


Fig. 41 $\phi - \Gamma$ plots for pyrazine in 0.03 M $NaClO_4$ at Hg for various q_M values.

PYRIDINE
T = 283 °K

q_M	μC	cm^{-2}
○	+6	
●	+4	
△	0	
□	-2	
▲	-4	
x	-6	

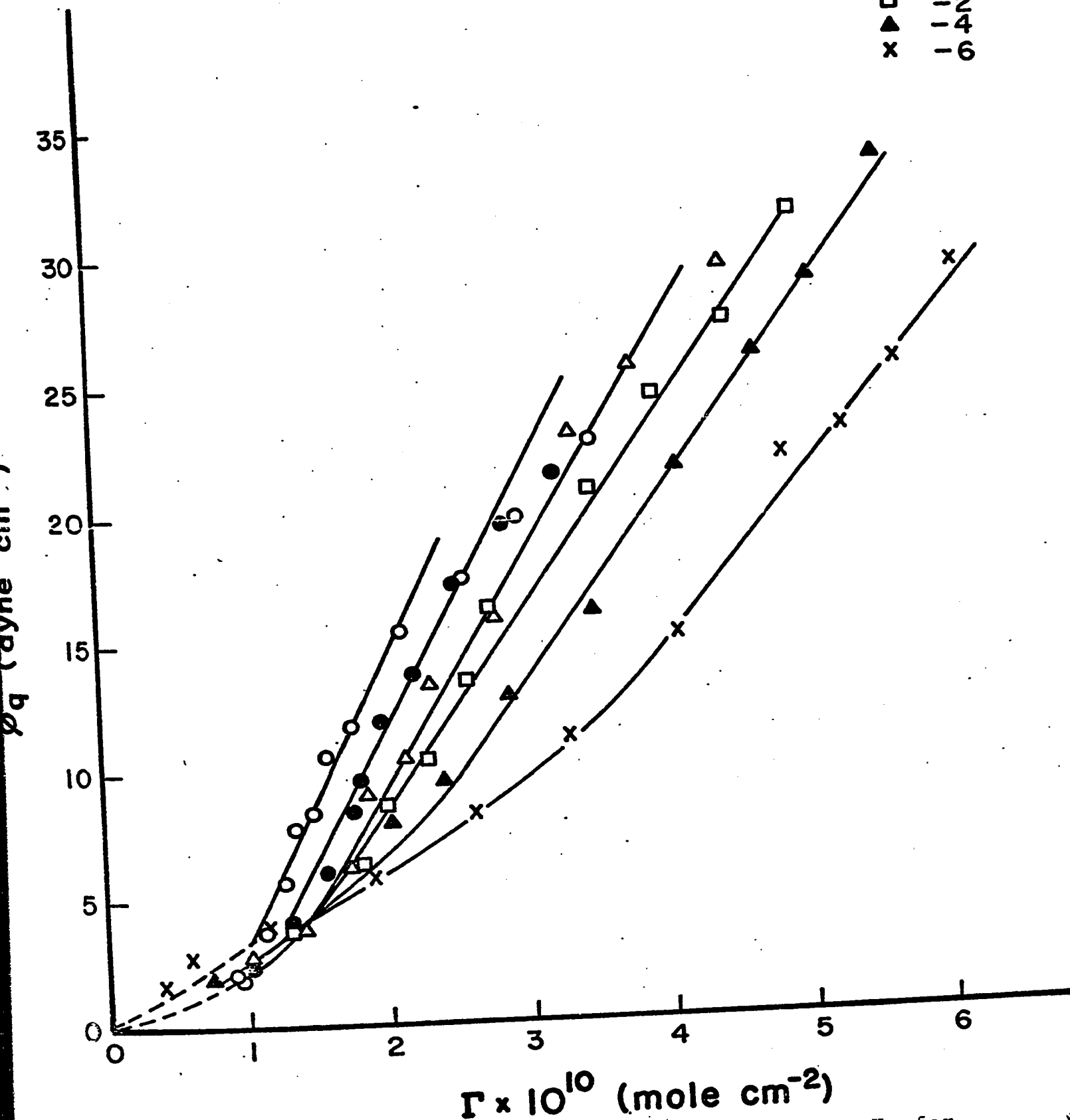


Fig. 42 ϕ_q - Γ plots for pyridine in 0.03 M $NaClO_4$ at Hg for various q_M values.

little change of orientation of pyrazine while pyridine becomes progressively more oriented by the field arising from the charged interface as $-q_M$ increases, and this causes lower ϕ_q as orientation becomes greater at more negative q_M . This effect is consistent with more negative ΔG_{ads}^0 , also evaluated in this work, as q_M becomes more negative and θ becomes larger.

In the case of pyridine, it appears (relative to the behavior of pyrazine) that a greater coverage can be accommodated, especially at higher negative q_M , without (or with less) repulsive interaction under conditions where neither type of molecule is oriented (as indicated from Figs. 41 and 42). Pyridine is a mono-functional H-bonding molecule, so less interference with other H-bonded pyridine molecules attached to water will arise in comparison with the case of pyrazine. Also, as q_M becomes more negative, the strength of H-bonding between oriented water molecules and pyridine N-centres can become stronger due to an inductive effect through the π -orbitals (in the "flat" orientation) from the negative metal surface (making N more basic). This would lead to relatively less easy orientation as q_M is made larger, except as the ratio of pyridine to water becomes greater at higher Γ , whereupon relatively sudden orientation arises, possibly with 2 molecules carrying a water molecule between them at the N centres. Also some relief of hydrophobic interaction with water would tend to be achieved in the side-by-side orientation.

The high Γ sections of the inflected $\phi_q - \Gamma$ relations of Fig. 42 shows a diminishing slope, $d\phi_q/d\Gamma$, as q_M becomes more negative. In relation to the slopes of the main parts of the $\phi_q - \Gamma$ lines for $q_M > 0$, and to the slopes of the $\phi_q - \Gamma$ lines for all q_M values in the case of pyrazine (Fig. 41), it is of interest to establish first if the lower slopes of the $\phi_q - \Gamma$ lines for pyridine originate because of attractive interactions or if the higher slope lines originate because of repulsive or equivalent interactions. For ideal behavior in the interface, $\phi_q = RT\Gamma$ or $d\phi_q/d\Gamma = RT = 2.476 \times 10^{10}$ erg mole⁻¹. Inspection of Figs. 41 and 42 shows that for pyrazine and for the high Γ sections of the pyridine behavior, the slopes $d\phi_q/d\Gamma$ are some four times larger than the value for ideal behavior beyond $\Gamma = 0.8 \times 10^{-10}$ mole cm⁻² indicating an appreciable second virial coefficient in the virial equation of state. For $q_M < 0$, the lower slope regions for pyridine (Fig. 42) therefore indicate less repulsive interactions which persist to higher Γ values, the more negative is q_M . This is entirely consistent with the EM results of Fig. 37 where pyridine orientation sets in only at progressively higher Γ as q_M becomes more negative.

In the case of pyrazine, the repulsive interaction becomes appreciable, but independent of q_M (Fig. 41), as

$\Gamma \times 10^{10} > \text{ca. } 0.8$. This is about 1/4 coverage. Construction of a model of the surface shows that pyrazine molecules each with one water molecule H-bonded to each N atom can just be accommodated without overlap up to ca. 1/4 coverage of the surface by pyrazine. Beyond that coverage, interference amongst the H-bonded water molecules must arise, giving the diminished free energy of adsorption indicated by Fig. 26 as θ increases. This will also give rise to the higher slope of the $\phi_q - \Gamma$ relation for pyrazine above the ideal value. The independence of $d\phi_q/d\Gamma$ on q_M , and the lack of an orientation contribution due to pyrazine in the EM plots of Fig. 35, shows that pyrazine itself is not oriented and that the interaction effect is independent of water orientation in the double-layer.

The above effects of q_M on orientation (e.g. in the EM plots or in the $\phi_q - \Gamma$ relations) will not arise in the case of pyrazine since there is no double-layer field effect tending to promote net orientation of this molecule.

D. Adsorption of Pyrazine and Pyridine at the Air/Water Interface

1. Comparison of isotherms for pyrazine and pyridine

The adsorption of pyrazine at the air-water interface may be compared with that of pyridine and also with that of pyrazine at the Hg/H₂O interface. The results are first shown in terms of Γ -log C plots in Fig. 16 (cf. Section B of Chapter III). Pyridine is initially more strongly adsorbed than pyrazine but shows an unexpected maximum in Γ at ca. 0.7 M. A similar maximum in adsorption at the Hg/H₂O interface is observed⁶⁵ at ca. 1.0 M. Two reasons may be considered for this maximum in Γ : (a) only the apparent surface excess is measured by $-(\partial\gamma/\partial\mu_2)_{T,E}$ since the chemical potential of solvent also begins to vary significantly when the adsorbate concentration exceeds ca. 1 M. Then both solute (2) and solvent (1) terms must be considered in the Gibbs equation which gives

$$-(\partial\gamma/\partial\mu_2)_{T,E} = \Gamma_2 - \frac{x_2}{x_1} \Gamma_1 \quad (101)$$

where Γ_1 is the surface excess of solvent and x_1 , x_2 are the mole fractions of solvent and solute, respectively. Also Γ_1 can be estimated in terms of the molecular area of solute and

solvent as $\Gamma_1 A_1 + \Gamma_2 A_2 = 1 \text{ cm}^2$. Hence the corrected Γ_2 can be evaluated⁶⁵. No reasonable values of areas of pyridine and water give a corrected curve of Γ_2 vs $\log C$ which reaches the expected constant limiting value corresponding to full and constant coverage. In the present experiments, $x_2 < 0.05$; the pyridine $(\partial\gamma/\partial\mu_2)_{T,E}$ falls $1.5 \times 10^{-10} \text{ mole cm}^{-2}$ below the maximum at this mole fraction. Hence $\frac{x_2}{x_1} \Gamma_1$ should be of this magnitude. $\frac{x_2}{x_1} > 0.05$, so that $\Gamma_1 < 30 \times 10^{-10} \text{ mole cm}^{-2}$. This is, however, unreasonable since the value of Γ_1 required for the correction is unrealistically large and is usually negative. For the air/water interface, the maximum reasonable correction is only some 25% of that required to eliminate the maximum. (b) The second reason for the maximum can be the neglect of non-ideality of the pyridine/water solution. Evaluation of activity coefficients for pyridine for an infinite dilution reference state was made* from the data of Cabani et al.⁷⁴ and the data are shown in Table II. Except in the experiments at the air/water interface at high pyridine concentrations, the activity coefficient corrections are small. The corrected form of Γ -log a relation for pyridine at the air/water interface at one temperature is shown in Fig. 16. Pyrazine shows no serious anomalies either at the air/water (Fig. 16) or the Hg/water interface up to comparable concentrations.

* The data were provided by Dr. J. D. Cox, National Physical Laboratory, London.

Table II

Activity coefficients for aqueous pyridine solutions

Molal concentration	Activity coefficient
0.10	0.942
0.2	0.887
0.4	0.791
0.6	0.710
0.8	0.641
1.0	0.582
1.5	0.470
2.0	0.389
2.5	0.333
3.0	0.292

2. Entropy and enthalpy of adsorption at the
air/water interface

The apparent isosteric entropies and enthalpies of adsorption of pyrazine and pyridine at the air-water interface may be obtained by use of the same procedures employed above for the Hg-water interface, i.e. evaluation of Γ as a function of concentration and ΔG_{ads}° as a function of θ . (The surface charge is not an independent variable in this case.) The trend of ΔS_{ads}° values with θ for pyridine was found to be quite different from that for pyrazine. At low θ , pyridine adsorption occurs with positive ΔS_{ads}° while with pyrazine, ΔS° is negative. The apparent standard isosteric entropies of adsorption at the air/water and Hg/H₂O interfaces are as shown in Table III for various isosteric conditions, i.e. constant θ values.

Table III

Comparison of standard* entropies of adsorption of pyrazine and pyridine at the air/water and Hg/H₂O (q_M=0) interfaces

		$\theta =$							
		0.1	0.15	0.2	0.3	0.4	0.5	0.6	
ΔS_{ads}^0 (air/water) (cal.mole ⁻¹ °K ⁻¹)	Pyridine	1.3	1.8	2	1.85	1.1	0.02	-0.6	
	Pyrazine	-4.4	-2.8	-1.7	-0.5	+0.3	0.9	-	
ΔS_{ads}^0 (Hg/H ₂ O, q _M =0) (cal.mole ⁻¹ °K ⁻¹)	Pyridine	-	-	-9.0	-8.0	-2.5	+2.0	-	
	Pyrazine	-	-14.5	-11.3	-3.5	+1.5	+4.0	-	

* Standard states for the ΔG_{ads}^0 and derived ΔS_{ads}^0 and ΔH_{ads}^0 quantities are the same as those for the Hg/H₂O interface considered earlier.

A substantial degree of compensation between $\Delta H_{\text{ads}}^{\circ}$ and $\Delta S_{\text{ads}}^{\circ}$ for various coverages also arises for the adsorption of both compounds at the air/water interface. The compensation temperatures T_c (slopes of the $\Delta H^{\circ}/\Delta S^{\circ}$ lines) are 300°K for pyridine and 450°K for pyrazine, a difference which reflects the difference between the interactions of these chemically similar molecules with water in the interphase.

E. Adsorption of DBO at the Hg Electrode

Here the adsorption of the more or less spherical and electrically symmetrical molecule DBO (see Section A.5 of Chapter III) will be considered.

1. Free energy of adsorption

$\Delta G_{\text{ads}}^{\circ}$ values were calculated at various coverages from the isotherm relation (77) for $x = 3$, and are shown as $f(q_M)$ in Fig. 43. Variation of $\Delta G_{\text{ads}}^{\circ}$ with q_M for DBO is small, being only 1 kcal compared to 2 kcal mole⁻¹ for pyrazine and pyridine over the range $\pm q_M = 10$ (cf. Figs. 21 and 22). Also the adsorption behavior is distinctly different from that of either pyrazine or pyridine. In the range of $q_M = +10$ to $+1 \mu\text{C cm}^{-2}$, $\Delta G_{\text{ads}}^{\circ}$ becomes more negative with θ , indicating apparent attractive interactions among DBO molecules in the interphase. Such effects could arise if one of the N atoms of DBO lies towards the positively charged surface, and the other is available for intermolecular H-bonding with

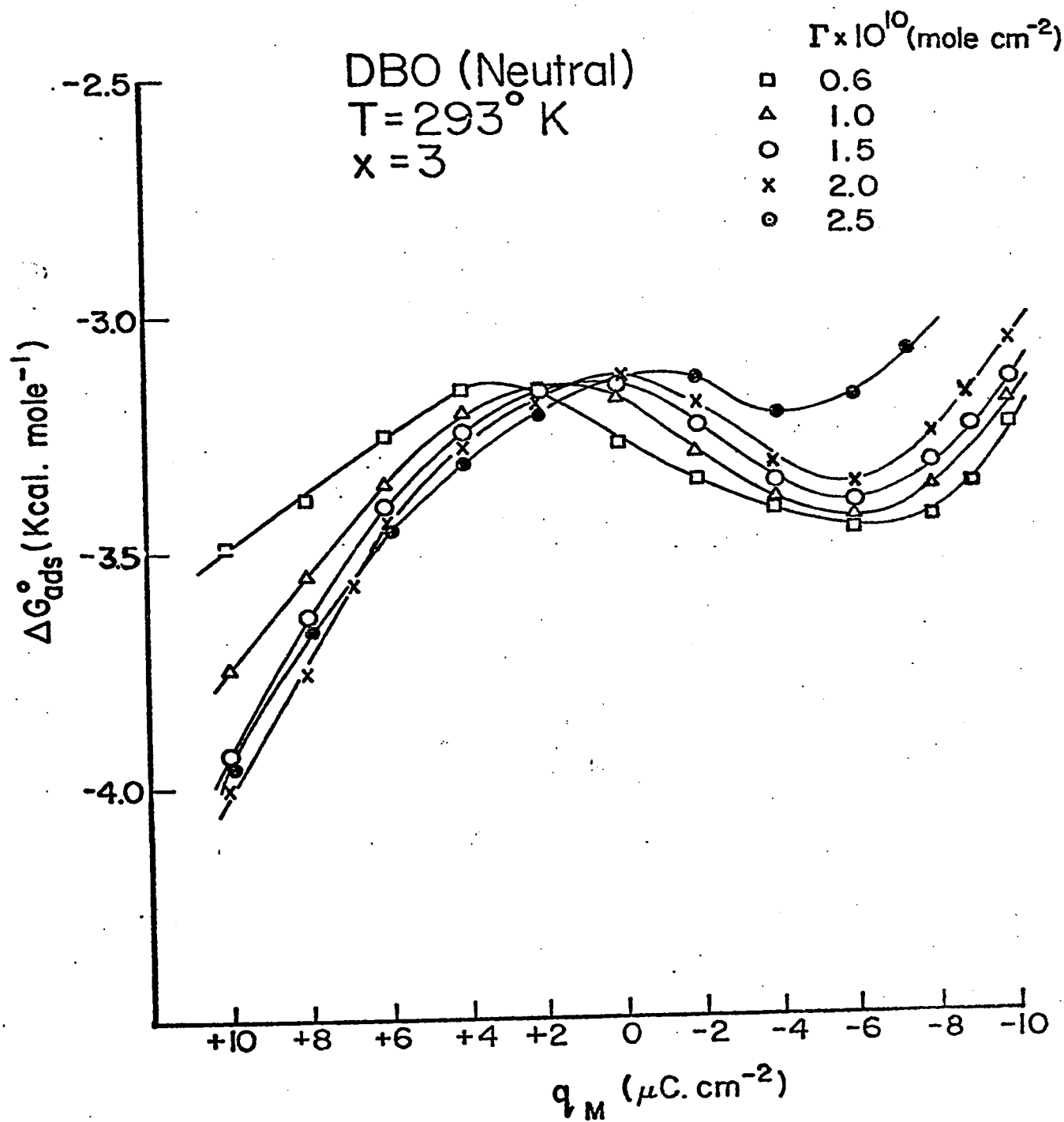


Fig. 43 Variation of $\Delta G_{\text{ads}}^\circ$ of DBO (neutral) at 20°C as $f(q_M)$ at various surface coverages.

water molecules (compare adsorption of pyridine at negative q_M). This orientation for DBO at positive q_M would be facilitated by the presence of the considerable electron density on the N atoms (cf. the adsorption⁶¹ of S-compounds at Hg). The experimental fact that the ΔG_{ads}^0 vs q_M curves coincide around a charge of $+1 \mu C cm^{-2}$, before showing apparent repulsive interactions among the molecules, indicates that the DBO molecule is in the process of gradual orientation as q_M diminishes from a value of $+10 \mu C cm^{-2}$. As q_M becomes more negative than $+1 \mu C cm^{-2}$, the molecule will tend to lie with the hydrocarbon part "on" the surface, and then exhibit repulsive interactions between N atoms of adjacent molecules on the surface.

The fact that the ΔG_{ads}^0 vs q_M curves for $q_M = +1$ to $-10 \mu C cm^{-2}$ have minima around $q_M = -6 \mu C cm^{-2}$, does not mean that water molecules have no orientation at that charge, and are therefore easily replaced. The minimum ΔG_{ads}^0 at $q_M = -6 \mu C cm^{-2}$ could be associated with maximum polarization and optimum orientation of DBO leading to strongest adsorption in the orientation considered at negative q_M (see above). When q_M is more negative than $-6 \mu C cm^{-2}$, water dipole-field interaction increases* and adsorption of DBO will tend to decrease in the usual way.

* Water molecules always tend to be preferentially adsorbed at high enough fields in the competitive adsorption process because one neutral molecule has to replace 3 to 4 water molecules so that the combined interaction of the water molecules with the surface field is ultimately greater.

The behavior of DBO is seen to be quite different from that of pyrazine. The reasons for this are probably to be found in (a) the greater basic character of the N atoms, i.e. the higher electron density on N in DBO than in pyrazine and (b) the absence of π -orbital interaction with the metal surface and a corresponding smaller electric polarizability. Both these factors will tend to make DBO more susceptible to orientation due to positive surface charge than would be the case for pyrazine which tends to lie flat at all q_M values.

2. Esin-Markov effects

Because of the complicated nature of adsorption of the DBO molecule, the ΔE_q vs Γ plots will be divided into two groups (a) for $q_M = +10$ to $-2 \mu\text{C cm}^{-2}$ and (b) $q_M = -2$ to $-10 \mu\text{C cm}^{-2}$, as shown in Figs. 44a and 44b. In contrast to the plots for pyrazine (Fig. 35), the shift of ΔE_q for DBO as q_M becomes positive (Fig. 44a) is in the opposite (positive) direction. This is consistent with the explanation given for both pyrazine and DBO adsorption. Pyrazine does not seem to have any significant interaction with the Hg surface through its N atoms, so that the surface-dipole potential change primarily arises from the replacement of oriented (O atoms towards Hg) water molecules, while for the DBO molecule the surface-dipole potential contribution comes both from replaced oriented solvent molecules and the DBO molecule

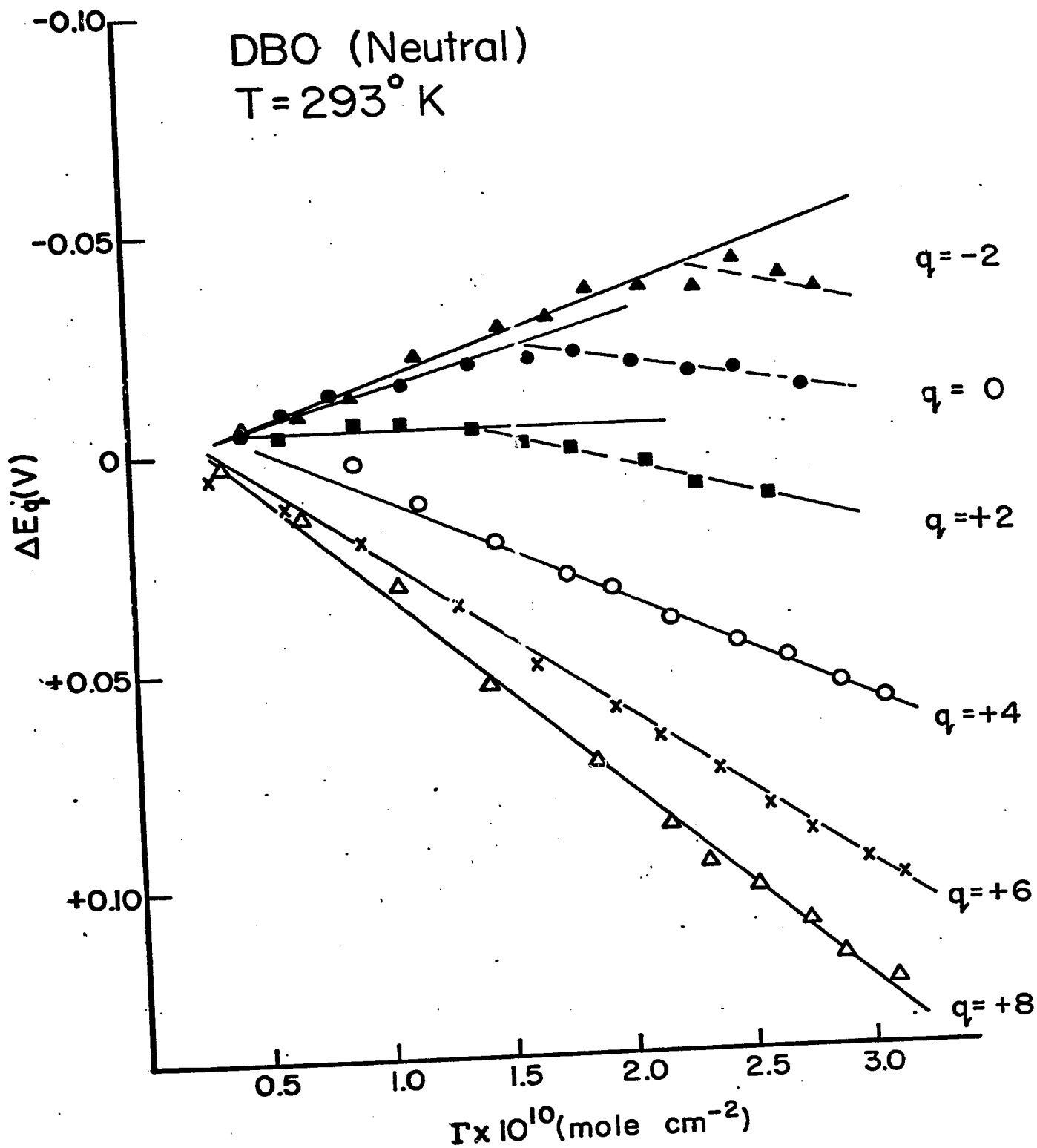


Fig. 44a Esin and Markov plots for DBO (neutral) adsorption at Hg as a function Γ at q_M values +8 to -2 $\mu\text{C cm}^{-2}$.

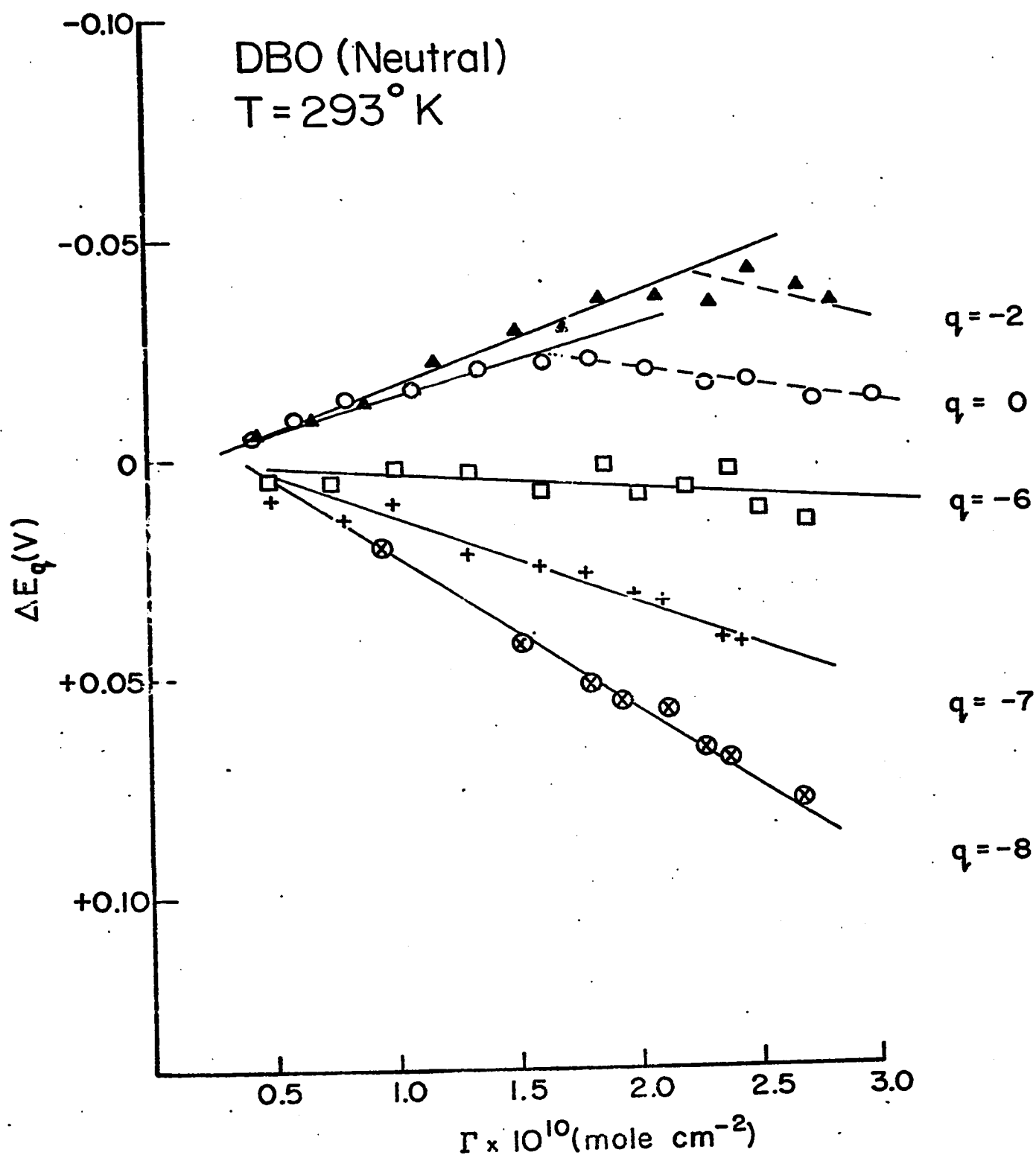


Fig. 44b Esin and Markov plots for DBO (neutral) adsorption at Hg as function Γ at q_M values -2 to -8 $\mu\text{C cm}^{-2}$.

itself oriented due to specific interaction of the negative N centre with the Hg surface when q_M is positive. According to such an interpretation, the DBO molecule interacts more strongly with the surface through one of its N atoms than does pyrazine, and thus ΔE_q changes in the positive direction (cf. change of direction of ΔE_q in pyridine adsorption at negative q_M). With increasing $-q_M$, ΔE_q becomes increasingly negative because, as DBO changes from upright (N atom towards Hg) to the flat (hydrocarbon part towards Hg) orientation, interaction with the surface diminishes. Around $q_M = +1 \mu C \text{ cm}^{-2}$, the surface dipole contributions from replaced water and adsorbed DBO molecules become balanced, producing zero ΔE_q at all θ . At $q_M = -2 \mu C \text{ cm}^{-2}$, where there is no net orientation of water molecules (cf. Section C.3(i) of this Chapter), the observed $-\Delta E_q$ change must mean that orientation polarization contributions to ΔE_q from DBO molecules become important. At $q_M = -6 \mu C \text{ cm}^{-2}$ (Fig. 44b) again the two surface dipole contributions from replaced water molecules and adsorbed DBO cancel each other, producing zero ΔE_q . At more extreme negative charges, e.g. as $q_M \rightarrow -8 \mu C \text{ cm}^{-2}$, the change of surface-dipole potential comes primarily from replacement of oriented water molecules (H atoms towards Hg) which thus produce a positive ΔE_q as found for pyrazine, pyridine and amyl alcohol when q_M is negative.

3. Surface pressure relations

In the case of DBO, changes of slope of the $\phi_q - \Gamma$ relations (Fig. 45) with q_M are not very significant but a tendency for ϕ_q to be lower at positive q_M (for a given Γ) is apparent. This is consistent with attractive interactions between the molecules when q_M is positive. Higher ϕ_q at more negative q_M is indicative of repulsive interactions among the molecules or equivalent solvent interaction effects.

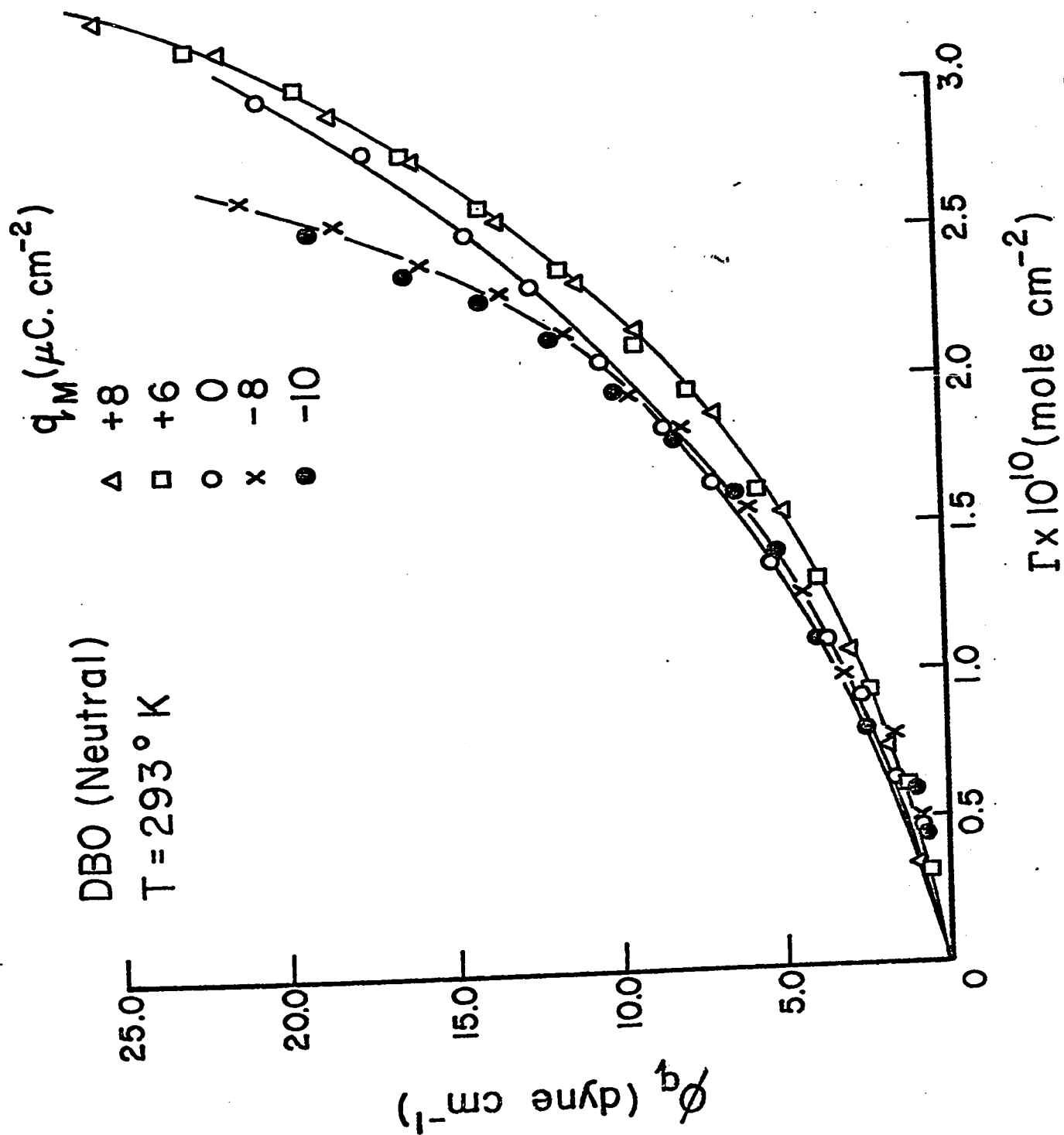


Fig. 45 ϕ_q - Γ plots for neutral DBO in 0.3 M $NaClO_4$ at Hg for various q_M values.

PART II: Adsorption of Organic Cations at the Hg Electrode

A. Introduction

Theories of ionic adsorption in the double-layer at Hg have been based (a) on the Poisson-Boltzmann distribution for the charge in the diffuse-layer and the corresponding ψ_1 potential at its inner limit³⁰ ("Outer Helmholtz Plane"), (b) on ionic repulsion forces⁶³ and finite ion size effects in the adsorption isotherm^{39,69} and (c) image effects associated with discrete charge models¹¹⁰. Most theoretical interpretations¹¹¹ of ionic adsorption at the Hg electrode have been concerned with relatively dilute monolayers of simple ions¹¹¹ for which solvation effects have been neglected. The number of points on which tests of isotherms have been based has often been insufficient^{59,63,111} to enable distinctions to be made between various forms of isotherms.

In this part of the thesis, the adsorption behavior of a number of organic cations up to appreciable coverages where the experimental adsorption isotherm is based on a relatively large number of points between the accessible limits of measurement of surface tension changes at the Hg electrode, has been examined. The interaction effects which are manifested at appreciable coverages have previously been treated^{59,63} in early work in terms of a simple ionic repulsion model and in later calculations in terms of repulsive

effects between ions taking into account electrostatic image effects¹¹¹. At coverages $\theta > 0.1$, however, average distances between adsorbed organic ions, e.g. pyridinium, are $< 17\text{\AA}$. This corresponds to an equivalent three-dimensional concentration of ca. 0.32 M. Towards full coverage, interionic distances correspond to much larger concentrations. In such solutions, effects due to overlap of solvation shell co-spheres¹¹² become substantial but have not previously been considered as a basis for two-dimensional interaction effects between adsorbed ions. As in the thermodynamic theory of three-dimensional solutions at high concentrations, e.g. of Stokes and Robinson¹¹³, these effects are to be added to the normal coulombic attraction or repulsion effects. For a number of organic ions, these interaction effects have been studied for the case of three-dimensional solutions in the water solvent in this laboratory, especially with regard to specificities in solute and solvent structure effects¹⁰⁴.

Estimates of these effects in the two dimensional interphase at a mercury electrode are presented and are based on two types of treatment: a) overlap of Born polarization co-spheres and b) energy changes of the ions due to the dielectric decrement which the ions themselves cause in the water solvent.

B. Treatment of Data

1. Methods of approach

For the purpose of evaluating the form of the dependence of interaction energy amongst adsorbed ions on their coverage at the electrode, it is again convenient (see p.127) to evaluate the coverage dependence of the apparent standard free energy of adsorption, ΔG_{ads}^0 , calculated from an isotherm based on an appropriate configurational function of θ taking into account the number of solvent molecules x which are displaced upon adsorption of the ion. For the organic ions considered in this work, x will be taken as 1 or 3 depending on the supposed location of the ion in the double-layer. Then, with the isotherm relation (77), ΔG_{ads}^0 is evaluated for various q_M values over a range of experimental θ values corresponding to adsorption equilibrium at bulk concentration C . The variation of ΔG_{ads}^0 with θ that is generally found for non-ideal interphases with interaction between the adsorbate ions or molecules can then be treated in terms of some molecular model^{54,59,63} of the interphase as discussed earlier (see p.91 and Section B, Part I of this Chapter).

2. N-methyl pyridinium perchlorate

Plots of the variation of ΔG_{ads}^0 with $\theta^{1/2}$ (cf.^{59,63}) and $\theta^{3/2}$ (cf.¹¹¹) are shown in Figs. 46a and b, calculated for $x = 3$, based on space-filling models. The results are plotted

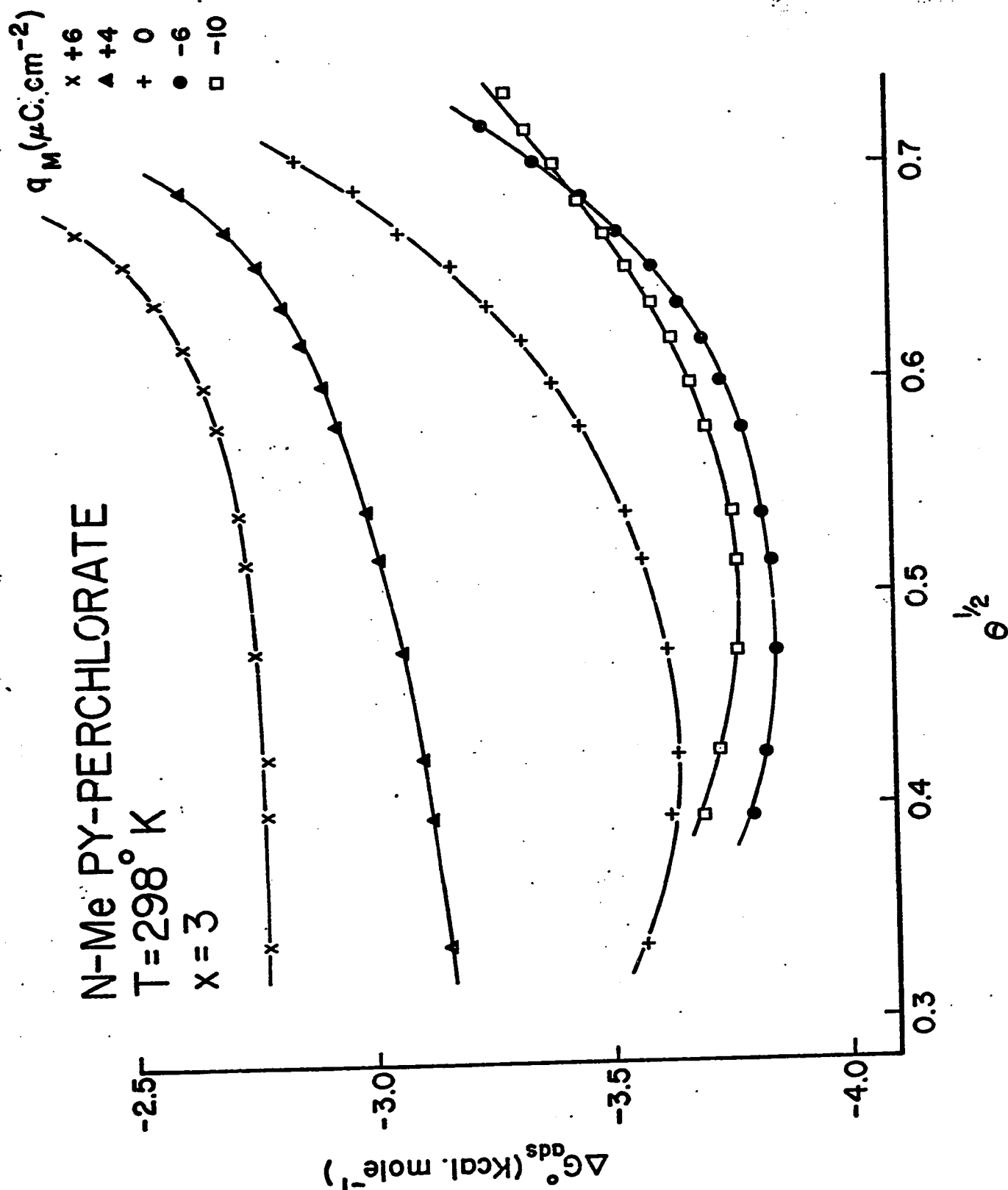


Fig. 46a Variation of ΔG_{ads}° with $\theta^{1/2}$ calculated from experimental data with the size factor $x = 3$ for N-methylpyridinium perchlorate.

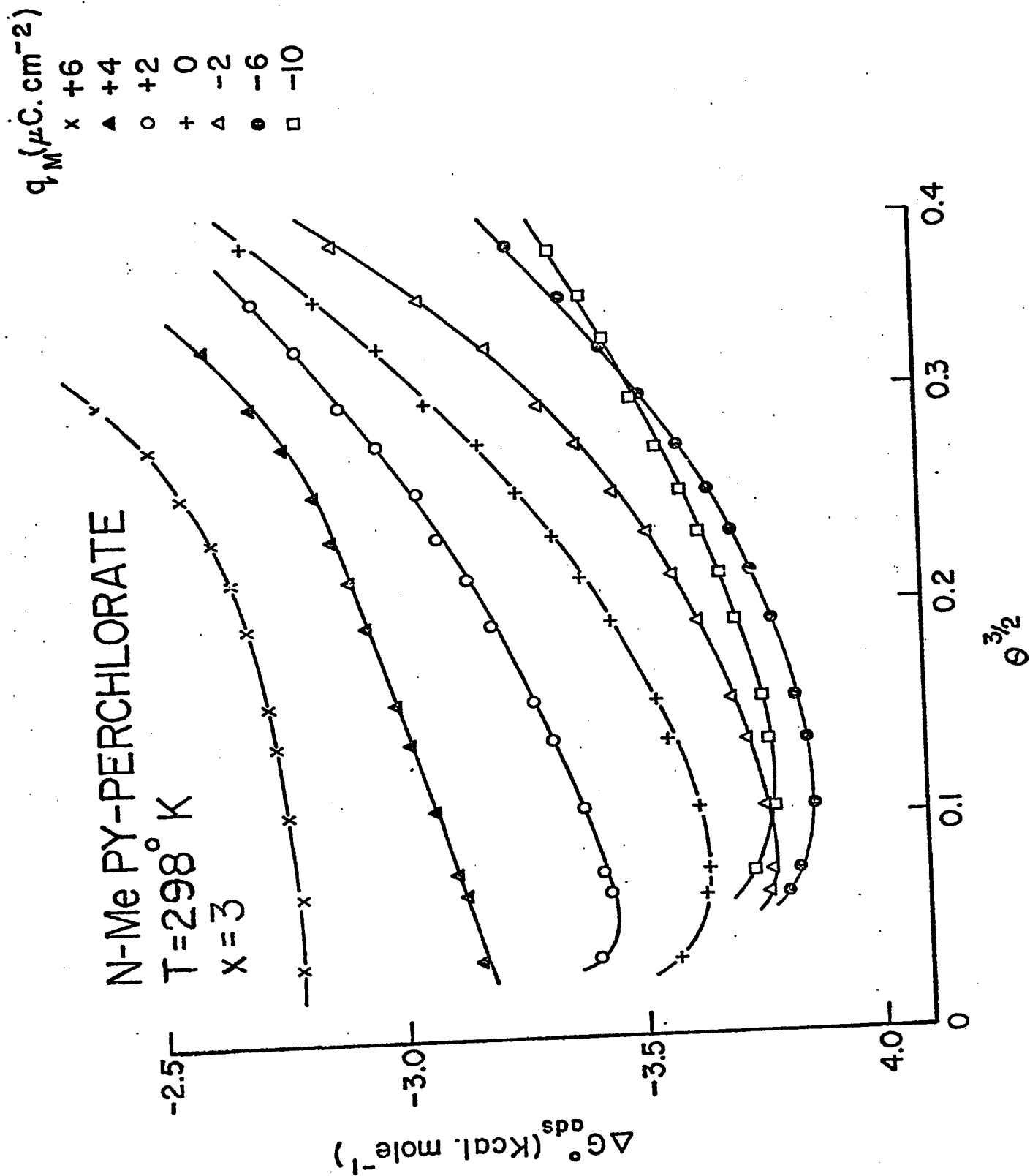


Fig. 46b Variation of $\Delta G^{\circ}_{\text{ads}}$ with $\theta^{3/2}$ calculated from experimental data with the size factor $x = 3$ for N-methyl pyridinium perchlorate.

for 7 values of q_M with points evaluated at 12 to 14 concentrations and equivalent θ values. It is clear that while ΔG_{ads}^0 becomes less negative with increasing θ (repulsive interaction effect), the relation is linear neither in $\theta^{1/2}$ nor in $\theta^{3/2}$.

A $\theta^{1/2}$ relation originates from first order coulombic repulsion effects while a $\theta^{3/2}$ function arises if repulsive interaction effects are calculated for the ionic charge and its image. The present results show that $|\Delta G_{ads}^0|$ decreases more rapidly than either a $\theta^{1/2}$ or $\theta^{3/2}$ function.

The Esin and Markov effects, calculated for various q_M values are shown in Fig. 47. They demonstrate substantial specific adsorption associated with the organic cation. Part of this effect may be due to solvent displacement¹¹⁴ if the organic residue enters the inner region of the double-layer where solvent orientation is charge dependent²⁵. This question will be considered below.

Fig. 48 shows the surface pressure plotted against the surface excess of N-methyl pyridine perchlorate based on experiments in which $HClO_4$ is in constant excess (cf. Chapter III). The ϕ_q and corresponding decrease of γ is hence due only to the organic cation. Also, the small liquid junction potential to the aq. HCl calomel electrode was almost constant. Fig. 48, and the related plot of $\phi_q A$ vs A which can be made where A is the area per mole ($1/\Gamma$) in the interphase, show that θ_q or $\phi_q A$ are independent of the surface charge q_M . This

N-Me PY-PERCHLORATE T=298° K

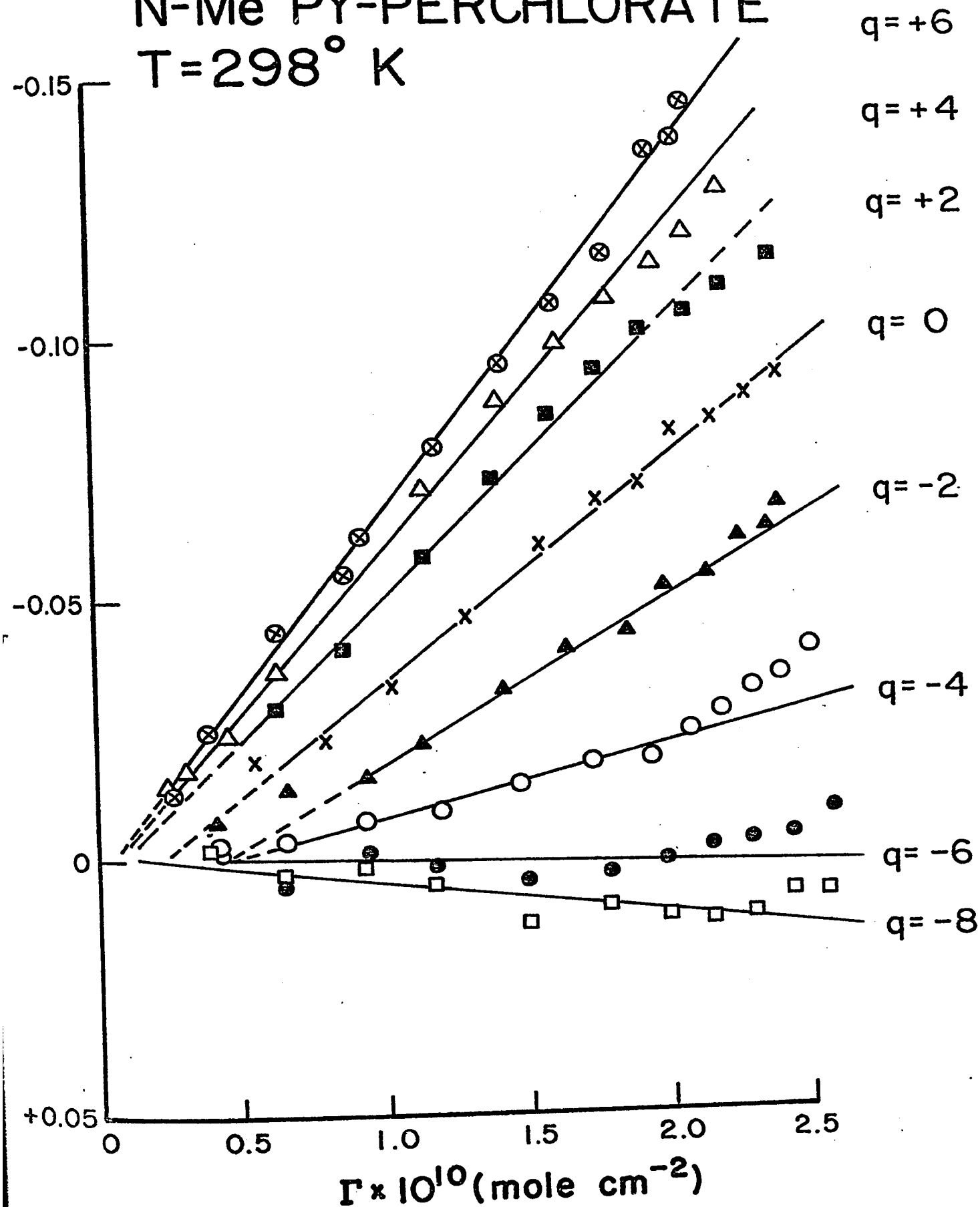


Fig. 47 Esin and Markov plots for N-methyl pyridinium perchlorate adsorption at Hg for various q_M values.

N-Me PY-PERCHLORATE

T = 298° K

$q_M (\mu C. cm^{-2})$

○ +6

△ +4

△ -2

x -8

ϕ_q (dyne cm^{-1})

30

25

20

15

10

5

0

0.5

1.0

1.5

2.0

2.5

$\Gamma \times 10^{10} (mole\ cm^{-2})$

Fig. 48 ϕ_q - Γ plots for N-methyl pyridinium perchlorate in 1M $HClO_4$ at Hg for various q_M values.

is to be contrasted with the behavior of neutral pyridine itself¹¹⁴ where the slopes of $\phi_q - \Gamma$ plots⁸⁰ depend on q_M and the Esin and Markov plots show distinguishable regions characteristic both of displacement of oriented solvent molecules and orientation of pyridine itself, depending on q_M and Γ (see Section C, Part I of this Chapter).

The dependence of ΔG_{ads}^0 calculated for given θ values, on q_M is shown in Fig. 49. As expected for cation adsorption, the ΔG_{ads}^0 becomes more negative with decreasing q_M down to ca. -6 to $-8 \mu C \text{ cm}^{-2}$ where there is a slight decrease again in $|\Delta G_{ads}^0|$ due probably to increasing competition with adsorption of oriented solvent molecules. The curves in Fig. 49 rise to higher, less negative ΔG_{ads}^0 values, as θ increases as shown in Figs. 46a and b.

3. Mono and dications of diazabicyclo-octane (DBO^+ and DBO^{++})

The plots of ΔG_{ads}^0 for the mono-positive cation of DBO as a function of q_M are shown in Figs. 50 and 51 for various Γ values with the data calculated taking $x = 1$ (Fig. 50) or $x = 3$ (Fig. 51). The reasons for the choice of these x values will be considered later. At higher Γ , ΔG_{ads}^0 data cannot reliably be derived for q_M values > 4 to 0 due to crowding together of the electrocapillary curves on the positive branches. The Esin and Markov plots are shown in Fig. 52a and, in contrast to those of Fig. 47 for the pyridine perchlorate solutions, show a tendency to reach a limiting ΔE_q

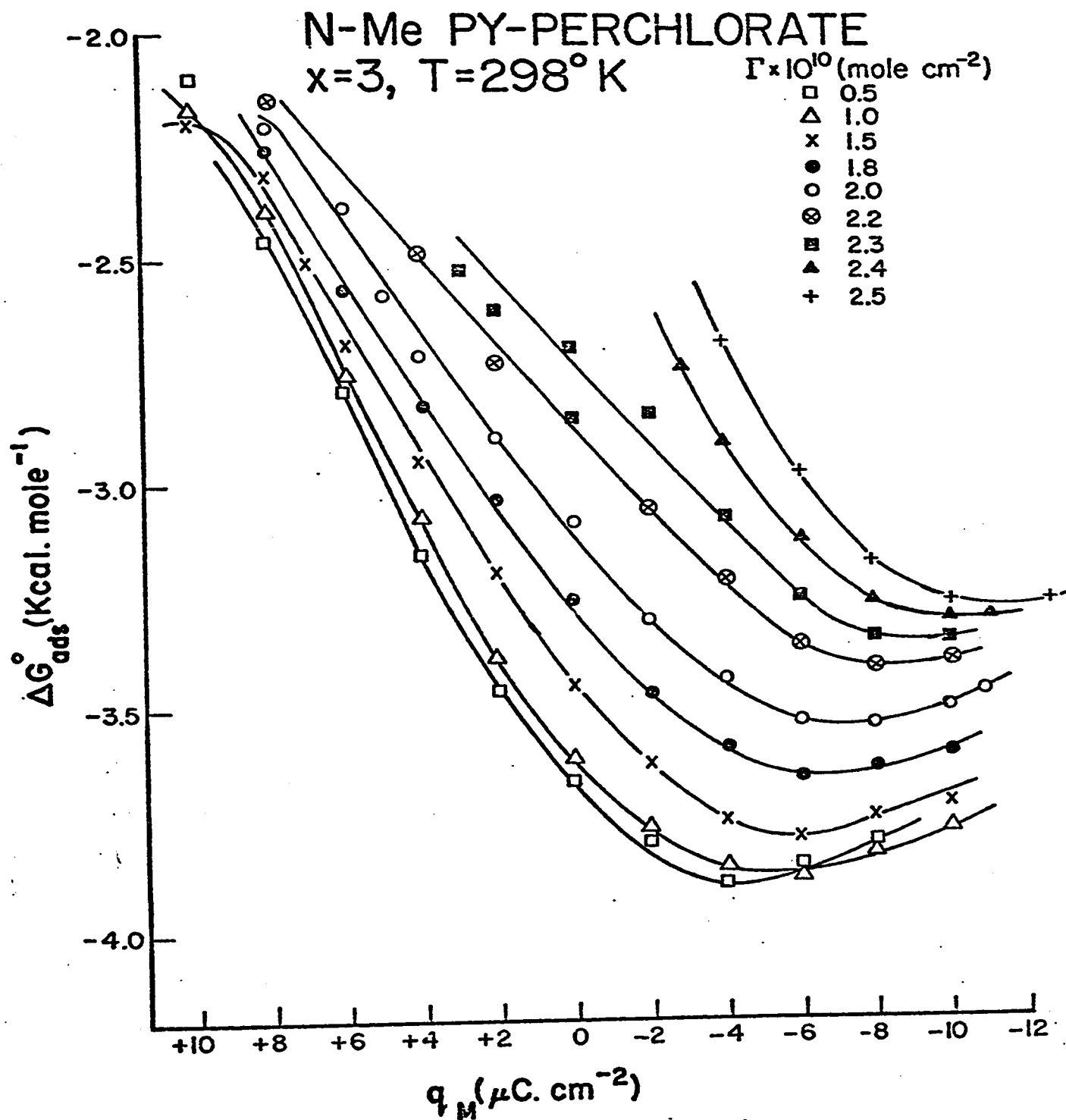


Fig. 49 Dependence of $\Delta G_{\text{ads}}^{\circ}$ on q_M for various Γ values for adsorption of N-methyl pyridinium perchlorate at Hg, calculated for $x = 3$.

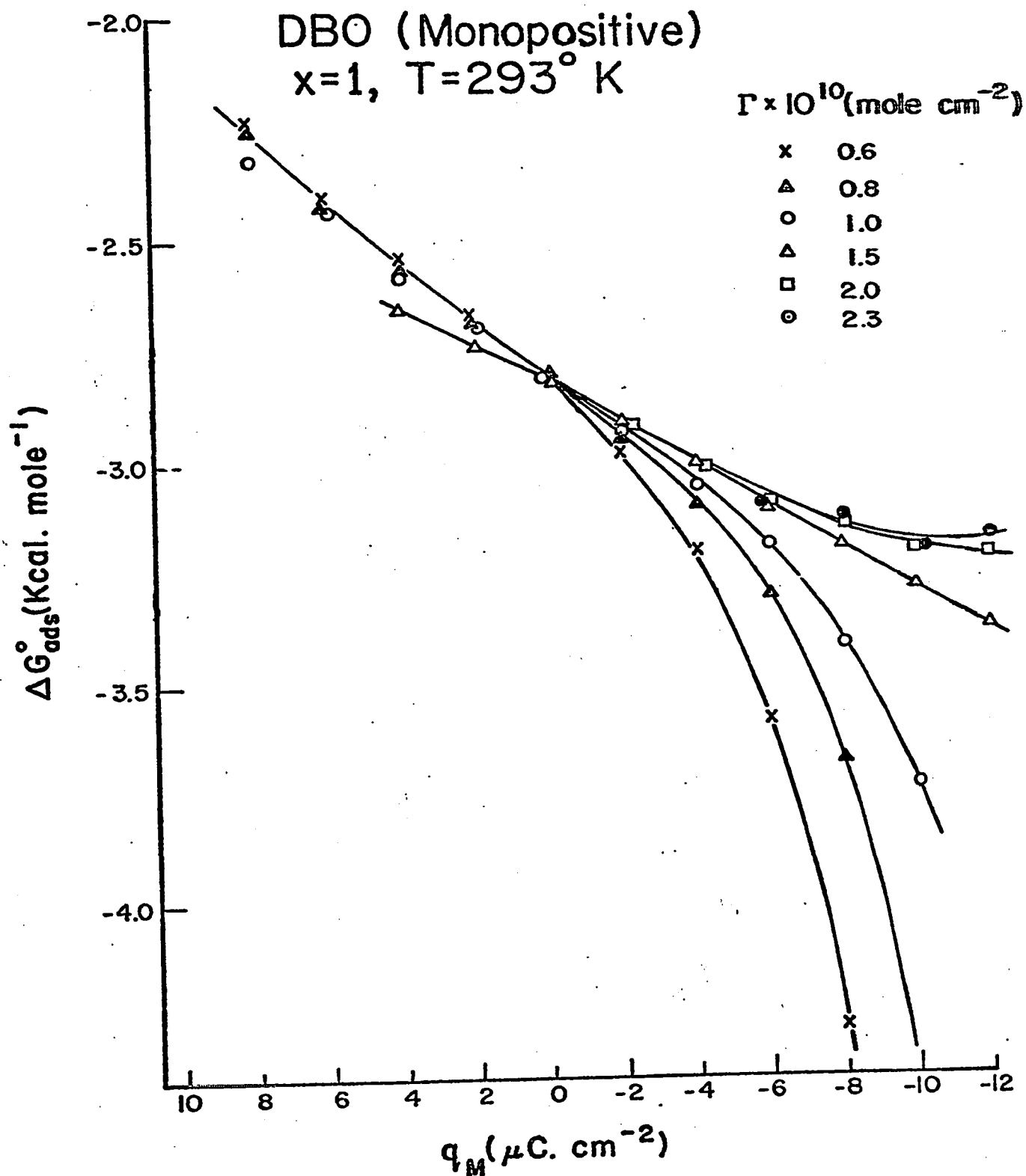


Fig. 50 Dependence of $\Delta G_{\text{ads}}^{\circ}$ on q_M for various θ values for adsorption of the monocation of DBO, calculated for $x = 1$.

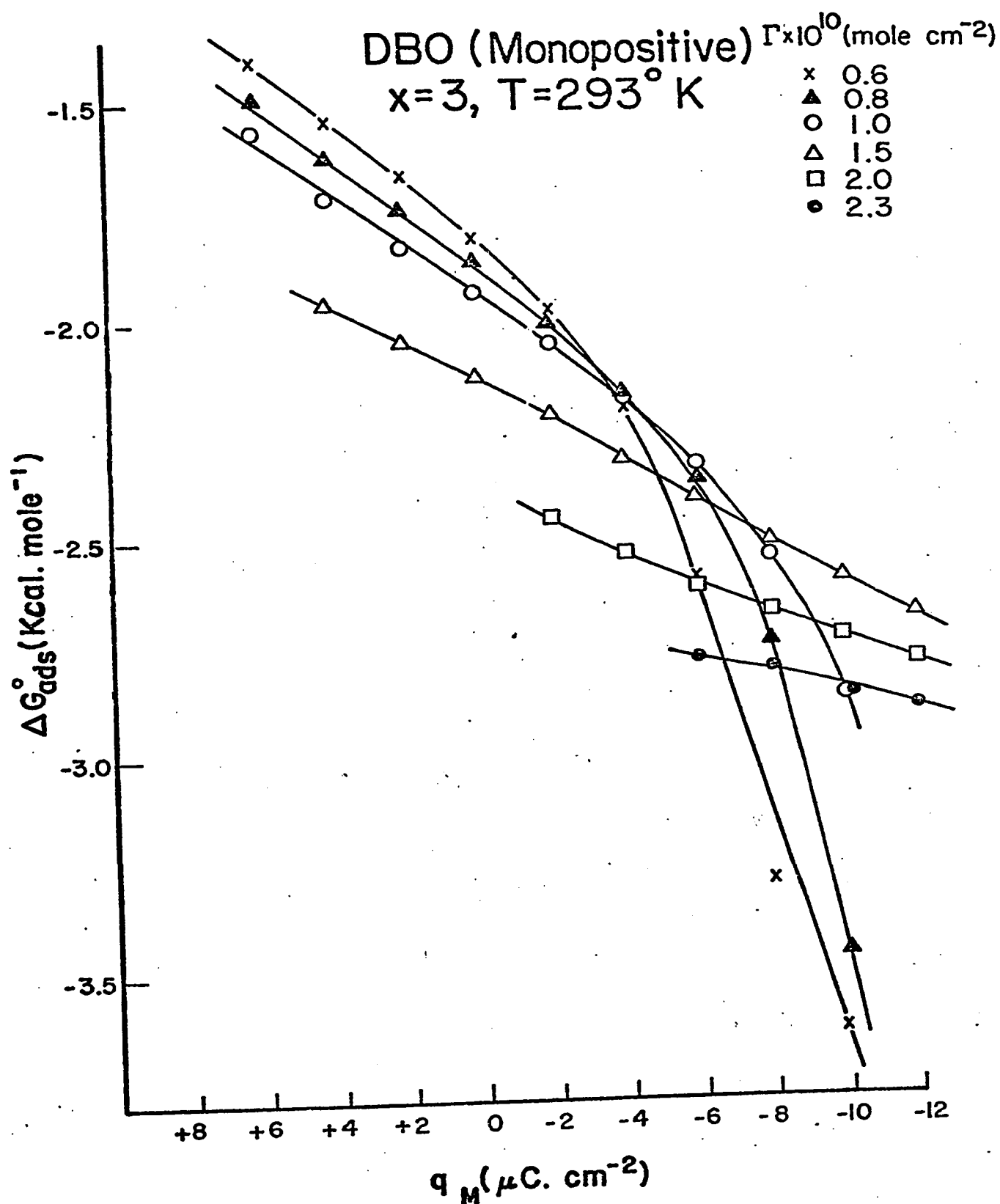


Fig. 51 Dependence of $\Delta G_{\text{ads}}^\circ$ on q_M for various θ values for adsorption of the monocation of DBO, calculated for $x = 3$.

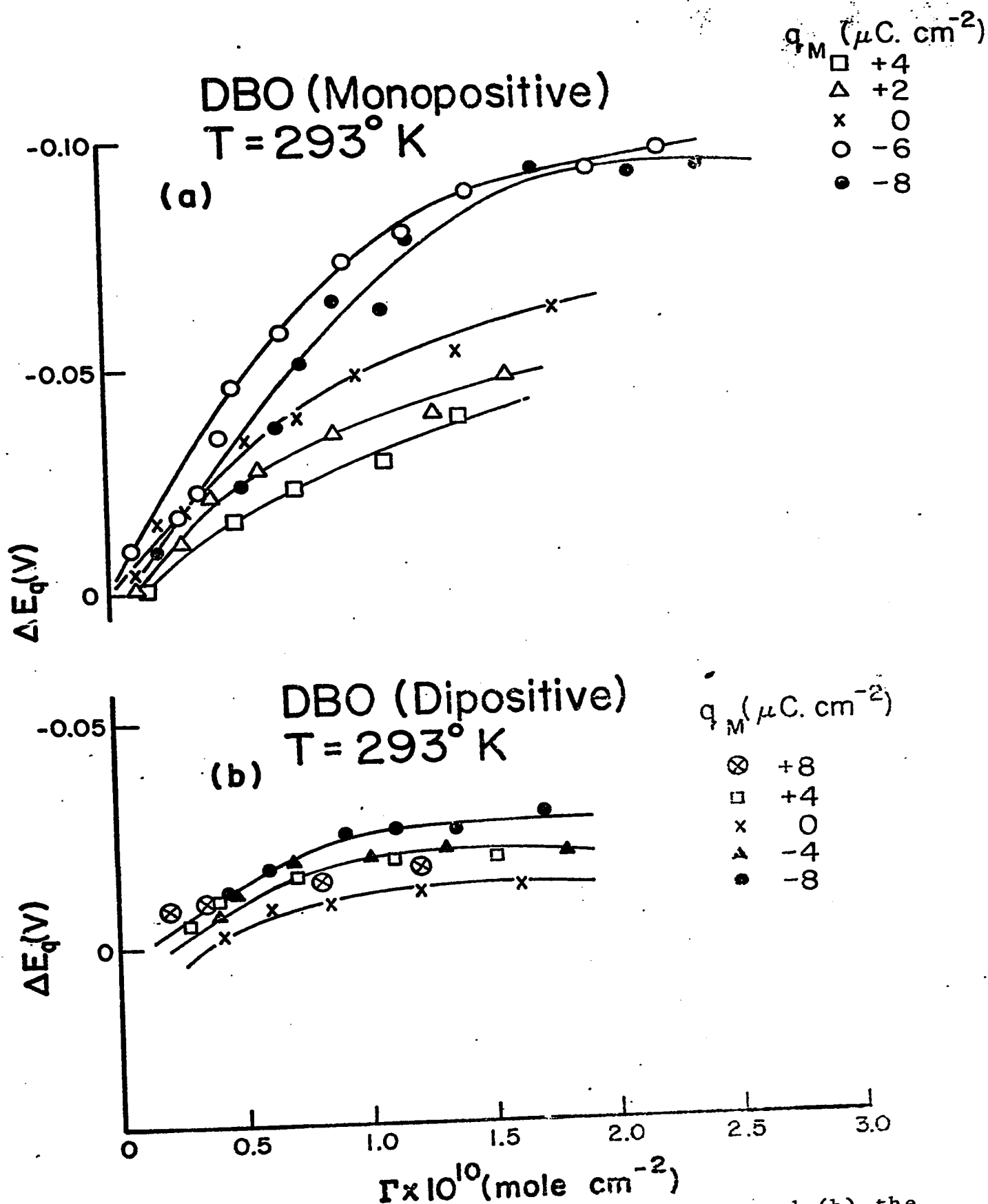


Fig. 52 Esin and Markov plots for (a) the mono and (b) the dications of DBO at various q_M values.

value with increasing Γ . We argue below that this may be due to the different location of the DBO cation from that of the pyridinium-type cation in the double-layer, and to the presence of co-adsorbed anions.

Corresponding graphs for ΔG_{ads}^0 as $f(q_M)$ with $x = 1$ or 3 are shown in Figs. 53a and b for the dipositive cation of DBO. For this ion, the EM effects are quite small (< 30 mV) and reach limiting values at each q_M with increasing Γ (Fig. 52b).

For the mono-positive DBO ion, the $\phi_q - \Gamma$ plots are as in Fig. 54a; they are almost linear but with increasing slope as q_M becomes more negative. Since the effect of surface charge on the $\phi_q - \Gamma$ slope does not show a maximum or minimum at $q_M = 0$ (or $-2 \mu C \text{ cm}^{-2}$ where net water orientation is zero), this variation of $d\phi_q/d\Gamma$ cannot be due to solvent orientation effects but rather to the orientation of the positive charge and to its proximity to the metal surface where, on the positive branch, effects of anion adsorption can become appreciable. The dipositive ion exhibits an essentially similar, but smaller dependence of ϕ_q on Γ and q_M (Fig. 54b).

C. Dependence of ΔG_{ads}^0 on Coverage

1. N-methyl pyridinium ions

The results of Fig. 46 show that there is no appreciable range of coverage values over which ΔG_{ads}^0 varies

DBO (Dipositive) $x=1$, $T=293^{\circ}\text{K}$

$\Gamma \times 10^{10} (\text{mole cm}^{-2})$

$\times$ 0.4
 $\square$ 0.6
 $\circ$ 0.8
 $\triangle$ 1.2
 $\bullet$ 1.5

(a)

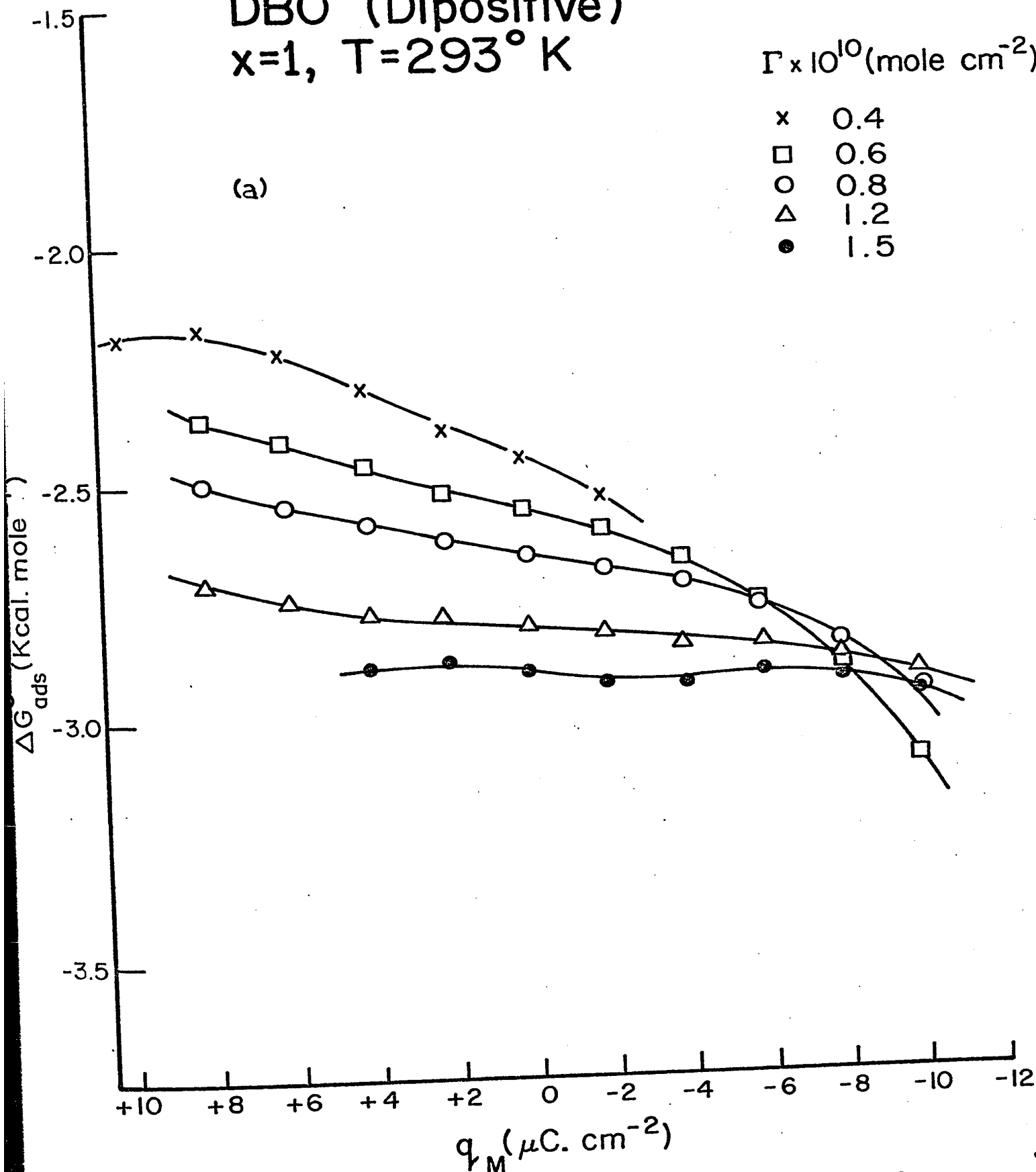


Fig. 53a Dependence of $\Delta G^{\circ}_{\text{ads}}$ on q_M for various θ values for adsorption of the dication of DBO calculated for $x = 1$.

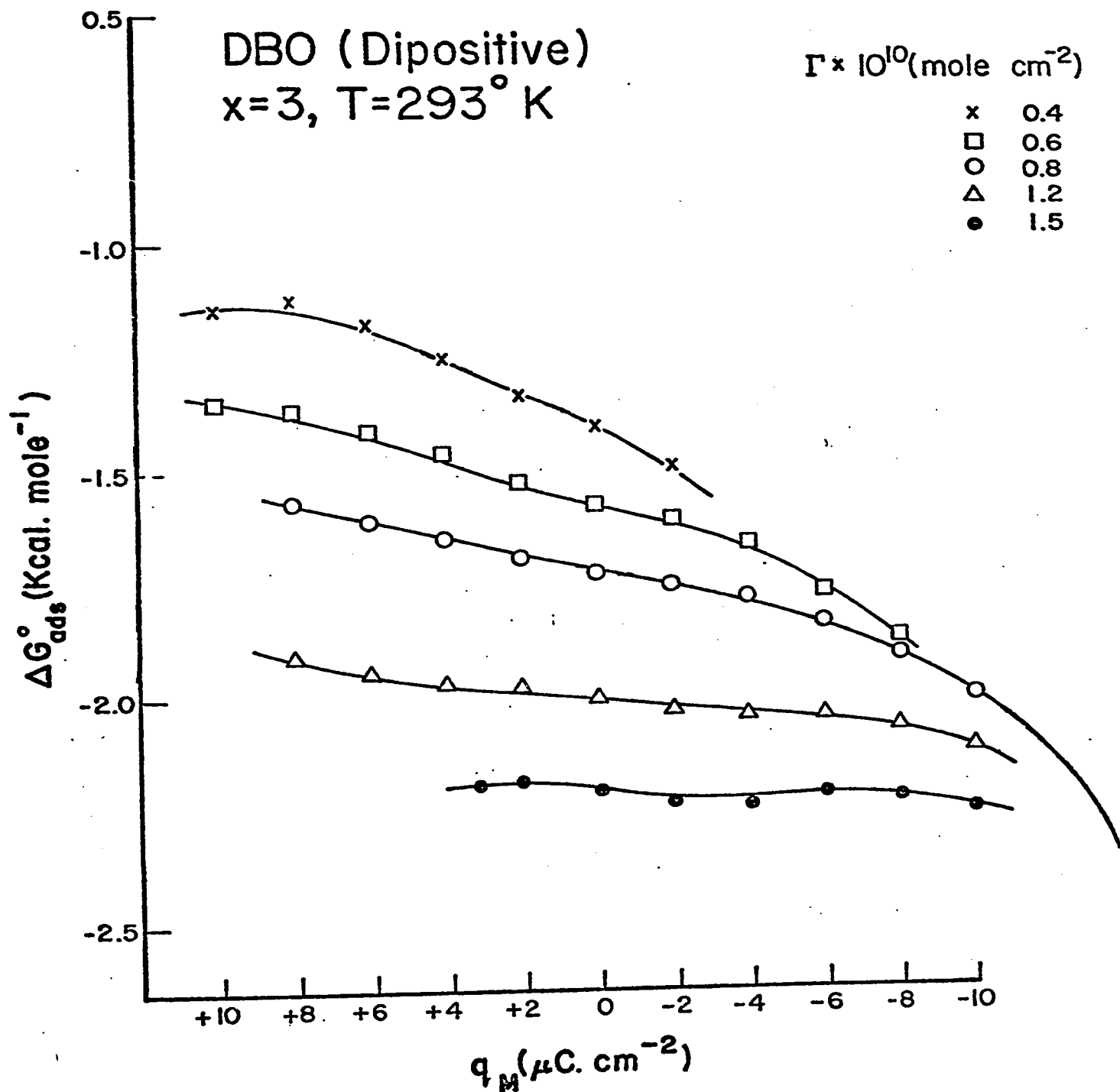


Fig. 53b Dependence of $\Delta G_{\text{ads}}^\circ$ on q_M for various θ values for adsorption of the dication of DBO calculated for $x = 3$.

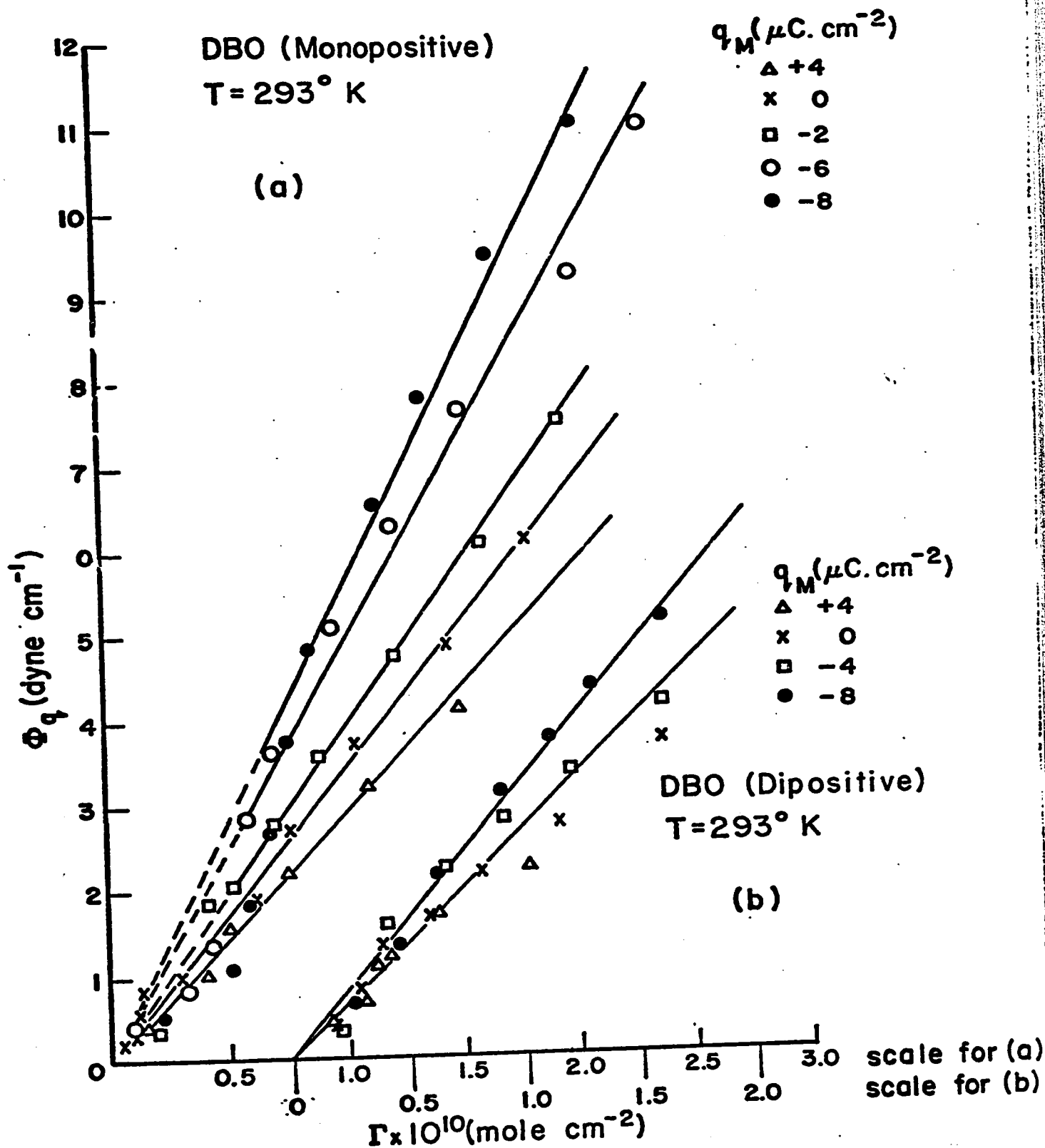


Fig. 54 ϕ_q - Γ plots for adsorption of DBO (a) monocation at Hg .
in 0.3 M KH_2PO_4 and (b) dication at Hg in 1 M aq. HClO_4 .

linearly with $\theta^{1/2}$ or $\theta^{3/2}$ as expected on simple models^{63,111} of ionic interaction in the interphase. The general trend (Fig. 46) is for ΔG_{ads}^0 to decrease more rapidly than corresponds to the $\theta^{3/2}$ relation, i.e., interactions within a system of adsorbed ions and their images¹¹¹. The $\theta^{1/2}$ and $\theta^{3/2}$ relations arise simply from coulombic interactions.

At appreciable coverages by specifically adsorbed ions, co-sphere interaction effects between hydration shells will arise and contribute an important new repulsive interaction term in the interphase, as in three-dimensional solutions at concentrations >ca. 1 M where activity coefficients can become >1 due to solvation effects. These effects may be estimated as follows by two methods:

(i) Partial loss of long-range Born solvation energy

A square lattice of adsorbed ions is considered first. The mean distance between two adjacent ions is represented by AB in Fig. 55a, where

$$AB = \left(\frac{1}{N_A \Gamma} \right)^{1/2} \quad (102)$$

for a surface concentration Γ mole cm^{-2} , and N_A is Avogadro's number. At finite coverages, the Born polarization energy G_B in the interphase due to the adsorbed cations, will be diminished due to overlap of spherical volume elements of the solvent polarized by neighboring ions. We assume co-sphere¹¹² effects are significant for Born energies $>kT$, i.e., for co-sphere radii r given by

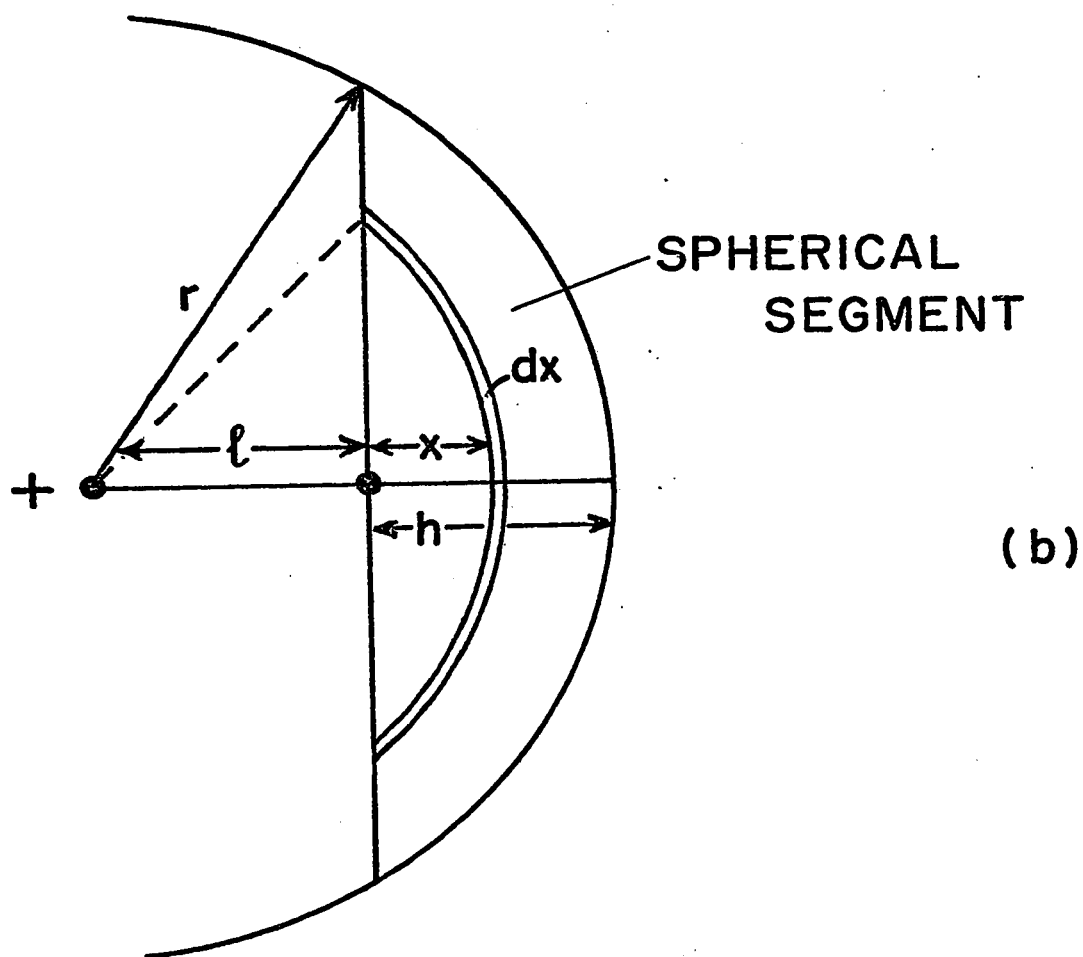
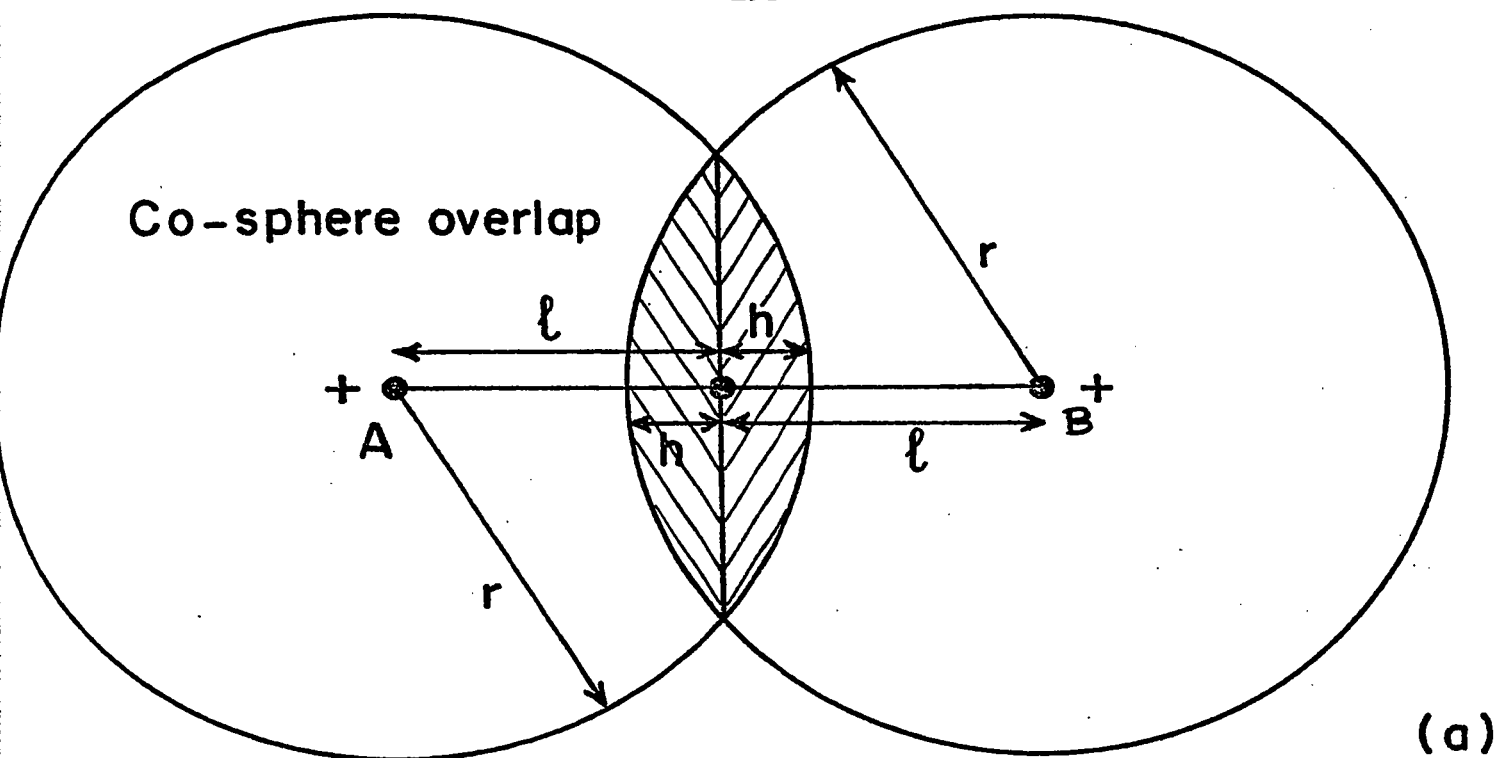


Fig. 55 Model for calculation of solvation energy change in an interphase due to ion solvation co-sphere overlap. (a) Overlapping co-spheres; and (b) integration over the spherical segment.

$$G_B = \frac{e^2}{2r\epsilon} = kT \quad \text{or} \quad r = \frac{e^2}{2\epsilon kT} \quad (103)$$

for univalent cations. Three values of ϵ will be considered, 10, 36 and 80. For overlapping spherical shell elements, the height h of the overlap segment (Fig. 55b) is

$$h = r - \frac{1}{2} \left(\frac{1}{N_A \Gamma} \right)^{1/2} \quad (104)$$

and $r = \ell + h$ where $2\ell = AB$ or $\ell = (1/4 N_A \Gamma)^{1/2}$. The polarization energy in a sphere as a function of distance from a centrally situated charge e is given¹¹⁵ by

$$W_h = \frac{1}{8\pi\epsilon} \int_x^\infty F^2 dV \quad (105)$$

for a volume element dV in a field F . For the situation shown in Fig. 55b,

$$dV = 2\pi(\ell+x)x dx \quad (106)$$

where x is measured along the height of the segment (Fig. 55b). Then (cf. ref.¹¹⁵)

$$W_h = \frac{1}{4\epsilon} \int_0^h \left[\frac{e}{(\ell+x)^2} \right]^2 (\ell+x)x dx \quad (107)$$

$$= \frac{e^2}{4\epsilon} \int_0^h \frac{x dx}{(\ell+x)^3} \quad (108)$$

The integral is easily evaluated giving for an overlap distance of $2h$

$$W_h = \frac{e^2}{4\epsilon} \cdot \frac{h^2}{2\ell(\ell+h)^2} \quad (109)$$

In terms of θ ,

$$W_h = \frac{e^2}{2\epsilon r^2} \left[r^2 \Gamma_{\max}^{1/2} \theta^{1/2} + \Gamma_{\max}^{-1/2} \theta^{-1/2} / 4 - r \right] \quad (110)$$

since $\theta = 1/4 \ell^2 \Gamma_{\max}$, $h^2 = (r-\ell)^2$ and $\ell+h = r$. Relations (109) or (110) will apply provided the extent of overlap of co-spheres is not too large. In the square lattice, the total overlap energy associated with each ion will be $\frac{1}{2}(8W_h)$; noting that for each interaction between a given pair of ions, 2 segments are involved, h will be dependent on surface concentration through equation (104).

Numerical evaluation of equation (109) was made and the results are shown in Fig. 56. The critical co-sphere "contact" distance defined for $G_B = kT$ obviously depends on ϵ . Results of calculations of $\epsilon = 10$ (curve (1)) and 36 (curve (2)) are shown in Fig. 56. For $\epsilon = 80$, $W_h = 0$ up to $\theta = 0.7$ since r is very small; for this case no realistic results arise. Low values of ϵ between 10 and 36 have been deduced⁴⁶ and considered previously²⁵ for the compact part of the double-layer. These values of ϵ evidently give values of W_h having the correct order of magnitude for the total overlap energy $4W_h$, especially for $\epsilon = 36$. In an hexagonal lattice, the overlap energies will be slightly different since the mean distance AB will then be given by $AB = \left(\frac{2}{\sqrt{3} N_A \Gamma} \right)^{1/2}$.

More specific solvent-structure co-sphere effects will also be significant (cf. the b coefficients of the linear

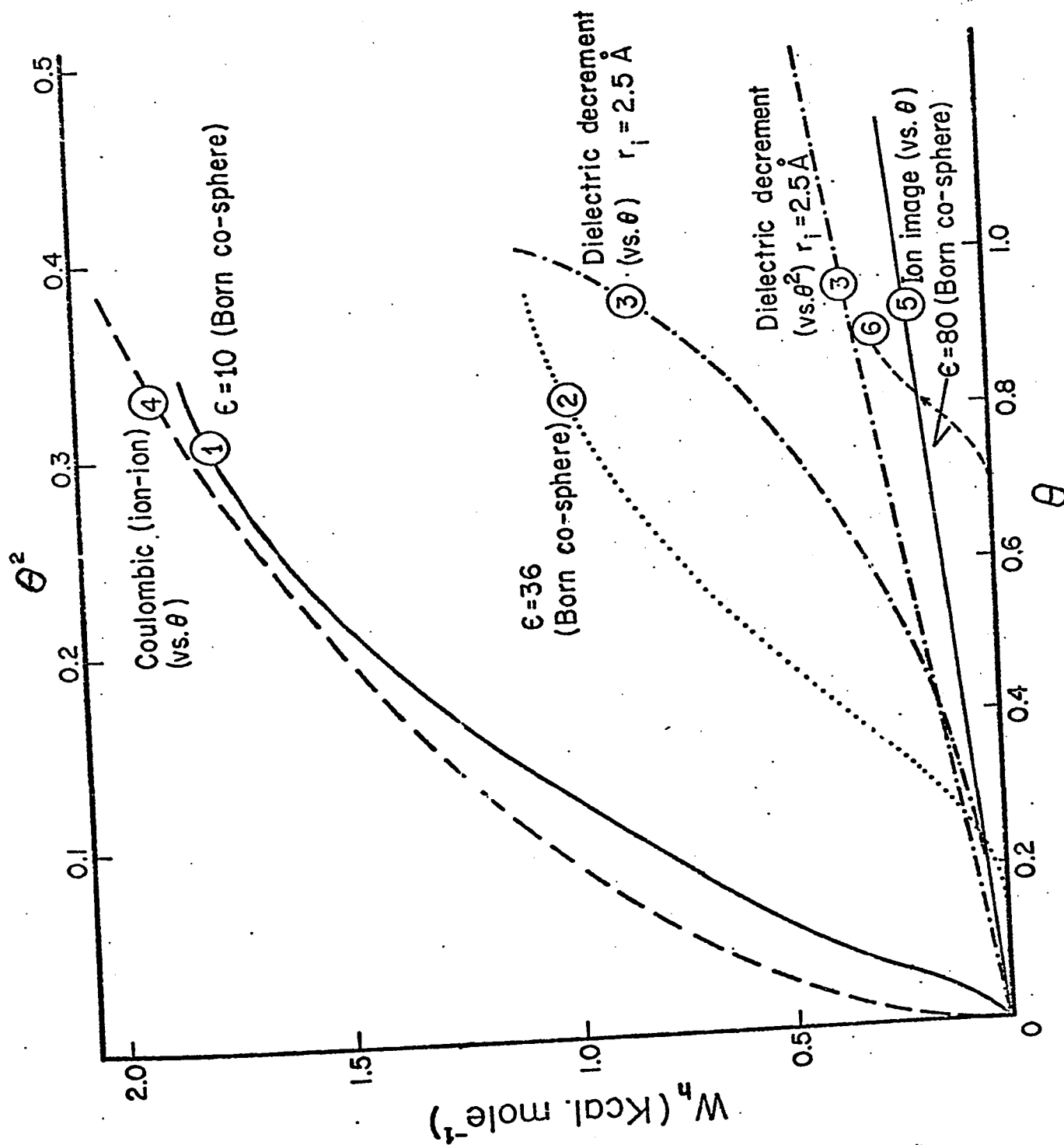


Fig. 56 Co-sphere overlap energy W_h as a function of coverage θ or θ^2 for various types of calculation. Also coulombic ion-ion and ion/image-ion/image interaction energies are shown.

term in concentration dependence of partial molar volumes¹¹⁶), e.g. due to H-bond breaking, but these are difficult to treat in any quantitative way at the present time.

The above calculations obviously give only a first order approximation for the overlap energy due to diminution of dielectric polarization energy. They probably give an upper limit to the effects since only along the line of centres AB in the overlap segment will the field vectors of the adjacent ions exactly cancel one another. An exact solution would, however, be extremely complex. Some indication that the method of calculation is not seriously in error may be shown by considering the problem in another way, as follows.

(ii) Change of polarization in terms of dielectric decrement

A more empirical approach is to calculate the change of self-energy of the ions which arises because of the decrease of dielectric constant which the ions themselves bring about in the solution. The N^+ centre in ionized pyridine or its N-Me derivative has about the radius of an Na^+ ion. It is appropriate therefore to use the mean ionic dielectric decrement (δ) value $\delta = 5.7$ for NaF since a datum for only the cation is required. In a three-dimensional solution, the mean interionic distance d (cf. Stokes and Robinson¹¹⁷) is given by $d = (1000/N_A C)^{1/3}$ for a molar concentration C . The effective dielectric constant $\bar{\epsilon}$ for various inter-ionic distances may then be related to this distance and used to evaluate the self-energy of ions in the two-dimensional

interphase at surface concentrations corresponding to the same inter-ionic distances.

The change ΔW_h of self-energy of the adsorbed ions of radii r_i due to their effect on the dielectric constant of the solvent in the interphase will be

$$-\Delta W_h = \frac{e^2}{2r_i} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_c} \right) \quad (111)$$

where $\epsilon_\infty = 80$ and ϵ_c is the dielectric constant at an ionic concentration C given by

$$\epsilon_c = \epsilon_\infty - \delta C \quad (112)$$

where δ is the molar dielectric decrement. Then equation (111) becomes

$$-\Delta W_h = \frac{e^2}{2r_i} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_\infty - \delta C} \right) \quad (113)$$

Ions in the two-dimensional interphase will be at the same inter-ionic distance as in a bulk solution of concentration C when

$$\left(\frac{1000}{N_A C} \right)^{1/3} = \left(\frac{1}{N_A \Gamma} \right)^{1/2} \quad (114)$$

i.e. when

$$C = \frac{1000}{N_A} (N_A \Gamma)^{3/2} \quad (115)$$

Hence, as a function of Γ ,

$$-\Delta W_h = \frac{e^2}{2r_i} \left[\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_\infty - \frac{\delta 1000}{N_A} (N_A \Gamma)^{3/2}} \right] \quad (116)$$

As previously, Γ can be expressed as a fractional coverage θ upon assignment of a value for $\Gamma_{\max}$, the surface excess for monolayer coverage, determined, e.g. by means of space-filling models.

The results of this calculation are compared with those of method (i) in Fig. 56, curve 3.

The hydration co-sphere effects have to be added to the coulombic effects arising from lateral ionic or ion - image interactions, as they do in a corresponding way in theories of ionic solutions¹¹³. For $\epsilon = 36$, such interactions give rise to curves (4) and (5) in Fig. 56. The coulombic interactions themselves, based on direct ion-ion repulsion, are rather too large to account for the diminution of $|\Delta G_{\text{ads}}^0|$ with θ while those calculated on the basis of the ion + image interactions¹¹¹ are too small in relation to the experimentally observed changes of ΔG_{ads}^0 with coverage (cf. also ref.¹¹¹). For the ion-image* calculations, an effective radius of the charge centre of $2.5 \text{ \AA}$ was taken, based on space-filling models, and the value of ϵ was taken as 36.

Both the direct coulombic interaction effects (curve 4, Fig. 56) and the Born co-sphere overlap effects

* Ion-image interaction energy U_i is given by the formula

$$U_i = \frac{e^2 r_i^2 \pi^{3/2} n_a^{3/2}}{4\epsilon} \left[1 - \frac{3}{4} r_i^2 \pi n_a \right],$$

n_a being the number of ions cm^{-2} on the surface.

(curves 1 and 2, Fig. 56) increase with a power of θ less than 1 (as also follows from equation (110) except at low θ). For $\epsilon = 36$, however, the effects are of the correct order of magnitude. The most correct form of the dependence of W_h on θ is obtained from the dielectric decrement, treatment, based on equation (116); this calculation shows that W_h increases with θ^2 as found experimentally.

D. Comparison of Adsorption Behavior of N-Me Pyridinium Perchlorate, DBO^+ and DBO^{++} ions

The adsorption behavior will be examined in terms of (a) the variation of ΔG_{ads}^0 with θ ; (b) the surface pressure as $f(q_M)$ and (c) the Esin and Markov effects. For DBO^+ , $-\Delta G_{\text{ads}}^0$ decreases in approximately the expected way (cf. the theoretical calculation, Fig. 56) with θ if q_M is appreciably negative. As q_M becomes 0 or positive, the decrease of $-\Delta G_{\text{ads}}^0$ disappears and eventually becomes reversed (Fig. 57a). The opposite trend arises with DBO^{++} ions; $-\Delta G_{\text{ads}}^0$ is least at $+8 \mu\text{C cm}^{-2}$ but increases with θ and this trend is smaller as q_M becomes negative ($-8 \mu\text{C cm}^{-2}$ in Fig. 57b). Thus, with DBO^+ , the lateral interactions are repulsive at negative q_M , zero at $q_M = 0$ to $-2 \mu\text{C cm}^{-2}$ and somewhat attractive as $q_M \rightarrow +4 \mu\text{C cm}^{-2}$.

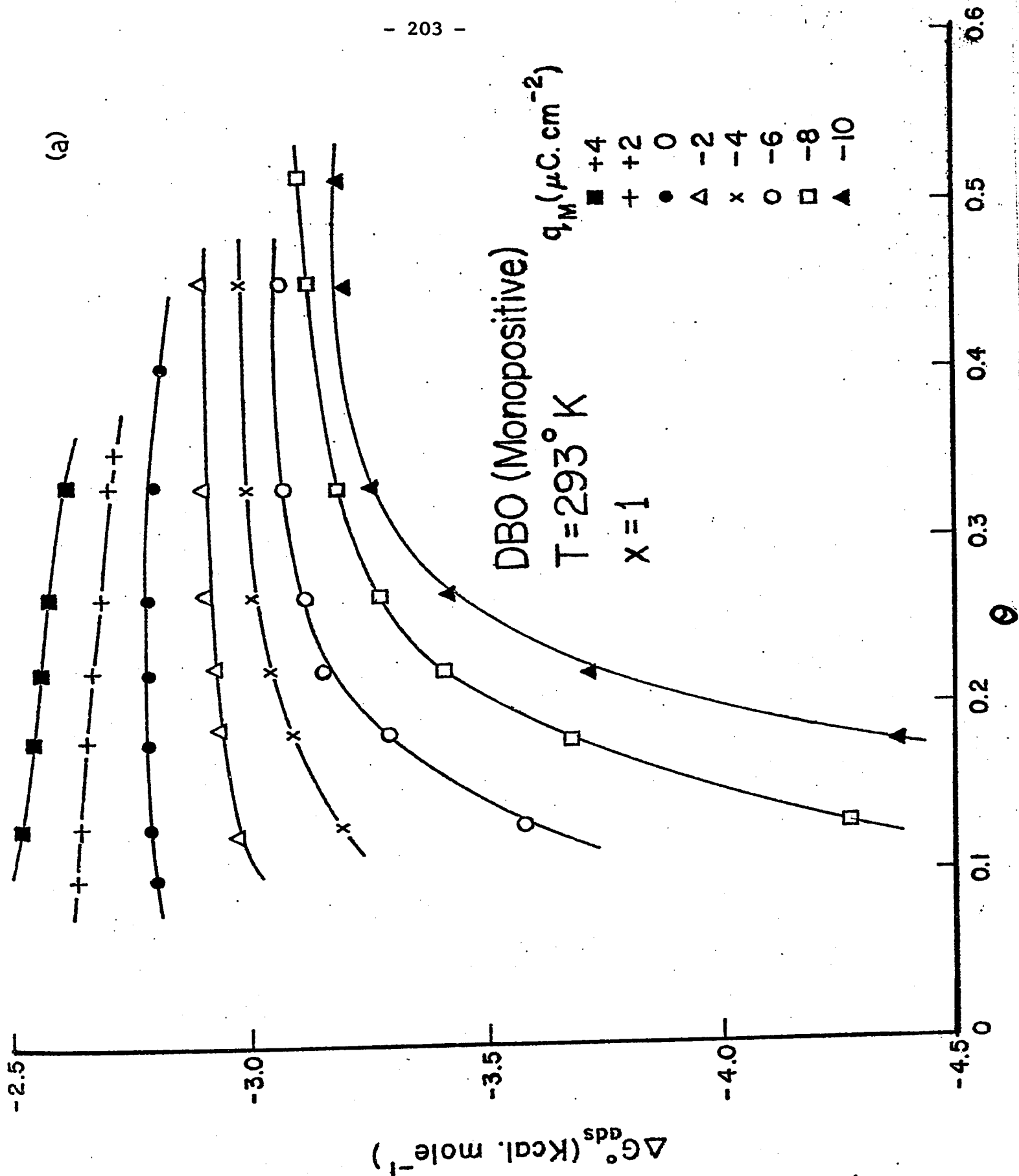


Fig. 57a Dependence of ΔG_{ads}° on θ for DBO monocation at various q_M values (calculated for $x = 1$).

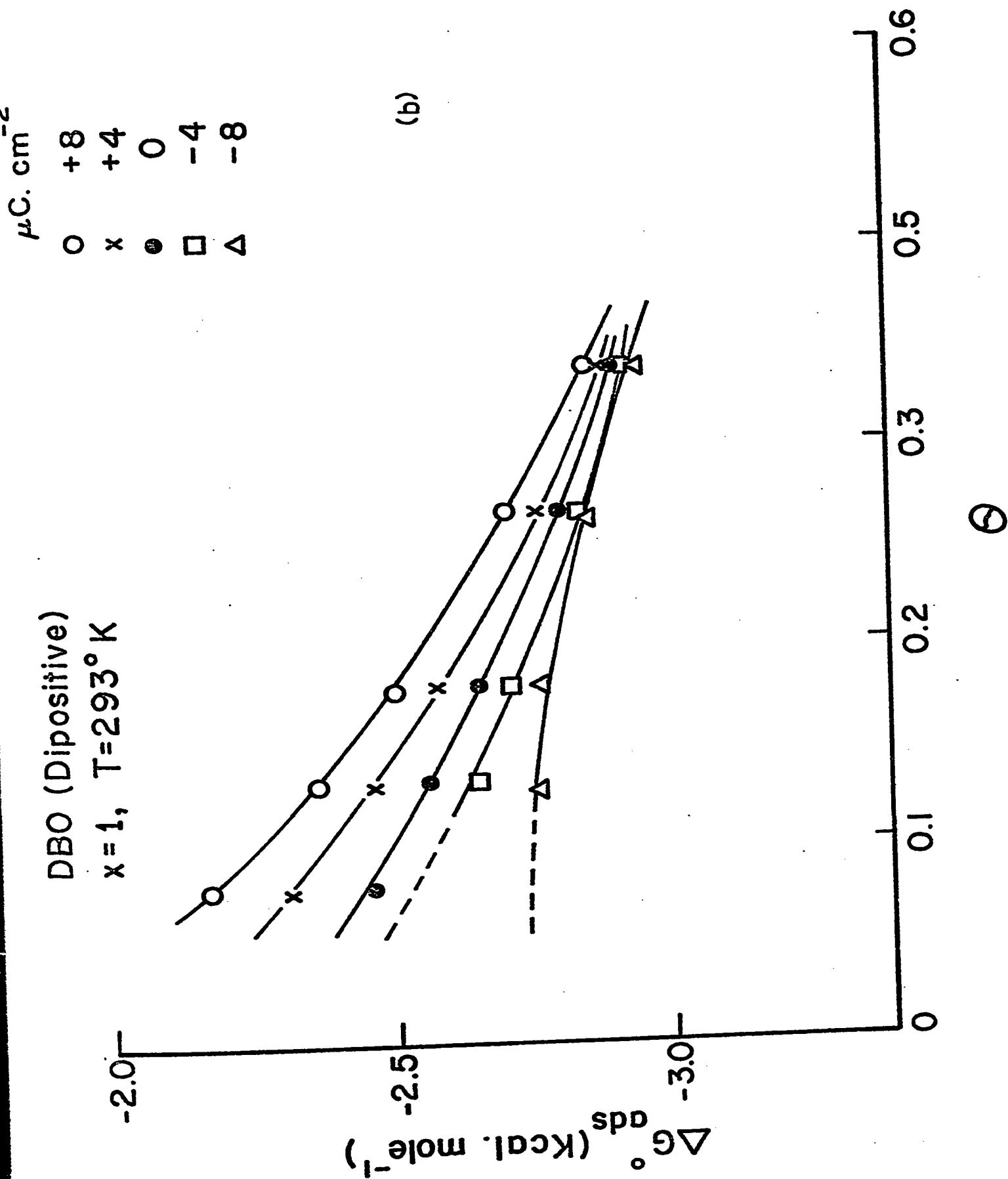


Fig. 57b Dependence of $\Delta G^{\circ}_{\text{ads}}$ on θ for DBO dication at various q_M values (calculated for $x=1$).

With DBO^{++} , on the other hand, the interactions are attractive for all q_M , the trend being relatively greater for positive q_M .

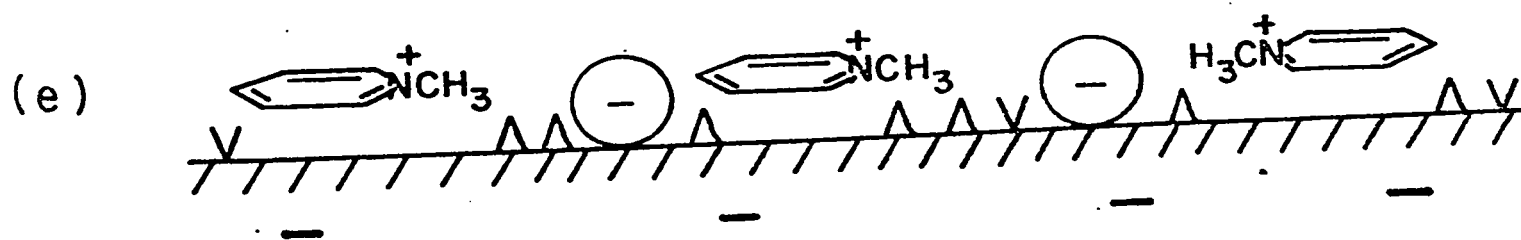
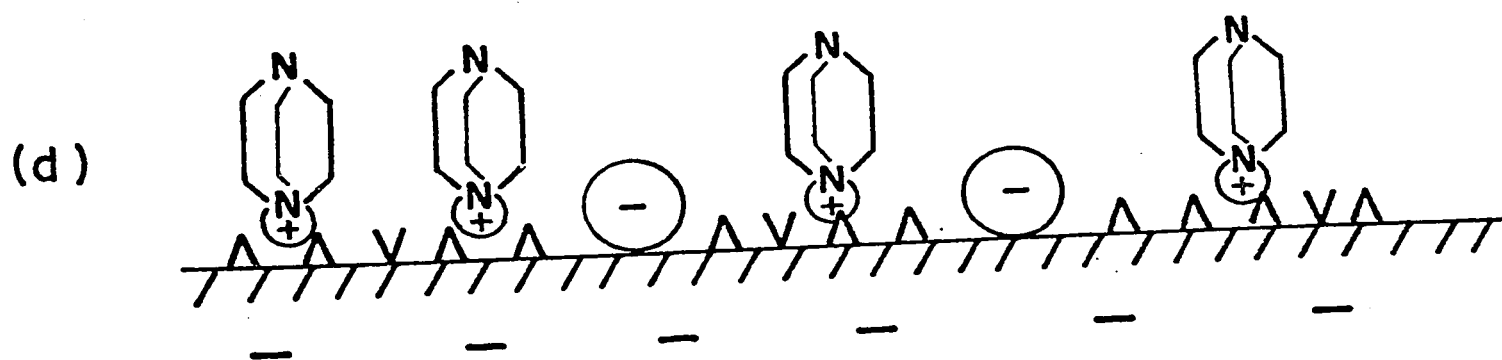
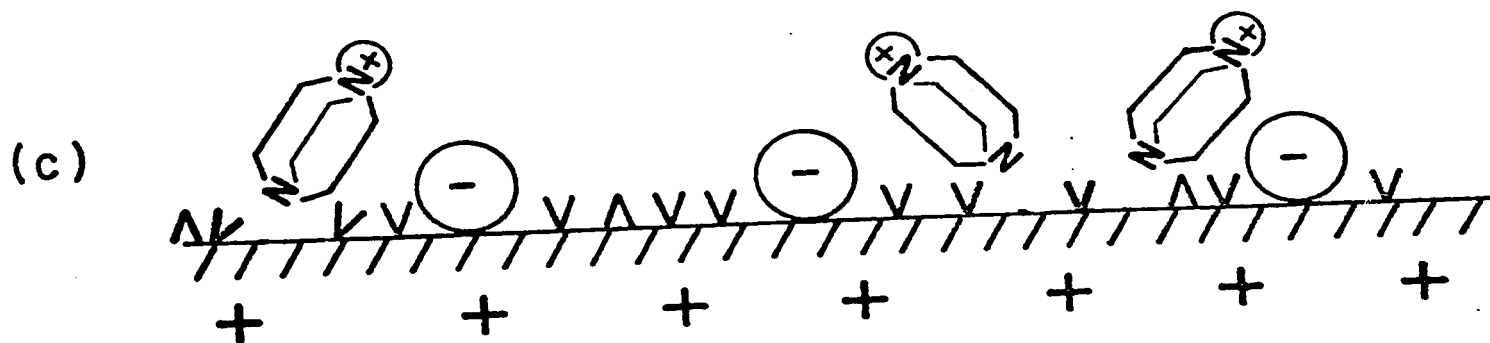
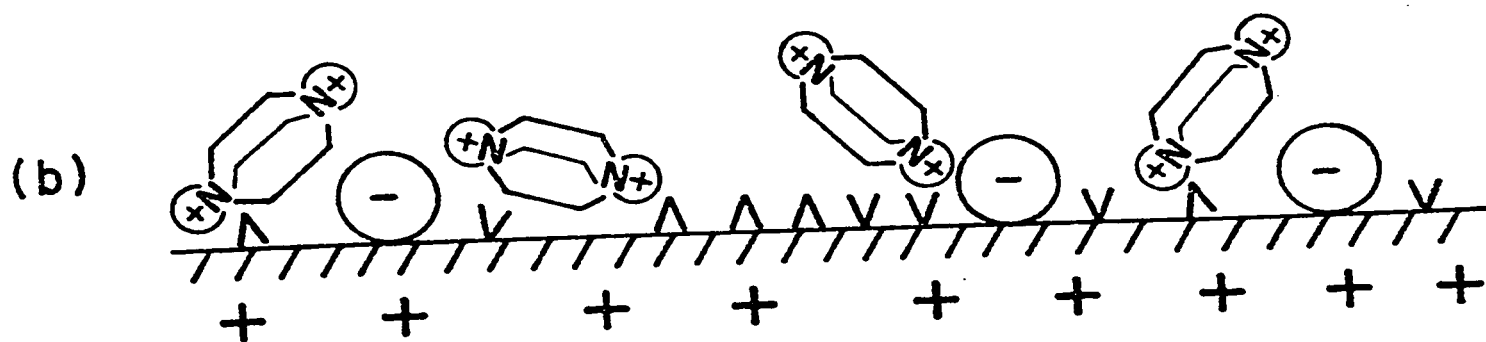
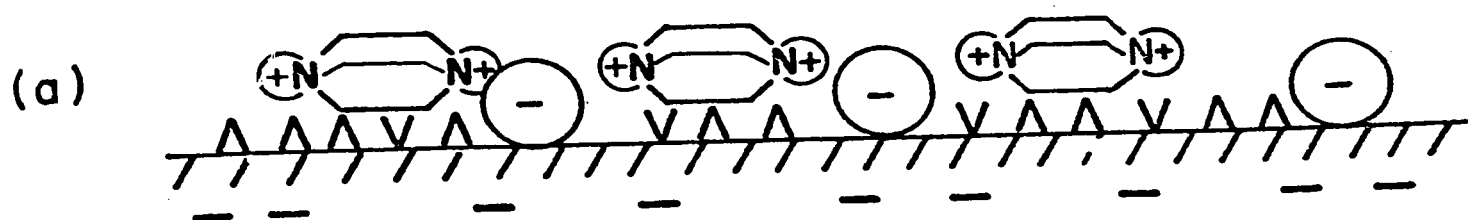
The most realistic way of explaining these trends is to suppose that at positive surface charges anion adsorption becomes important but the cations, being specifically (hydrophobically) adsorbed, are not displaced from the surface. Dication-anion pairs in the case of DBO^{++} then give rise to the strongest attractive effects with increasing coverage of the organic cation and with larger positive q_M . At low θ , however, the $-\Delta G_{\text{ads}}^0$ is smallest at the most positive q_M as expected for a cation but changes relatively more rapidly with θ as θ increases and anion pair interactions become more important. With the mono-positive ion, the same effects arise on a diminished scale at positive q_M while at negative q_M , anions can become completely displaced in this case, so that normal coulombic and hydration co-sphere repulsive interactions predominate (see the lines for $q_M = -10$ to $-6 \mu\text{C cm}^{-2}$ in Fig. 57a for DBO^+ ions).

With the dipositive ion, the orientation shown in Fig. 58a will tend to be adopted at large negative q_M while that of Fig. 58b may be preferred at more positive q_M as anions populate the inner Helmholtz layer. For DBO^+ , the mean orientation shown in Fig. 58c is probable at positive q_M while at negative q_M , with anions expelled, the mono-positive ions will be oriented as in Fig. 58d with maximum inter-ionic repulsion in the interphase.

Fig. 58

Models of adsorption and orientation of water and various N-containing ions at Hg.

- (a) DBO dication at negative q_M with some anion pairing.
- (b) DBO dication at positive q_M with interaction with adsorbed anions.
- (c) DBO monocation at positive q_M with smaller interaction with adsorbed anions.
- (d) Repulsive interaction between oriented DBO monocations at negative q_M .
- (e) Orientation and solvent displacement by N-Me pyridinium⁺ ion in the "flat" orientation at Hg.



These proposals are consistent with the surface pressure behavior shown in Figs. 54a and 54b. For DBO^+ and DBO^{++} , the $\phi_q - \Gamma$ plots are charge-dependent but since DBO^{++} is a symmetrical ion, the charge dependence of ϕ_q cannot be primarily due to orientation of the ions themselves; it must be due more to co-adsorption of anions. ϕ_q is smaller both for DBO^+ and DBO^{++} when q_q is positive, as required if anion co-adsorption determines the lateral interactions. Also all the $\phi_q - \Gamma$ lines for DBO^{++} have lower slopes than the corresponding lines for DBO^+ , indicating the greater role of anion attraction effects.

These aspects of the adsorption behavior of these ions are consistent with the Esin and Markov plots of Fig. 52. The DBO^{++} ion gives smaller ΔE_q changes than the DBO^+ ion for comparable extents of adsorption (Γ) and this can only arise if the DBO^{++} ion adsorption is associated with simultaneous anion adsorption, as postulated above.

The adsorption of N-Me-Py ClO_4 exhibits strikingly different behavior. The $\Delta G_{\text{ads}}^0 - \theta$ plots indicate repulsive interactions at all q_M from -10 to +6 $\mu\text{C cm}^{-2}$ and the $\phi_q - \Gamma$ relations are almost independent of q_M (Fig. 48). This indicates (a) little tendency for the pyridinium-type ion to become oriented with changing q_M , presumably due to π -orbital interaction⁵⁹ with the metal and (b) less involvement of co-adsorbed anions.

The Esin and Markov plots (Fig. 47) are also quite

different from those for DBO^+ , as ΔE_q is of opposite sign e.g. for $q_M = -8 \mu\text{C cm}^{-2}$ and for $q_M = +4 \mu\text{C cm}^{-2}$, the ΔE_q is much larger in the case of N-Me-Py ClO_4 than for DBO^+ . The N-Me-Py ClO_4 salt behaves much more like a neutral molecule such as pyridine or pyrazine for which the EM effects at low Γ is primarily due to displacement of oriented solvent dipoles at q_M values other than $-2 \mu\text{C cm}^{-2}$ where net solvent orientation is zero^{37,114}. At $q_M = -2$, therefore, the EM effect for the N-Me-Py ClO_4 is that due to the cation itself (since ClO_4^- is in excess and present in the supporting electrolyte). Since at charges other than $-2 \mu\text{C cm}^{-2}$, the ΔE_q shift is opposite to that for DBO^+ , it must be concluded that the N-Me-Py ClO_4 lies flat and displaces oriented water (Fig. 58e) like other specifically adsorbed neutral molecules^{25,37,114} while DBO^+ and DBO^{++} behave more like simple cations with hydration shells and thus do not displace oriented water to a comparable extent, since the oriented water layer at the electrode forms part of their own hydration shells. The large and unusual EM effects with the pyridinium salt are hence due to comparable contributions from specifically adsorbed charge and displacement of field-oriented solvent dipoles.

With the N-Me-Py ClO_4 salt, the absence of effects that could be associated with ion-pair interaction with anions presumably arises because the N^+ center is relatively protected by the Me group at the quaternary N. Independence of the $\phi_q - \Gamma$ plots on q_M and hence anion adsorption is hence rationalized.

APPENDIX I

Surface excess quantities of various compounds studied at the Hg electrode at different temperatures, and for various q_M values.

In all Tables, Γ is expressed in mole cm^{-2} and q_M in $\mu\text{C cm}^{-2}$.

Table I

Pyrazine T = 281°K

Values of C corresponding to various values of Γ and q_M

q_M $\Gamma \times 10^{10}$	+8	+6	+4	+2	0	-2	-4	-6	-8
0.8	0.0304	0.0147	0.0070	0.0037	0.0030	0.0031	0.0045	0.0052	0.0099
0.9	0.0402	0.0212	0.0109	0.0062	0.0036	0.0045	0.0059	0.0074	0.0131
1.0	0.0526	0.0290	0.0158	0.0093	0.0059	0.0062	0.0076	0.0101	0.0172
1.2	0.0804	0.0491	0.0287	0.0177	0.0122	0.0111	0.0122	0.0174	0.0281
1.4	0.119	0.0765	0.0469	0.0301	0.0216	0.0184	0.0193	0.0281	0.0441
1.6	0.169	0.113	0.0722	0.0477	0.0352	0.0291	0.0296	0.0433	0.0667
1.8	0.233	0.161	0.106	0.0720	0.0542	0.0443	0.0445	0.0643	0.0983
2.0	0.315	0.223	0.151	0.105	0.0803	0.0655	0.0658	0.0929	0.141
2.2	0.418	0.302	0.210	0.149	0.115	0.0945	0.0956	0.131	0.200
2.4	0.500	0.402	0.286	0.206	0.162	0.133	0.137	0.182	0.278
2.8	-	0.500	0.382	0.280	0.223	0.185	0.194	0.248	0.382

Table II

Pyrazine $T = 293^{\circ}\text{K}$ Values of C corresponding to various values of Γ and q_M

q_M $\Gamma \times 10^{10}$	+8	+6	+4	+2	0	-2	-4	-6	-8
0.8	0.0284	0.0194	0.0104	0.003	0.003	0.003	0.003	0.005	0.0122
0.9	0.0530	0.0285	0.0177	0.0072	0.0045	0.0036	0.0053	0.0085	0.0180
1.0	0.0698	0.0395	0.0257	0.0121	0.0076	0.0067	0.0082	0.0127	0.0252
1.2	0.112	0.0681	0.0461	0.0253	0.0164	0.0147	0.0162	0.0244	0.0445
1.4	0.168	0.108	0.0732	0.0442	0.0298	0.0267	0.0282	0.0412	0.0725
1.6	0.243	0.161	0.109	0.0708	0.0498	0.0437	0.0454	0.0650	0.112
1.8	0.340	0.232	0.155	0.107	0.0782	0.0674	0.0695	0.0977	0.165
2.0	0.465	0.325	0.214	0.156	0.118	0.0996	0.102	0.142	0.238
2.2	-	0.445	0.289	0.220	0.172	0.142	0.147	0.200	0.334
2.4	-	-	0.381	0.303	0.245	0.198	0.205	0.276	0.459
2.6	-	-	0.495	0.409	0.342	0.271	0.282	0.373	0.500

Table III

Pyrazine T = 308°K

Values of C corresponding to various values of Γ and q_M

q_M $\Gamma \times 10^{10}$	+8	+6	+4	+2	0	-2	-4	-6	-8
0.8	0.0632	0.0343	0.0182	0.0085	0.003	0.003	0.0067	0.0121	0.0265
0.9	0.0813	0.0473	0.0274	0.0156	0.010	0.0087	0.0113	0.0185	0.0367
1.0	0.102	0.0622	0.0375	0.0233	0.0160	0.014	0.0164	0.0260	0.0484
1.2	0.151	0.0994	0.0635	0.0425	0.031	0.0266	0.0295	0.0435	0.0763
1.4	0.215	0.148	0.0980	0.0679	0.050	0.0436	0.0471	0.0666	0.112
1.6	0.294	0.211	0.143	0.101	0.077	0.0658	0.0705	0.0963	0.158
1.8	0.392	0.290	0.201	0.145	0.110	0.0947	0.101	0.134	0.215
2.0	0.500	0.390	0.273	0.199	0.154	0.132	0.140	0.181	0.285
2.2	-	0.500	0.365	0.268	0.208	0.178	0.189	0.239	0.371
2.4	-	-	0.477	0.354	0.276	0.236	0.251	0.310	0.476
2.6	-	-	-	0.459	0.360	0.307	0.328	0.396	-

Table IV

Pyrazine T = 323°K

Values of C corresponding to various values of Γ and q_M

q_M $\Gamma \times 10^{10}$	+8	+6	+4	+2	0	-2	-4	-6	-8
0.6	0.0423	0.0246	0.0146	0.003	-	-	-	0.0112	0.0223
0.8	0.0775	0.0484	0.0342	0.0205	0.0168	0.0148	0.0168	0.0251	0.0418
0.9	0.0992	0.0630	0.0453	0.0286	0.0231	0.0206	0.0229	0.0330	0.0535
1.0	0.124	0.0798	0.0580	0.0379	0.0311	0.0271	0.0297	0.042	0.0666
1.2	0.186	0.121	0.0876	0.060	0.0494	0.0427	0.0460	0.0625	0.0981
1.4	0.265	0.1744	0.125	0.0895	0.0712	0.0624	0.0664	0.0884	0.137
1.6	0.366	0.242	0.171	0.126	0.0987	0.0866	0.0922	0.120	0.187
1.8	0.494	0.327	0.228	0.173	0.132	0.116	0.124	0.159	0.247
2.0	-	0.433	0.297	0.230	0.173	0.153	0.162	0.206	0.320
2.2	-	-	0.380	0.301	0.222	0.197	0.208	0.262	0.408
2.4	-	-	0.479	0.387	0.280	0.250	0.264	0.328	0.500
2.6	-	-	-	0.490	0.349	0.313	0.330	0.407	-

Table V

Pyrazine T = 338°K

Values of C corresponding to various values of Γ and q_M

q_M $\Gamma \times 10^{10}$	+8	+6	+4	+2	0	-2	-4	-6	-8
0.6	0.0567	0.0393	0.0291	0.0221	0.0163	0.0149	0.0168	0.0238	0.0409
0.8	0.0950	0.0663	0.0499	0.0383	0.0304	0.0276	0.0299	0.0404	0.0653
0.9	0.119	0.0833	0.0624	0.0478	0.0384	0.0349	0.0372	0.0503	0.0797
1.0	0.147	0.102	0.109	0.0586	0.0473	0.0430	0.0462	0.0613	0.0956
1.2	0.215	0.147	0.149	0.0835	0.0680	0.0621	0.0665	0.0873	0.133
1.4	0.304	0.205	0.199	0.114	0.0934	0.0852	0.0925	0.119	0.178
1.6	0.417	0.277	0.260	0.151	0.124	0.113	0.122	0.159	0.233
1.8	0.500	0.367	0.333	0.195	0.160	0.147	0.159	0.206	0.298
2.0	-	0.477	0.420	0.247	0.204	0.187	0.203	0.263	0.375
2.2	-	-	0.500	0.310	0.255	0.235	0.256	0.331	0.467
2.4	-	-	-	0.383	0.316	0.291	0.318	0.412	0.500
2.6	-	-	-	0.468	0.386	0.356	0.392	0.500	-

Table VI

Pyridine T = 283°K

Values of C corresponding to various values of Γ and q_M

q_M $\Gamma \times 10^{10}$	+8	+6	+4	+2	0	-2	-4	-6	-8
0.4	0.0013	0.0013	0.0014	0.015	0.0015	0.0016	0.0014	-	-
0.6	0.002	0.0017	0.0017	0.0017	0.0018	0.0019	0.0022	0.0047	0.0083
0.8	0.0038	0.0023	0.0021	0.0021	0.0022	0.0024	0.0033	0.0062	0.0097
1.0	0.0105	0.0033	0.0026	0.0026	0.0027	0.0031	0.0045	0.0077	0.0112
1.2	0.0234	0.0062	0.0034	0.0034	0.0035	0.0041	0.0061	0.0093	0.0128
1.5	0.0470	0.0291	0.0059	0.0059	0.0057	0.0066	0.0090	0.0120	0.0154
1.8	0.0745	0.0626	0.0148	0.0148	0.0110	0.0112	0.0128	0.0150	0.0182
2.0	0.095	0.086	0.0326	0.0326	0.0188	0.0159	0.0160	0.0173	0.020
2.5	0.154	0.151	0.090	0.090	0.0561	0.0356	0.0267	0.0243	0.0263
3.0	0.225	0.225	0.160	0.160	0.109	0.0676	0.0429	0.0334	0.0337
4.0	0.407	0.407	0.323	0.323	0.249	0.171	0.101	0.0626	0.0548
5.0	-	-	-	-	0.439	0.332	0.219	0.123	0.0913

Table VII

Pyridine* T = 298°K

Values of C corresponding to various values of Γ and q_M

q_M $\Gamma \times 10^{10}$	+8	+6	+4	+2	0	-2	-4	-6	-8
0.4	0.0043	0.0033	0.0030	0.0030	0.0030	0.0037	0.0050	0.0063	0.0078
0.6	0.0081	0.0054	0.0043	0.0038	0.0038	0.0046	0.0058	0.0072	0.0089
0.8	0.0130	0.0832	0.0062	0.0052	0.0050	0.0057	0.0069	0.0083	0.0102
1.0	0.0194	0.0124	0.0088	0.0071	0.0066	0.0071	0.0081	0.0094	0.0116
1.2	0.0275	0.0180	0.0123	0.0097	0.0086	0.0088	0.0096	0.0108	0.0132
1.5	0.0437	0.0301	0.0201	0.153	0.0129	0.0121	0.0122	0.0132	0.0160
1.8	0.0660	0.0485	0.0324	0.0238	0.191	0.0166	0.0157	0.0162	0.0193
2.0	0.0850	0.0654	0.0443	0.0319	0.0247	0.0205	0.0186	0.0186	0.0220
2.5	0.0151	0.132	0.0939	0.0650	0.0465	0.0347	0.0283	0.0263	0.0300
3.0	0.254	0.250	0.193	0.130	0.0861	0.0585	0.0432	0.0373	0.0407
3.4	0.371	0.404	0.337	0.222	0.139	0.0885	0.0609	0.0496	0.0519
4.0	-	-	-	0.487	0.281	0.164	0.102	0.0762	0.0744
5.0	-	-	-	-	-	0.452	0.247	0.158	0.134

* The data for 298°K are not from the same runs as those for 283, 313 and 328°K, and therefore may not be quite consistent with the other three temperatures.

Table VIII

Pyridine T = 313°K

Values of C corresponding to various values of Γ and q_M

q_M $\Gamma \times 10^{10}$	+8	+6	+4	+2	0	-2	-4	-6	-8
0.4	0.0021	0.0018	0.0018	0.0018	0.0017	0.0016	0.0017	0.0039	0.0070
0.6	0.0039	0.0027	0.0024	0.0023	0.0022	0.0023	0.0032	0.0062	0.0098
0.8	0.0170	0.0485	0.0037	0.0040	0.0031	0.0035	0.0052	0.0085	0.0126
1.0	0.0392	0.0155	0.0067	0.0050	0.0046	0.0054	0.0075	0.0110	0.0157
1.2	0.0607	0.0386	0.0157	0.0088	0.0075	0.0082	0.0104	0.0138	0.0191
1.5	0.0945	0.0750	0.0434	0.0243	0.0168	0.0150	0.0159	0.0186	0.0247
1.8	0.131	0.114	0.0782	0.0506	0.0333	0.0250	0.0231	0.0243	0.0312
2.0	0.157	0.143	0.104	0.0716	0.0476	0.0337	0.0289	0.0288	0.0360
2.5	0.230	0.222	0.179	0.134	0.0935	0.0632	0.0477	0.0424	0.050
3.0	0.314	0.314	0.270	0.211	0.153	0.104	0.0742	0.0607	0.0673
3.4	0.389	0.398	0.354	0.283	0.211	0.147	0.102	0.0797	0.0839
4.0	-	-	0.460	0.409	0.315	0.229	0.158	0.117	0.114
5.0	-	-	-	-	-	0.421	0.303	0.218	0.183

Table IX

Pyridine T = 328°K

Values of C corresponding to various values of Γ and q_M

q_M $\Gamma \times 10^{10}$	+8	+6	+4	+2	0	-2	-4	-6	-8
0.4	0.0025	0.0024	0.0022	0.0020	0.0018	0.0019	0.0024	0.0037	0.0061
0.6	0.0046	0.0036	0.0032	0.0029	0.0028	0.0031	0.0043	0.0069	0.0114
0.8	0.0442	0.0095	0.0057	0.0048	0.0045	0.0052	0.0071	0.0105	0.0169
1.0	0.0691	0.0406	0.0162	0.0097	0.0081	0.0086	0.0106	0.0146	0.0227
1.2	0.0922	0.0668	0.0369	0.0206	0.0145	0.0137	0.0150	0.0193	0.0288
1.5	0.139	0.118	0.0704	0.0447	0.0298	0.0244	0.0233	0.0274	0.0387
1.8	0.163	0.145	0.106	0.0738	0.0505	0.0386	0.0337	0.0370	0.0496
2.0	0.189	0.174	0.132	0.0955	0.0669	0.0501	0.0420	0.0443	0.0574
2.5	0.256	0.250	0.204	0.158	0.117	0.0861	0.0678	0.0657	0.0789
3.0	0.330	0.336	0.287	0.233	0.180	0.1330	0.102	0.0921	0.104
3.4	0.394	0.412	0.361	0.302	0.240	0.179	0.135	0.117	0.125
4.0	-	-	0.460	0.422	0.349	0.264	0.199	0.163	0.163
5.0	-	-	-	-	-	0.452	0.346	0.263	0.237

Table X

n-Amyl alcohol T = 283°K

Values of C corresponding to various values of Γ and q_M

q_M	+8	+6	+4	+2	0	-2	-4	-6	-8
$\Gamma \times 10^{10}$									
0.4	0.0074	0.0053	0.0042	0.0036	0.0033	0.0032	0.0025	-	0.0088
0.6	0.0093	0.0063	0.0047	0.0039	0.0036	0.0034	0.0032	-	0.0088
0.8	0.0115	0.0075	0.0054	0.0043	0.0038	0.0037	0.0039	0.0057	0.0106
1.0	0.0142	0.0088	0.0061	0.0047	0.0040	0.0039	0.0045	0.0069	0.0125
1.2	0.0178	0.0104	0.0069	0.0052	0.0043	0.0043	0.0051	0.0080	0.0144
1.5	0.124	0.0135	0.0083	0.0060	0.0048	0.0048	0.0060	0.0097	0.0177
1.8	-	0.0179	0.0102	0.0070	0.0054	0.0053	0.0070	0.0115	0.0217
2.0	-	0.0223	0.0118	0.0078	0.0059	0.0058	0.0077	0.0129	0.0250
2.5	-	0.124 (2.2)	0.0177	0.0103	0.0072	0.0070	0.0098	0.0169	0.0379
3.2	-	-	0.124 (3.0)	0.0168	0.0101	0.0094	0.0137	0.0257	0.124 (2.6)
4.0	-	-	-	0.124 (3.8)	0.0171	0.0141	0.0210	0.124 (3.6)	-
4.8	-	-	-	-	0.124 (4.4)	0.124	0.124 (4.4)	-	-

Note: Numbers in the brackets represent the values of Γ corresponding to the immediate above value of C, e.g. in column $q_M=+6$ the last value of C is 0.124, the corresponding value of Γ is not 2.5 but 2.2 as shown inside the bracket.

Table XI
n-Amyl alcohol T = 293°K
Values of C corresponding to various values of Γ and q_M

q_M $\Gamma \times 10^{10}$	+8	+6	+4	+2	0	-2	-4	-6	-8
0.4	0.0062	0.0051	0.0041	0.0033	0.0032	0.0031	0.0028	-	-
0.6	0.0091	0.0064	0.0048	0.0037	0.0034	0.0034	0.0034	0.0025	0.0074
0.8	0.0129	0.0079	0.0056	0.0042	0.0037	0.0036	0.0039	0.0053	0.0096
1.0	0.0181	0.0097	0.0065	0.0047	0.0040	0.0039	0.0045	0.0065	0.0119
1.2	0.0260	0.0118	0.0075	0.0052	0.0043	0.0043	0.0050	0.0076	0.0144
1.5	0.0542	0.0160	0.0093	0.0062	0.0048	0.0048	0.0059	0.0095	0.0187
1.8	0.124 (1.6)	0.0219	0.0117	0.0074	0.0055	0.0054	0.0069	0.0115	0.0239
2.0	-	0.0280	0.0135	0.0083	0.0060	0.0059	0.0077	0.0131	0.0282
2.5	-	0.124 (2.3)	0.0205	0.0114	0.0075	0.0073	0.0099	0.0178	0.0438
3.2	-	-	0.124	0.0193	0.0109	0.0100	0.0142	0.0293	0.124
4.0	-	-	-	0.124	0.0190	0.0151	0.0230	0.124 (3.6)	-
4.8	-	-	-	-	0.124 (4.6)	0.124	0.124 (4.4)	-	-

Note: See footnote in Table X

Table XII
n-Amyl alcohol T = 303°K
Values of C corresponding to various values of Γ and q_M

q_M $\Gamma \times 10^{10}$	+8	+6	+4	+2	0	-2	-4	-6	-8
0.4	0.0056	0.0046	0.0040	0.0035	0.0034	0.0033	0.0028	-	-
0.6	0.0091	0.0062	0.0048	0.0040	0.0036	0.0035	0.0034	0.0042	0.0075
0.8	0.0139	0.0079	0.0057	0.0045	0.0039	0.0038	0.0041	0.0056	0.0099
1.0	0.0206	0.0101	0.0066	0.0050	0.0043	0.0042	0.0047	0.0068	0.0125
1.2	0.0302	0.0126	0.0078	0.0057	0.0046	0.0045	0.0053	0.0081	0.0154
1.5	0.0558	0.0177	0.0099	0.0068	0.0052	0.0051	0.0063	0.0100	0.0205
1.8	0.120	0.0254	0.0126	0.0082	0.0060	0.0058	0.0074	0.0123	0.0268
2.0	-	0.0333	0.0149	0.0092	0.0065	0.0063	0.0083	0.0140	0.0320
2.5	-	0.124 (2.4)	0.0235	0.0127	0.0083	0.0078	0.0107	0.0195	0.0501
3.2	-	-	0.124	0.0212	0.0121	0.0109	0.0157	0.0341	0.105
4.0	-	-	-	0.124	0.0212	0.0170	0.0265	0.124 (3.4)	0.124 (3.4)
4.8	-	-	-	-	0.124 (4.4)	0.124 (4.6)	0.124 (4.2)	-	-

Note: See footnote in Table X

Table XIII
n-Amyl alcohol T = 318°K
Values of C corresponding to various values of Γ and q_M

q_M $\Gamma \times 10^{10}$	+8	+6	+4	+2	0	-2	-4	-6	-8
0.4	0.0081	0.0062	0.0047	0.0037	0.0033	0.0034	-	-	0.0084
0.6	0.0121	0.0083	0.0060	0.0047	0.0039	0.0039	0.0045	0.0069	0.0106
0.8	0.0169	0.0105	0.0072	0.0055	0.0045	0.0044	0.0054	0.0081	0.0129
1.0	0.0235	0.0129	0.0086	0.0064	0.0051	0.0049	0.0063	0.0094	0.0152
1.2	0.0331	0.0158	0.0100	0.0073	0.0057	0.0055	0.0071	0.0106	0.0179
1.5	0.0678	0.0213	0.0125	0.0088	0.0067	0.0064	0.0084	0.0127	0.0228
1.8	0.124 (1.6)	0.0295	0.0157	0.0105	0.0078	0.0074	0.0097	0.0150	0.0291
2.0	-	0.0381	0.0182	0.0118	0.0086	0.0081	0.0107	0.0168	0.0348
2.5	-	0.124 (2.3)	0.0275	0.0158	0.0110	0.0101	0.0136	0.0225	0.0668
3.2	-	-	0.24 (3.0)	0.0251	0.0157	0.141	0.0190	0.124 (3.0)	0.124 (2.6)
4.0	-	-	-	0.124 (3.6)	0.0259	0.0216	0.124	-	-
4.8	-	-	-	-	0.124 (4.2)	0.124 (4.4)	-	-	-

Note: See footnote in Table X

Table XIV
n-Amyl alcohol T = 333°K
Values of C corresponding to various values of Γ and q_M

q_M $\Gamma \times 10^{10}$	+8	+6	+4	+2	0	-2	-4	-6	-8
0.4	0.0086	0.0070	0.0056	0.0045	0.0039	0.0038	0.0025	0.0069	0.0105
0.6	0.0162	0.0099	0.0074	0.0059	0.0049	0.0047	0.0058	0.0086	0.0134
0.8	0.0269	0.0133	0.0092	0.0071	0.0058	0.0055	0.0069	0.0102	0.0165
1.0	0.0406	0.0174	0.0112	0.0083	0.0067	0.0063	0.0079	0.0119	0.0202
1.2	0.0573	0.0224	0.0134	0.0096	0.0076	0.0071	0.0090	0.0137	0.0244
1.5	0.088	0.0327	0.0172	0.0118	0.0090	0.0084	0.0108	0.0168	0.0327
1.8	0.124	0.0489	0.0222	0.0143	0.0106	0.0098	0.0128	0.0205	0.0449
2.0	-	0.0665	0.0264	0.0163	0.0118	0.0109	0.0143	0.0235	0.0577
2.5	-	0.124 (2.3)	0.0441	0.0225	0.0153	0.0141	0.0188	0.0347 (2.3)	0.124 (2.3)
3.2	-	-	0.124 (2.8)	0.0395	0.0226	0.0205	0.0289	0.124 (2.8)	-
4.0	-	-	-	0.124 (3.4)	0.124	0.0360	0.124 (3.8)	-	-
4.8	-	-	-	-	-	0.124 (4.2)	-	-	-

Note: See footnote in Table X

Table XV

DBO (Neutral) T = 293°K

Values of C corresponding to various values of Γ and q_M

q_M $\Gamma \times 10^{10}$	+10	+8	+6	+4	+2	0	-2	-4	-6	-8	-10
0.4	0.0033	0.0035	0.0040	0.0043	0.0036	0.0003	-	-	-	-	-
0.6	0.0039	0.0046	0.0058	0.0068	0.0067	0.0055	0.0049	0.0044	0.0041	0.0039	0.0059
0.8	0.0046	0.0060	0.0081	0.0100	0.0105	0.0097	0.0080	0.0070	0.0065	0.0070	0.0098
1.0	0.0056	0.0079	0.0112	0.0143	0.0156	0.0151	0.0124	0.0105	0.0098	0.0109	0.0149
1.2	0.0069	0.0106	0.0153	0.0199	0.0223	0.0225	0.0185	0.0154	0.0143	0.0162	0.0220
1.5	0.0098	0.0164	0.0244	0.0321	0.0369	0.0389	0.0326	0.0265	0.0246	0.0284	0.0384
1.8	0.0147	0.0262	0.0389	0.0510	0.0600	0.0648	0.0566	0.0454	0.0421	0.0496	0.0679
2.0	0.0202	0.0363	0.0534	0.0695	0.0826	0.0903	0.0819	0.0658	0.0615	0.0735	0.103
2.2	0.0291	0.0511	0.0740	0.0953	0.114	0.125	0.120	0.0975	0.0928	0.114	0.166
2.5	0.0555	0.0882	0.124	0.157	0.192	0.206	0.220	0.191	0.203	0.296	0.500
3.0	0.195	0.251	0.353	0.420	0.500	0.500	-	-	-	-	-

Table XVI

N-Me pyridinium perchlorate T = 298°K

Values of C corresponding to various values of Γ and q_M

q_M $\Gamma \times 10^{10}$	+10	+8	+6	+4	+2	0	-2	-4	-6	-8	-10
0.2	0.0122	0.0058	0.0032	0.001	0.0012	0.0011	-	-	-	-	0.0011
0.4	0.0245	0.0132	0.0076	0.0041	0.0025	0.0019	0.0015	0.0014	0.014	0.0016	0.0017
0.6	0.0412	0.0239	0.0132	0.0076	0.0045	0.0031	0.0024	0.0022	0.0022	0.0024	0.0026
0.8	0.0638	0.0397	0.0211	0.0126	0.0075	0.0050	0.0039	0.0034	0.0034	0.0036	0.0040
1.0	0.0937	0.0628	0.0324	0.0198	0.0122	0.0080	0.0061	0.0052	0.0051	0.0055	0.0060
1.2	0.1327	0.0962	0.0492	0.0306	0.0194	0.0126	0.0096	0.0080	0.0078	0.0083	0.0092
1.5	0.213	0.176	0.0929	0.0583	0.0388	0.0259	0.0191	0.0160	0.0150	0.0157	0.0174
1.8	0.327	0.312	0.190	0.116	0.0808	0.0562	0.0402	0.0333	0.0301	0.0307	0.0334
2.0	0.428	0.455	0.350	0.199	0.139	0.101	0.0714	0.0582	0.0502	0.0496	0.0524
2.2	0.553	0.661	0.750	0.413	0.267	0.210	0.148	0.112	0.0895	0.0835	0.0837
2.5	-	-	-	-	-	-	0.750	0.750	0.305	0.213	0.177

Table XVII

DBO (Monopositive) $T = 293^{\circ}\text{K}$

Values of C corresponding to various values of Γ and q_M

q_M	+6	+4	+2	0	-2	-4	-6	-8	-10	-12
$\Gamma \times 10^{10}$										
0.2	0.049	0.039	0.0267	0.015	0.0031	0.0022	0.0018	-	-	-
0.4	0.0921	0.0747	0.0582	0.0432	0.0284	0.0123	0.0038	0.0022	0.0019	0.0018
0.6	0.137	0.110	0.0883	0.0691	0.0516	0.0350	0.018	0.0054	0.0028	0.0023
0.8	0.187	0.147	0.120	0.098	0.0769	0.0585	0.0412	0.0224	0.0060	0.0034
1.0	0.242	0.188	0.154	0.129	0.105	0.084	0.0653	0.045	0.026	0.0063
1.2	0.290	0.231	0.191	0.162	0.135	0.112	0.0915	0.071	0.055	0.0280
1.5	-	0.290	0.252	0.218	0.187	0.159	0.135	0.115	0.099	0.0845
1.8	-	-	-	0.281	0.247	0.212	0.184	0.165	0.145	0.141
2.0	-	-	-	-	0.290	0.251	0.220	0.202	0.181	0.181
2.2	-	-	-	-	-	0.290	0.258	0.243	0.218	0.224
2.5	-	-	-	-	-	-	-	0.290	0.278	0.290

Table XVIII

DBO (Dipositive) T = 293°K

Values of C corresponding to various values of Γ and q_M

q_M $\Gamma \times 10^{10}$	+8	+6	+4	+2	0	-2	-4	-6	-8	-10
0.2	0.107	0.0940	0.0181	0.0564	0.0156	0.0150	0.0147	0.0145	0.0142	0.0137
0.4	0.128	0.117	0.102	0.0890	0.0795	0.0683	0.0268	0.0273	0.0249	0.0200
0.6	0.145	0.134	0.122	0.112	0.103	0.0973	0.0878	0.0722	0.0585	0.0413
0.8	0.161	0.150	0.139	0.132	0.134	0.118	0.112	0.102	0.090	0.076
1.0	0.176	0.165	0.156	0.150	0.143	0.137	0.132	0.127	0.117	0.106
1.2	0.189	0.178	0.171	0.169	0.161	0.154	0.151	0.151	0.144	0.133
1.5	-	0.198	0.193	0.195	0.187	0.179	0.178	0.185	0.182	0.172
1.8	-	-	-	-	-	0.200	0.200	-	-	-

CLAIMS TO ORIGINAL RESEARCH

1. Electrochemical adsorption studies on several neutral organic molecules and organic cations have been made at a sufficient number of closely spaced concentration intervals, so as to be able to obtain adsorption parameters with much increased accuracy in comparison with that in previous work.
2. The extent of orientation of water molecules in the Hg/solution interphase has been quantitatively evaluated as $f(q_M)$. The results suggest that orientation of the water dipoles, in the region of charge accessible by experiment, is only partial. Probably there are co-operative effects amongst groups of solvent molecules.

Interpretations of the adsorption parameters for pyrazine also lead to evaluation of the parameter, U_c , characterizing interactions among water molecules in the interphase as a function of charge on the surface, q_M .

3. With the proper choice of the interaction parameter for water dipoles, it has been shown that $\Delta G_{ads}^0 - q_M$ relations for pyrazine can be calculated theoretically and are in very good agreement with the experimental behavior.
4. Water molecules on a charged Hg surface have been shown to have zero net orientation at $q_M = -2$ and, at $q_M = 0 \mu C \text{ cm}^{-2}$ water molecules are partially oriented with the oxygen atom towards the surface.

5. Evaluation of the adsorption parameters $\Delta G_{\text{ads}}^{\circ}$, ΔE_q , ϕ_q , $\Delta S_{\text{ads}}^{\circ}$ and $\Delta H_{\text{ads}}^{\circ}$ for pyrazine shows that this molecule interacts with the surface in the same way at all charges. The molecule is therefore most probably adsorbed in a "flat" orientation.
6. Pyridine adsorbs in the "flat" orientation, like pyrazine, at positive surface charges, but at negative charges, depending on coverage, the molecule orients from the flat to the upright position (with the N atom way from the surface).
7. The adsorption parameters for pyrazine and pyridine at the Hg surface for $q_M = 0$ have been compared with those for the two molecules at the air/water interface; the comparison supports some of the interpretations given to the adsorption behavior of these molecules.
8. n-Amyl alcohol, which has its dipole moment mainly in the functional group, adsorbs with the hydrocarbon chain on the surface at the both positive and negative charges. The hydrophobic character of the carbon chain in n-amyl alcohol is more important in its adsorption than any field-dipole interactions.
9. 1,4-diazabicyclo-octane (DBO), a molecule with a spherical shape and having no net dipole moment like pyrazine, has different adsorption characteristics than those for pyrazine because of the presence of considerable electron density on the two N atoms of the molecule and absence of

of π -orbitals. At positive charges, the molecule adsorbs with one of the N atoms towards the surface and at negative charges, the axis of the molecule passing through the two N atoms tends to lie parallel with the surface. The dependence of ΔG_{ads}^0 , ΔE_q and ϕ_q on q_M and θ are all consistent with these proposed orientations.

10. From adsorption studies on selected organic cations, it has been shown that solvation co-sphere overlap effects and cation-anion pairing are important, depending on the value of the surface charge. It has been shown from theoretical considerations that solvation co-sphere interaction effects, can, in fact become the main term in the 2-dimensional interaction energy between specifically adsorbed ions of the same sign of charge. Models for adsorption of the different kinds of organic cations are proposed.
11. A new isotherm relation applicable to substitutional adsorption of molecules of different sizes has been rigorously derived.
12. A derivation for the so-called "Flory-Huggins" isotherm, which has been intuitively used by many authors without derivation, has been provided. It has been shown that the so-called Flory-Huggins isotherm, frequently used and previously named after Flory and Huggins, is inappropriate since a different form results from proper evaluation of "Flory-Huggins" statistics.

REFERENCES

1. C. Herring, p.312, Metal Interfaces, Am.Inst.Metals, 1954.
2. B.E. Conway, J.E. Desnoyers and A.C. Smith, Phil. Trans. Roy. Soc. (London), A256, 389 (1964).
3. D. Eisenberg and W. Kauzmann, The Structure and Properties of Water, Oxford at the Clarendon Press, 1969.
4. S. Rice and P. Gray, The Statistical Mechanics of Simple Liquids, Interscience, N. Y. 1965.
5. G.W. Stewart, Phys. Rev., 37, 9 (1931).
6. J.D. Bernal and R.H. Fowler, J. Chem. Phys., 1, 515 (1933).
7. J. Morgan and B.E. Warren, J. Chem. Phys., 6, 666 (1938).
8. A.H. Narten, M.D. Danford and H.A. Levy, Oak Ridge National Lab. Report ORNL 3937; Disc. Faraday Soc., 43, 97 (1967).
9. L. Pauling, Hydrogen Bonding, Pergamon Press, London, 1959.
10. R.A. Horne, Water and Aqueous Solutions, Wiley Interscience, 1971.
11. H.S. Frank and A.S. Quist, J. Chem. Phys., 34, 604 (1961).
12. B. Kamb, p.507, Structural Chemistry and Molecular Biology, Eds. A. Rich and N. Davidson, Freeman, San Francisco, 1968.
13. H.S. Frank and W.Y. Wen, Disc. Faraday Soc., 24, 133 (1957).
14. O.Y. Samoilov, Structure of Aqueous Electrolyte Solutions and the Hydration of Ions, Consultant Bureau, N.Y. 1965.
15. J.A. Pople, Proc. Roy. Soc. (London), A205, 163 (1951).
16. J.D. Bernal, Proc. Roy. Soc. (London), A280, 299 (1964).

17. M. Falk and T.A. Ford, Can. J. Chem., 44, 1699 (1966).
18. E.U. Frank and K. Roth, Disc. Faraday Soc., 43, 108 (1967).
19. T.T. Wall and D.F. Hornig, J. Chem. Phys., 43, 2079 (1965).
20. G.E. Walrafen, J. Chem. Phys., 48, 244 (1968).
21. G.E. Walrafen, J. Chem. Phys., 46, 1870 (1967).
22. R.P. Marchi and H. Eyring, J. Phys. Chem., Ithaca, 68,
221 (1964).
23. R.J. Watts-Tobin, Phil. Mag., 6, 133 (1961).
24. J. O'M. Bockris and A.K.N. Reddy, Modern Electrochemistry,
Vol. 2, Section 7.4, Plenum Press, N. Y., 1970.
25. J. O'M. Bockris, M.A.V. Devanathan and K. Müller, Proc.
Roy. Soc. (London), A274, 55 (1963).
26. H.L.F. Helmholtz, Ann. Physik., 7, 337 (1879).
27. G. Gouy, J. de Phys., 9, 457 (1910); Annales de Phys.,
7, 129 (1917).
28. D.L. Chapman, Phil. Mag., 25, 470 (1913).
29. O. Stern, Z. Elektrochem., 30, 508 (1924).
30. D.C. Grahame, Chem. Rev., 41, 441 (1947).
31. T.N. Anderson and J.O'M. Bockris, Electrochimica Acta,
9, 347 (1964).
32. R. Parsons, J. Electroanal. Chem., 8, 93 (1964).
33. C. Giomini and L. Rampazzo, J. Phys. Chem., 76, 707 (1972).
34. J. Lawrence and R. Parsons, J. Phys. Chem., 73, 3577 (1969).
35. R. Payne, J. Electrochem. Soc., 113, 999 (1966).
36. B.E. Conway and L.G.M. Gordon, J. Phys. Chem., 73,
3609 (1969).

37. B.E. Conway, H.P. Dhar and S. Gottesfeld, J. Colloid and Interface Science, In press (1973).
38. A.N. Frumkin, Z. Fur Physik, 35, 792 (1926); Z. Phys. Chem., 116, 466 (1925).
39. R. Parsons, J. Electroanal. Chem., 5, 397 (1963).
40. J.A.V. Butler, Proc. Roy. Soc. (London), A113, 594 (1927); A122, 399 (1929).
41. W. Lorenz and F. Möckel, Z. Elektrochem., 60, 507 (1956).
42. D.C. Grahame, J. Am. Chem. Soc., 76, 4819 (1954); 79, 2093 (1957).
43. J.R. Macdonald, J. Chem. Phys., 22, 1857 (1954).
44. R.G. Barradas and J.M. Sedlak, Electrochim. Acta, 17, 683 (1972).
45. C. Kemball, Proc. Roy. Soc. (London), A90, 117 (1947).
46. B.E. Conway, J.O'M. Bockris and A.I. Ammar, Trans. Faraday Soc., 47, 756 (1951).
47. N.F. Mott and R.J. Watts-Tobin, Electrochim. Acta, 4, 79 (1961).
48. N.F. Mott, R. Parsons and R.J. Watts-Tobin, Phil. Mag., 7, 483 (1962).
49. M.J. Austin and R. Parsons, Proc. Chem. Soc., 239 (1961).
50. J.R. Macdonald and C.A. Barlow, J. Chem. Phys., 36, 3062 (1962).
51. D.C. Grahame, Z. Elektrochem., 59, 364 (1956).
52. A.N. Frumkin and B.B. Damaskin, p.149, Modern Aspects of Electrochemistry, Vol. 3, Eds. J.O'M. Bockris and B.E. Conway, Butterworths, London, 1965.

53. B.B. Damaskin, J. Electroanal. Chem., 23, 431 (1969).
54. J.O'M. Bockris, E. Gileadi and K. Müller, Electrochim. Acta, 12, 1301 (1967).
55. R.G. Barradas and J.M. Sedlak, Electrochim. Acta, 16, 2091 (1971).
56. M.A.V. Devanathan and B.V. Tilak, Chem. Rev., 65, 635 (1965).
57. G.J. Hills and R. Payne, Trans. Faraday Soc., 61, 326 (1965); J. Phys. Chem., 73, 3591 (1969).
58. E. Blomgren, J.O'M. Bockris and C. Jesch, J. Phys. Chem., 65, 2000 (1961).
59. B.E. Conway and R.G. Barradas, Electrochim. Acta, 5, 319 (1961); 5, 349 (1961).
60. L.G.M. Gordon, Ph.D. Thesis, University of Ottawa, 1969.
61. F.W. Shapink, M. Oudeman, K.W. Leo and J.N. Helle, Trans. Faraday Soc., 56, 415 (1960).
62. S. Minc and J. Andrzejczak, J. Electroanal. Chem., 17, 101 (1968).
63. E. Blomgren and J.O'M. Bockris, J. Phys. Chem., 63, 1475 (1959).
64. J.O'M. Bockris and D.A.J. Swinkells, J. Electroanal. Soc., 111, 736 (1964).
65. R.G. Barradas, P.G. Hamilton and B.E. Conway, J. Phys. Chem., 69, 3411 (1965).
66. B.E. Conway and L.G.M. Gordon, J. Electroanal. Chem., 15, 7 (1967).

67. L.G.M. Gordon, J. Halpern and B.E. Conway, J. Electroanal. Chem., 21, P3 (1969).
68. A.W. Adamson, Physical Chemistry of Surfaces, 2nd Edition, Chapter I, Interscience Publishers, N.Y., 1967.
69. R. Parsons, Trans. Faraday Soc., 51, 1518 (1955).
70. R. Parsons and M.A.V. Devanathan, Trans. Faraday Soc., 49, 673 (1953).
71. R. Parsons and K.M. Joshi, Electrochim. Acta, 4, 129 (1961).
72. M.A.V. Devanathan and S.G. Canagaratna, Electrochim. Acta, 8, 77 (1963).
73. R. Payne, J. Electroanal. Chem., 15, 95 (1967); cf. J.O'M. Bockris, K. Müller, H. Wroblowa and Z. Kovač, J. Electroanal. Chem., 15, 101 (1967).
74. S. Cabani, G. Conti and L. Lepori, Trans. Faraday Soc., 67, 1933 (1971).
75. J. Lawrence, R. Parsons and R. Payne, J. Electroanal. Chem., 16, 193 (1968).
76. J. Reilly and W.N. Rae, Physico Chemical Methods, Vol. I, 5th edition, p.641, Methuen and Co. Ltd., London, 1954.
77. M. Breiter and P. Delahay, J. Am. Chem. Soc., 81, 2938 (1959).
78. (a) A.N. Frumkin and V.I. Melik-Gaikazyan, Doklady. Akad. Nauk SSSR, 77, 855 (1951); (b) V.I. Melik-Gaikazyan, Zhur. Fiz. Khim., 26, 560 (1952).
79. P.M. Ginnings and R. Baum, J. Am. Chem. Soc., 59, 1111 (1937).

80. B.E. Conway, R.G. Barradas, P.G. Hamilton and J.M. Parry, J. Electroanal. Chem., 10, 485 (1965).
81. R.G. Barradas, P.G. Hamilton and B.E. Conway, Coll. Czech. Chem. Comm., 32, 1790 (1967).
82. B.E. Conway and E. Gileadi, Trans. Faraday Soc., 58, 2493 (1962).
83. D.H. Everett, Trans. Faraday Soc., 46, 453 (1951).
84. H. Tompa, Polymer Solutions, p.78, Butterworths Scientific Publication, London, 1956; T.L. Hill, Introduction to Statistical Thermodynamics, Addison Wesley Co., San Francisco, 1962.
85. E.A. Guggenheim, Proc. Roy. Soc. (London), A183, 203 (1944); cf. R.H. Fowler and G.S. Rushbrooke, Trans. Faraday Soc., 33, 1272 (1937).
86. W.J.C. Orr, Trans. Faraday Soc., 40, 320 (1944).
87. A.N. Frumkin, J. Electroanal. Chem., 7, 152 (1964).
88. A. Zhukovitskii, Acta Physicochim. U.R.S.S., 19, 176 (1944); see also Zhur. Fiz. Khim., 18, 214 (1944).
89. J.M. Parry and R. Parsons, J. Electrochem. Soc., 113, 992 (1966).
90. P.J. Flory, J. Chem. Phys., 10, 51 (1942); M.L. Huggins, J. Phys. Chem., 46, 151 (1942); also Ann. N.Y. Acad. Sci., 43, 1 (1942).
91. B.B. Damaskin, O.A. Petrii and V.V. Batrakov, Adsorption of Organic Compounds on Electrodes, Plenum Press, N.Y., 1971.

92. E.A. Guggenheim, Mixtures, Chapter 10, Clarendon Press, Oxford, 1952.
93. J.M. Honig, p.371, Solid-Gas Interface, Ed. E.A. Flood, Marcel Dekkar Inc., N.Y., 1967.
94. G.S. Hartley and C.Robinson, Trans. Faraday Soc., 48, 847 (1952); C.Robinson and E.J. Ambrose, Trans. Faraday Soc., 48, 854 (1952).
95. D. Schuhmann, J. Chem. Phys., 64, 1399 (1967).
96. B.E. Conway and R. Verrall, J. Phys. Chem., 70, 1473 (1966).
97. E. Dutkiewicz, J.D. Garnish and R. Parsons, J. Electroanal. Chem., 16, 505 (1968).
98. B. Kastening and L. Holleck, Talanta, 12, 1259 (1965).
99. E.A. Guggenheim, J. Chem. Phys., 4, 689 (1936).
100. B.B. Damaskin, V.M. Gerovich, I.P. Gladkikh and R.I. Kaganovich, Zhur. Fiz. Khim., 38, 2495 (1964).
101. R. Parsons, Modern Aspects of Electrochemistry, Vol. I, Chapter 3, Eds. J.O'M. Bockris and B.E. Conway, Butterworths, 1954.
102. B.E. Conway, E. Gileadi and M. Dzieciuch, Electrochim. Acta, 8, 143 (1963).
103. W.N. Hansen, Surface Science, 16, 205 (1969).
104. B.E. Conway and L.H. Laliberté, J. Phys. Chem., 72, 4317 (1968).
105. W.N. Anderson and R. Parson, p.45, Second International Congress on Surface Activity, Vol. III, Ed. J. Schulman, Butterworths, London, 1957.

106. P. Ruetschi, Z. Phys. Chem., N.F., 14, 277 (1958);
W.J. Canady, H.M. Papée and K.J. Laidler, Trans.
Faraday Soc., 54, 502 (1958); see also R. Lumrey and
S. Rajender, Biopolymers, 9, 1125 (1970).
107. B.E. Conway, D.J. MacKinnon and B.V. Tilak, Trans.
Faraday Soc., 66, 1203 (1970).
108. L. Gierst, p.294, Trans. Symposium on Electrode Pro-
cesses, The Electrochemical Soc., 1958, Ed. E. Yeager,
John Wiley, 1960.
109. B.E. Conway, Theory and Principles of Electrode Processes,
p.73, Ronald Press Co., N.Y., 1964.
110. D.C. Grahame, Z. Elektrochem., 59, 773 (1955).
111. H. Wroblowa and K. Müller, J. Phys. Chem., 73, 3528 (1969).
112. R.W. Gurney, Ionic Processes in Solution, p.4, McGraw
Hill Book Co., 1953.
113. R.H. Stokes and R.A. Robinson, J. Am. Chem. Soc., 70,
1870 (1948).
114. B.E. Conway and H.P. Dhar, Croatica Chim. Acta, in press
(Proceedings of the Summer School on Surface Chemistry,
Rovinj, Yugoslavia, 1972).
115. C.J. Böttcher, Dielectric Polarization, Elsevier, 1952.
116. O. Redlich and D. Meyer, Chem. Rev., 64, 221 (1964).
117. R.H. Stokes and R.A. Robinson, Electrolyte Solutions,
Butterworths, London, 1955.
118. E.A. Guggenheim and N.K. Adam, Proc. Roy. Soc. (London),
A139, 218 (1933).

119. R. Payne, p.43, Techniques of Electrochemistry, Eds. E. Yeager and A.J. Salkind, Wiley-Interscience, 1972.
120. J.N. Butler, J. Phys. Chem., 69, 3817 (1965).
121. I. Morcos and H. Fischer, J. Electroanal. Chem., 17, 7 (1968); 20, 479 (1969).