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BINARY EQUILIBRIUM FOR THE LIQUID-LIQUID EXTRACTION OF COBALT AND NICKEL

BY

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in the
Department of Chemical Engineering

ABSTRACT

The thesis entitled 'Binary Equilibrium for the Liquid-liquid Extraction of Cobalt and Nickel' deals with a systematic study of equilibrium for the extraction of cobalt and nickel by di-(2-ethyl hexyl)-phosphoric acid (D2EHPA) in kerosene from an aqueous sulfate medium.

The method of solvent extraction has acquired a great importance in recent years because of its increased application in hydrometallurgy and the nuclear industry. It is used for the separation and recovery of numerous metals. One of the important applications of solvent extraction is in the recovery and separation of cobalt and nickel.

Acidic organophosphorous extractants are frequently used to extract metal from acidic solutions by cation exchange reaction. Dialkyl phosphoric acids, particularly, D2EHPA are widely used amongst these extractants.

The subject matter of this study was to collect the equilibrium data for the extraction of cobalt and nickel from an aqueous sulfate medium using D2EHPA in kerosene. The data have been correlated numerically by different correlations and curve fitting techniques. An attempt has been made to predict binary equilibria from the pure component isotherms.

20% and 40% (by volume) D2EHPA diluted in kerosene was used to extract cobalt and nickel from aqueous metal sulfate solutions. 5% Tributyl phosphate (TBP) was used as a third phase modifier. D2EHPA was pre-equilibrated with varying amounts of ammonia and the resulting ammonium salt of D2EHPA was used for the extraction. The initial metal ion concentration in the aqueous phase was kept at 10 g/l (approximately) and the initial pH was adjusted at 4.0. The phase ratio variation method was used to obtain the equilibrium data. The ratio (aqueous/organic) was varied from 0.5 to 10.0. After the shake-out tests, the two phases were separated and the metal ion concentration in the two phases was determined using an Atomic Absorption Spectrophotometer.

The experimental data were correlated numerically using semi-empirical and empirical correlations. It was found that quadratic and cubic approximations did not fit the data well. A Freundlich extraction isotherm gave a better fitting than the polynomial approximations. A Langmuir extraction isotherm however, gave the best fit for both pure component and binary mixtures. These isotherms enabled binary extraction equilibria to be predicted.

The apparent equilibrium constant was calculated at various saturation levels of D2EHPA with ammonia by fitting the data using the linear least squares method. The equilibrium constant decreased with the increase in saturation level of D2EHPA with ammonia.

Interfacial tensions between the organic phase and the aqueous phase and the viscosity of the organic phase were measured at a varying metal loading in the organic phase. An increase in these properties was observed as the organic phase metal loading increasd. Polymer formation in the organic phase was considered to have caused these changes.

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Chapter I

INTRODUCTION

The application of solvent extraction for the recovery of metals on a large scale has grown in recent years. Initially solvent extraction was used for the recovery of metals such as in the separation of uranium from leach liquors and the treatment of spent reactor fuel to separate plutonium and in the recovery and separation of rare earths (2). A great variety of metals can now be considered for treatment of solvent extraction (3).

As the advantages of solvent extraction became apparent, the development of the extractants such as alkyl phosphoric acids and chelating reagents took place. This has enabled the application of solvent extraction to the recovery of less valuable but important metals such as vanadium, copper, cobalt, and nickel (35).

At present, copper is being recovered on a large scale using LIX reagents (35). Extractants used for the recovery of less valuable metals include chelating reagents, the alkylphosphoric acids, carboxylic acids, sulfonium chlorides, hydroximes and LIX and KELEX reagents (2).

One important application of solvent extraction is the recovery of cobalt and nickel. The cobalt and nickel ores and concentrates can be leached with ammonia or acid. In the acid sulfate leaching process, the leached slurry is neutralized to remove metals such as iron or arsenic. Any copper present is precipitated out with iron powder. The leach liquor now containing cobalt and nickel may be used for solvent extraction. Cobalt and nickel can be recovered and separated using di-(2-ethylhexyl) phosphoric acid (D2EHPA) in kerosene and this process was the subject for this research work.

Before any liquid-liquid extraction process can be evaluated, it is necessary to obtain complete liquid-liquid equilibrium data for each system. Such data are needed to enable extraction efficiencies, solvent requirements and equipment design calculations to be carried out. Equilibrium data for solvent extraction are generally determined experimentally due to the lack of suitable correlations to predict equilibrium values for highly non -ideal liquid-liquid systems (18).

The process of solvent extraction is an equilibrium process which in simplified form can be represented by the following equation;

$$M + \bar{E} \rightleftarrows \overline{ME} \quad \text{.....1.1}$$

where M and E represent metal and extractant respectively. The first step is the extraction of metal, M, from an aqueous phase to an organic phase by an extractant, E, (extraction stage) as the complex ME. This process requires the equilibrium to be shifted to the right. The second step is the reverse of the first and is termed stripping. Thus solvent extraction is a simple process requiring a shift in equilibrium between extraction and stripping processes. The reversibility of the process is achieved by control of the aqueous phase pH.

Equilibrium studies for the solvent extraction of cobalt and nickel in D2EHPA have been carried out by Golding et. al. (20) using 10% D2EHPA (by volume) as an extractant. They found that the presence of a second metal affected the metal uptake of the first and the selectivity for cobalt uptake in the presence of nickel was 1.46. This investigation was undertaken to

1. extend the work further to higher D2EHPA concentration.

2. correlate the equilibrium data semi-empirically and empirically to predict (a) pure component and binary isotherms (b) equilibrium curves for binary solutions using pure component equilibrium data.

3. determine the effect of metal loading on organic phase physical properties.

4. determine separation factor, K_{Ni}^{Co}, and apparent equilibrium constant, k, for the different systems.

Chapter II

LITERATURE REVIEW

Generally solvent extraction has been applied where distillation techniques are not suitable for separation. Treybal (47, 48) has discussed the general applications of solvent extraction techniques for recovery and separation of metals. Hughes (21) studied the recovery of metals from secondary sources, that is, solvent extraction routes. The hydrometallurgists have made successful uses of liquid-liquid extraction for the separation of uranium and subsequent treatment of spent reactor fuel to separate plutonium from fission products (2). This basic work led to the use of dialkylamines to treat acid sulfate media and tributyl phosphate (TBP) to treat acid media.

A good review of all major publications in liquid-liquid extraction is presented by Klinzing et. al. (27). Bailes et. al. (2) have considered the solvents, extractants (inert, acidic and solvating) , chelating extractants, ionic extractants, modifiers and diluents in the liquid-liquid extraction. Flett and Spink (16) have reviewed solvent extraction of copper, cobalt, nickel, uranium, rare earths, molybdenum, tungsten, vanadium, chromium, cadmium and zinc. Flett (15) has reviewed the application of solvent extraction for the recovery of metals with particular emphasis on cobalt, nickel and copper. A survey of advancement in liquid-liquid extraction during 1963-65 has been prepared by Ellis and Beckman (14). Contributions pertinent to the fundamental understanding of the liquid-liquid extraction mass transfer operations were reviewed. Experimental techniques for measuring miscibility limits and compositions of co-existing phases for liquid-liquid systems have been reviewed by Gerster (19). He approaches approaches for screening solvents used in solvent extraction processes.

Vermeulen et. al. (49) discussed fundamental factors in performance and equilibrium behaviour. They explained the concept of equilibrium curves and their uses in extraction, adsorption and ion-exchange. The equilibrium curves are divided into five types depending upon which curves are convex or concave. Different types of isotherms and models are also suggested by them to fit the equilibrium data. Bouboulis (8) has described various types of diluents used in the extraction of cobalt and nickel. He examined the effect of the organic solvent composition on the separation of cobalt and nickel from acidic solutions. It was concluded that in the absence of TBP, any of the diluents like ESCAID 100, ESCAID 200, or Aromatic 150 (SOLVESSO 150) would be more than satisfactory. However a highly aromatic diluent such as Aromatic 150 or 180 (SOLVESSO 150 or 180) was preferred when TBP is used as a third phase modifier.

The problem of phase equilibria was also discussed by McCabe and Smith (30).

Ritcey and Ashbrook (37) discussed applications of solvent extraction in metals recovery They studied the extraction in two classes (i) in general (ii) in particular for the recovery and separation of cobalt and nickel. Ottertum and Strandell (33) investigated the solvent extraction of vanadium (IV) with D2EHPA and TBP giving more stress on co-extraction of iron along with Va(IV). Sabot and Bauer (40) studied liquid-liquid extraction of nickel (II) by dialkylphosphorodithioic acids. They also discussed the influence of extractant alkyl-group and suggested a reaction mechanism for distribution of extractant and the metal. Cook and Szmokaluk (12) studied refining of cobalt and nickel sulfate solutions by solvent extraction using D2EHPA. They observed that D2EHPA gave the best results for the coextraction of copper, iron, zinc and manganese found in the various sulfate feed solutions. They performed the shakeout tests (qualitatively) with D2EHPA diluted with kerosene type diluents and isodecanol as a third phase inhibitor. It was also observed that cobalt is more favorably extracted at pH in the range of 5 to 8.

Ritcey, Ashbrook and Lucas (38) have given an account of development of a solvent extraction process for the separation of cobalt from nickel. A short description of preparation of synthetic solution for solvent extraction was given. They also described a simplified chemistry of solvent extraction process, the solvent system and bench scale tests. Extraction isotherms for cobalt and nickel at various concentrations of D2EHPA were given. A scale-up method of a solvent extraction process was also described.

Mass transfer during solvent extraction of various metals has been studied (20). It has been observed that the metal uptake in the organic phase is a function of equilibrium pH. In some extraction systems, a synergistic effect is observed when mixture of extractants is used (20). This effect can be used for preferential extraction or separation of metals. Satake (41) has reported liquid-liquid extraction of copper oxinate in naphthalene from aqueous phase at 90 C. Equilibrium diagrams for the beneficiation of copper by liquid-liquid extraction were studied by Ruiz (39) using LIX 64 and KELEX 120 in kerosene. Tatsuya et. al. (45) have given formation and two phase equilibriums of cobalt and zinc complexes with B-diketones in solvent extraction systems. Equilibrium and kinetic studies for solvent extraction of copper has also been reported by Lee (28). Kinetic studies of solvent extraction of metal complexes and equilibrium and rate of solvent extraction of iron perchlorate with trioctylphosphine oxide in hexane have been considered by Tatsuya et. al. (45).

Bauer et. al. (4) have carried out measurement and correlation of solvent extraction equilibrium of copper by KELEX 100. They used statistical modelling procedures to correlate the experimental data. Tatsuya et. al. (46) have reported solvent extraction of nickel (II) B-diketonates and their trioctylphosphine oxide adducts. They compared formation constants of Ni(II) chelates with those of corresponding Co(II) and Cu(II) complexes. Kinetics and mechanism of solvent extraction of Ti(IV) from acidic aqueous solutions with Di-(2-ethyl hexyl) phosphoric acid in benzene is reported by Islam and Bi[illegible]was (23). They also proposed the reaction for the extraction of Ti(IV) and evaluated the extraction equilibrium constant.

The mechanism of mass transfer of solutes across liquid-liquid interfaces has been studied by Lewis (29) in which he determined the individual transfer coefficients for binary systems using a new type of mass transfer cell. Houghton et. al. (26) have developed a set of differential equations for the mass transfer with chemical reaction. A numerical technique to solve the equations is also described. They (25) also studied rates of forced convection mass transfer. The significance of total mass analysis in the study of the solvent extraction of metal complexes was explained by Berger (6). Hughes and Leaver (22) have considered the equilibria established between Aliquat 336 and various metal-anions involving chromium, vanadium, and the chloride and hydroxide anions. They also tried to develop mathematical model for binary equilibria.

Golding et. al. (20) studied the equilibrium and mass transfer behaviour for the separation of cobalt and nickel in D2EHPA. The experimental conditions were (i) total metal ion concentration of $\approx$ 10 g/l (0.17 mol/l), (ii) initial pH of aqueous phase = 4.0 and (iii) equilibration of 10% D2EHPA with ammonia at a level of 105%. TBP (5% by volume) was used as a third phase modifier. It was concluded (20) that

1. The metal uptake of one component is greatly influenced by the presence of the other metal.
2. The equilibrium pH varies over the range of aqueous to organic ratio, with higher pH values being obsvered at low aqueous to organic volumetric ratio.
3. Cobalt is slightly more favorably extracted than nickel (by comparison of extraction isotherms).

Sharma and Baird (43) have reported solvent extraction of copper with D2EHPA. Equilibrium data for the distribution of copper between aqueous solution and a 20% solution of D2EHPA in kerosene were obtained by shake-flask experiments. They observed that the capacity of the organic phase for copper was greatly improved when the ammonium salt of D2EHPA was used. They suggested the overall chemical equation for the extraction process as

$$Cu^{2+} + 2\overline{EH} \rightleftharpoons \overline{E_2Cu} + 2H^{+} \qquad .....2.1$$

This simplified representation of the true mechanism of the reaction was not adequate as the organic phase metal loading was found to be higher than extractant concentration. They also tried to correlate equilibrium constant for the reaction proposed in terms of organic and aqueous phase metal concentrations, initial saturation level of D2EHPA and the aqueous to organic phase ratio. However, it seems that this approach was suitable only for a certain level of saturation of D2EHPA with ammonia.

Brisk and McManamey (9) have described the theoretical aspects of the problem involving the liquid-liquid extraction. They suggested the reaction mechanisms for low and high metal concentrations in the organic phase (less than 0.1 mole of metal per mole of extractant). D2EHPA behaves as a dimeric molecule in non-polar solvents such as kerosene. Thus the extraction reaction for divalent metal ion becomes,

$$M^{2+} + 2(\overline{E_2H_2}) \longrightarrow (\overline{ME_2.E_2H_2}) + 2H^{+} \qquad .....2.2$$

They concluded from their experiments that this relationship was not adequate to explain the mechanism at higher metal loadings, for which a complex relationship involving polymeric species was proposed.

$$\overline{(ME_2)_{r-1} \cdot H_2E_2} + \overline{E_2H_2} + M^{2+} \dashrightarrow \overline{(ME_2)_r \cdot E_2H_2} + 2H^{+} \quad .....2.3$$

where r represents degree of polymerisation. They also noted from their studies that the cobalt and nickel complexes polymerised to higher degree as compared to the copper complex. The degree of polymerisation, however, could not be evaluated.

In the above paper Brisk and McManamey (10) tried to find out possible evidence of polymerisation by measuring viscosity of the organic phase as a function of the metal loading in the organic phase. They also provided further evidence of polymerisation by noting the change in color of the cobalt complex in the organic phase. Addition of acetone to the saturated organic phase resulted in precipitation of blue solid, which was insoluble in water. They concluded that this solid may be a long chain polymer of the cobalt-D2EHPA complex.

Forrest and Hughes (17, 18) studied the modelling of equilibrium data for the liquid-liquid extraction of metals. In the first part of the paper (17), a survey of existing models was carried out. Description of chemically based models, semi-empirical models and totally empirical models was given. In semi-empirical models, they have considered the analogies to adsorption and vapor-liquid equilibria, while totally empirical models are concerned with polynomial fitting of the equilibrium data. In a second paper, Forrest and Hughes (18) tried models for the copper/LIX 64N and chromate/Aliquat 336. Various models were fitted to the experimental data, and it was concluded for representing surfaces that the polynomial approximation gave the best fit.

Smutz et. al. (44) correlated multicomponent equilibrium data for the extraction of lanthanides with D2EHPA. They considered all empirical models for the prediction of single component and multicomponent equilibrium data. The models were developed considering analogy with vapor-liquid equilibria. A model for binary system predicts the total organic concentration as a function of mole fraction of components in the aqueous phase and equilibrium acidity at a given total metal ion concentration. Some numerical examples were given which explain the utility of the model.

Berger and Graff (5) have given some mathematical considerations in the treatment of the equilibria for the solvent extraction of metals with dibasic ligands. The paper is mainly concerned with derivation of mathematical relationship to show that the solvent extraction of metals with dibasic acids may be considered to be an extension of the monobasic case. They have developed generalized equations for the extraction of metals with mono and dibasic acids, considering polymerisation, if any, of the metal in the organic phase. A thermodynamic equilibrium model to predict the cobalt distribution coefficient in the cobaltous chloride-hydrochloric acid-water-TBP liquid-liquid extraction was given by Nevarez and Bautista (32) by considering the theory of mononuclear complexes equilibria. The application of their model is limited since (i) the complexes formed must be mononuclear and properly identified and (ii) the mechanism of their extraction into a suitable organic solvent must be known. A distributed parameter model for liquid-liquid extraction was solved by Burge and Clements (11) to obtain the frequency response for a countercurrent liquid extraction column.

Brisk and McManamey (10) have, as previously noted, reported that the metal polymer formation can significantly affect organic phase physical properties. This can be expected to change mass transfer rates for the extraction of most of the metals. Viscosity and interfacial tension plays an important role in designing of plate and pulse sieve extraction columns. The significance of surface activity in solvent extraction reagents is explained by Cox and Flett (13). Interfacial activity could be demonstrated by measuring interfacial tension, interfacial potential and interfacial viscosity.

Chapter III

THEORY

3.1 CHEMISTRY OF SOLVENT EXTRACTION PROCESS

D2EHPA is classified as a liquid cation exchanger in which the cobalt/nickel cation is exchanged for hydrogen ions of the solvent. The extraction is pH dependent as shown in figure 1. During the extraction of cobalt/nickel using the acid form of D2EHPA, hydrogen ions are liberated from the solvent (due to cation-exchange reaction). As a result, the pH range for maximum cobalt/nickel extraction (pH 4.5 approx. and higher) cannot be maintained, because the aqueous phase becomes more acidic as the metal is extracted. Ritcey et. al. (38) showed that the use of an alkali salt of the D2EHPA solvent maintained the desired pH for optimum extraction. As suggested by Ritcey et. al. (38) and Sharma and Baird (43), cobalt/nickel in acidic solution, under the conditions considered here, are certainly in the +2 oxidation state. One mole of D2EHPA extracted a maximum of 0.5 mole of cobalt/nickel, and liberated one mole of hydrogen ion. They have suggested the following mechanism:

Equilibration of D2EHPA solvent with ammonium hydroxide.

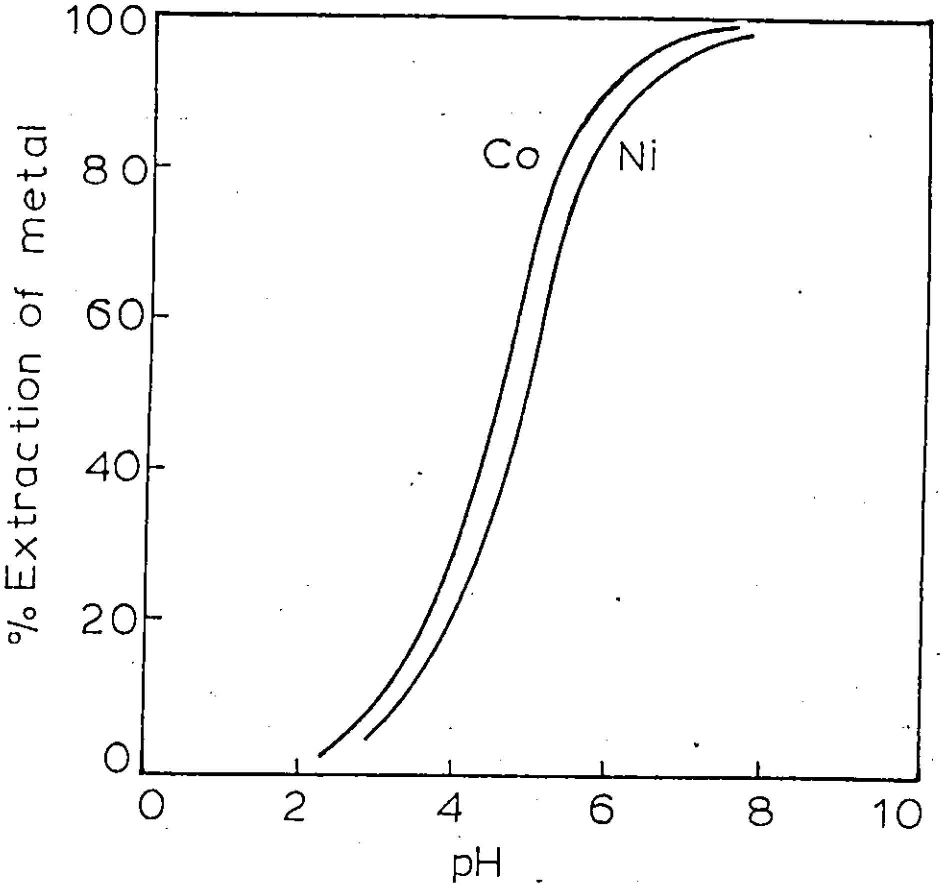
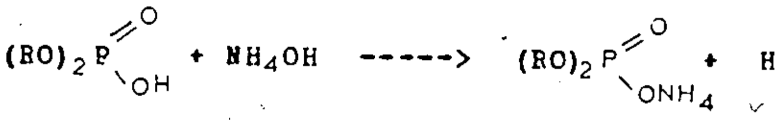
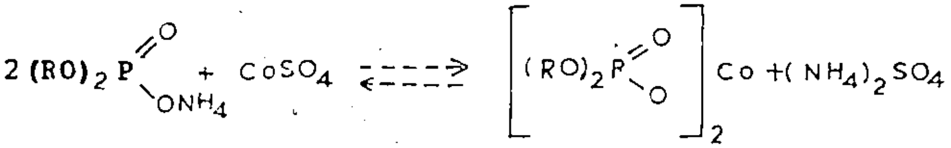


Fig. 1 % Extraction of cobalt and nickel as a function of equilibrium pH



$$(RO)_2P(=O)OH + NH_4OH \dashrightarrow (RO)_2P(=O)ONH_4 + H_2O \quad .....3.1$$

Extraction of Cobalt:



$$2(RO)_2P(=O)ONH_4 + CoSO_4 \rightleftharpoons \left[(RO)_2P(=O)O\right]_2Co + (NH_4)_2SO_4 \quad .....3.2$$

similar equations can be written for the extraction of nickel. The overall chemical equation for cobalt extraction can be taken as:

$$Co^{2+} + \overline{2EH} \dashrightarrow \overline{E_2Co} + 2H^{+} \quad .....3.3$$

where the overbar denotes a species in the organic phase. D2EHPA has one active hydrogen atom and is written as EH.

It should be emphasized that the above chemical equation is a simplified one. Representation of the D2EHPA-Co/Ni complex in the organic phase in these equations as 2:1::organic:metal complex does not imply that this is the actual species present. Brisk and McManamey (9) concluded from their experiments that a dimerised species of D2EHPA in kerosene was present which took part in the extraction. However, this was also not adequate to explain the equilibrium data at higher metal loading in the organic phase. A complex relationship involving polymeric species was proposed by Brisk and McManamey (9). Thus, the actual cobalt complex in the organic phase may be a dimerised, or even a polymerised complex.

Although the true mechanism of the reaction was not as simple as given in equation 3.2, Sharma and Baird (43) assumed that the activity coefficients were unity and developed equations to predict equilibrium constant.

$$K_H = \frac{C_O \cdot C_H^2}{C_A \cdot C_E^2} \qquad \text{.....3.4}$$

The equilibrium ratio of metal (organic to aqueous) declined as the pH fell. To maintain a certain pH range the extractant, D2EHPA, was converted to its ammonium salt in the organic phase,

$$\overline{EH} + NH_4^+ \rightleftharpoons \overline{ENH_4} + H^+ \qquad \text{.....3.5}$$

and for this reaction,

$$K_N = \frac{C_H \cdot C_{ON}}{C_E \cdot C_{AN}} \qquad \text{.....3.6}$$

When the ammoniated extractant was used to extract metal according to:

$$Co^{2+} + \overline{2ENH_4} \rightleftharpoons \overline{E_2Co} + 2NH_4^+ \qquad \text{.....3.7}$$

and

$$k = \frac{C_O . C_{AN}^2}{C_A . C_{ON}^2} = \frac{K_H}{K_N^2} \qquad .....3.8$$

A simplified expression for k in terms of the experimentally measured quantities was derived as follows:

An ammonia balance gave:

$$V_A C_{AN} = V_O (C_{ON_1} - C_{ON}) \qquad .....3.9$$

An ion balance on the aqueous phase provided,

$$C_{AN} = 2(C_{A_1} - C_A) \qquad .....3.10$$

from equations 3.9 and 3.10 the equilibrium distribution of ammonia between the phases was:

$$C_{ON}/C_{AN} = \frac{C_{ON_1}}{2(C_{A_1} - C_A)} - V_A/V_O \qquad .....3.11$$

A metal balance gave:

$$V_A (C_{A_1} - C_A) = V_O C_O \qquad .....3.12$$

Substitution for $(C_{A_1} - C_A)$ from equation 3.12 into 3.11 gave the ammonia distribution in terms of C_{ON_1} and C_O

$$C_{ON}/C_{AN} = (V_A/V_O)(C_{ON_1}/2C_O - 1) \qquad .....3.13$$

substituting equation 3.13 in 3.8,

$$k = (C_O/C_A)\,[\,(V_A/V_O)(C_{ON_1}/2C_O - 1)\,] \qquad .....3.14$$

or

$$(V_O/V_A)(C_O/C_A)^{1/2} = (k)^{1/2}\left[\frac{C_{ON_1}}{2C_O} - 1\right] \qquad .....3.15$$

Thus k can be evaluated by plotting $(V_O/V_A)(C_O/C_A)$ against $C_{ON_1}/2C_O$. The data points for the lowest ammonia loading ($C_{ON_1} < 0.07$ mol/l) did not confirm well because in this case the equilibrium with free D2EHPA cannot be neglected. The pH also fell below the desired range for extraction after equilibration and so the assumption in equation 3.10 that neglects changes in C_H compared to C_{AN} was not valid.

Some of the data for the highest ammonia level (C_{ON_1} > 1.5 mol/l) also deviated from euqation 3.15. This may be due to the observed formation of turbidity in the aqueous phase after equilibration with the highly ammoniated D2EHPA and a precipitate formed. According to above approach the stoichiometric extraction corresponds to a maximum molar ratio of metal to extractant of 0.5:1, but the experimentally observed value was higher. This could be due to the presence of TBP which itself is an extractant. It also appears to suggest that the extracted species may exist as a polymeric complex with the alkyl phosphoric acid as a bridging ligand.

Brisk and McManamey (9) have studied the liquid extraction of metal mixtures from sulfate solutions by an alkylphosphoric acid. According to them, at low metal concentrations in the organic phase (L less than 0.1) D2EHPA behaved as a dimeric molecule in non-polar solvents such as kerosene, and the simple extraction reaction became (for divalent metal ions):

$$M^{2+} + 2\overline{(H_2X_2)} \rightleftarrows \overline{(MX_2.H_2X_2)} + 2H^{+} \quad .....3.16$$

Equation 3.16 implies that the maximum value of L is 0.25. However, values up to and over 0.5 were obtained experimentally when higher loading of organic phase was the case. As percentage of D2EHPA increased, the organic phase metal loading per mole of the extractant D2EHPA, L, decreased.

This may be explained on the basis of the formation of a metal-reagent polymer. Typical steps in the formation of this polymer may be described as

$$\overline{(MX_2.H_2X_2)} + \overline{(H_2X_2)} + M^{2+} \rightleftarrows \overline{[(MX_2)\ .H_2X_2]} + 2H^{+} \quad .....3.17$$

$$\overline{[(MX_2)_{r-1}.\ H_2X_2]} + \overline{(H_2X_2)} + M^{2+} \rightleftarrows \overline{[(MX_2)_r.H_2X_2]} + 2H^{+} \quad .....3.18$$

where r is related to polymer size.

When r is 1, only the monomeric complex $(MX_2.H_2X_2)$ is formed implying the formation of a single large polymer. As suggested in the equation 3.18, when the polymer is formed a large number of hydrogen ions are generated, thus lowering the pH of the aqueous phase at equilibrium.

Brisk and McManamey (10) have discussed the existance of such polymers in reference to the viscosity of the organic phase. The specific viscosity was related to mean polymer size of the molecule by the relationship

$$\eta = \beta . r_m^2 \qquad .....3.19$$

where β is a constant.

Further qualitative evidence of polymer formation was provided by the appearance of the organic phase at equilibrium (10). The blue colored complex of cobalt turned to deep violet as the metal loading in the organic phase increased. This complex was insoluble in water but soluble in excess of acetone. Brisk and McManamey (10) suggested that this solid may be a long chain polymer of Co-D2EHPA complex.

3.2 MODELLING OF EQUILIBRIUM DATA

There are two types of models, (i) mechanistic and (ii) empirical.

1. Mechanistic models have physical or chemical basis on which they are constructed. An extrapolation can be done for the required information from data with some confidence. They are sometimes simple but often complex.

2. Empirical models are made to simulate the real situation. They have little confidence on extrapolation of data. The form of the empirical model is made as simple as possible.

The approaches which have been made to the representation of metal equilibria fall into three main catagories (17): (i) Chemically based models, which seek to model the data on the basis of the known chemistry of the extraction. These can be made thermodynamically rigorous if activity data are employed. (ii) Semi-empirical models using analogies between gas adsorption and vapor-liquid equilibria. (iii) Totally empirical models which use generalised mathematical expressions such as polynomials.

1. Chemically based models: Initial attempts at modelling equilibrium data were based on the extraction equation. Forrest and Hughes (18) tried to correlate the equilibrium data for the extraction of copper and chromium. Application of the chemical model as suggested in equation 3.8 suffers from two severe limitations. In the first case the solutions are not thermodynamically rigorous and concentrations should be replaced by activities. If activity data are not used a second limitation is imposed on equation 3.8 for now k need not necessarily remain constant and for the system

considered, it may change by a factor of ten or more. The value of, k, an apparent equilibrium constant, is only an average of the individual k values over a given concentration range. To conclude, the method is only as good as the proposed reaction equation.

2. Semi-empirical models: The transfer of solute between two liquid phases has analogies to other two-phase systems where, for instance, a solute is adsorbed by a solid from a gas phase. Ellis (14) noted the similarity between the shape of the adsorption isotherm and the shape of the distribution isotherm for solvent extraction systems involving chemical reaction. He assumed that the curvature was due to the reaction between the extracted substance and the extractant, so that, as more material is extracted the amount of available extractant decreases. This was analogous to the conditions considered by Langmuir in the derivation of the equation for the adsorption isotherm. In the case of the Langmuir equation for solid-gas equilibria the curvature is due to the decrease in surface area available for adsorption as the surface becomes covered with the adsorbed solute. In the liquid-liquid extraction Langmuir extraction isotherm is expressed in the form:

$$y = \frac{\theta_1 . \theta_2 . x}{1 + \theta_2 . x} \quad .....3.20$$

where y is the concentration of the metal in the organic phase and x is the concentration of the metal in the aqueous phase. Parameter θ_1 represents the maximum organic phase metal loading and parameter θ_2 represents an equilibrium constant.

One form of the Freundlich equation, expressed in terms of cobalt/nickel concentration, is

$$y = \theta_1 x^{\theta_2} \quad .....3.21$$

where x and y have definitions given in the previous case, and θ_1 and θ_2 are the parameters of the model. This power relationship is of the Freundlich adsorption isotherm equation type.

3. Empirical models: The cobalt/nickel concentrations in the organic phase must be described by atleast two independent variables. A generalised polynomial can be written as,

$$y = \sum_{i=0}^{n} \sum_{j=0}^{m} a_{ij} x^i \, [NH_3]^j_{aq(initially)} \quad .....3.22$$

Second and third order polynomials were tested on the constant sulfuric acid concentration data by Forrest and Hughes (18). for the extraction of copper and chromium. The following polynomials were used.

$$y = a_1 x + a_2 x^3 + a_3 x^3 \quad \text{(cubic)} \qquad .....3.23$$

$$y = a_1 x + a_2 x^2 \quad \text{(quadratic)} \qquad .....3.24$$

For one component systems equilibrium can be represented by a simple curve. These curves are a function of temperature and pH. Typical isotherms are shown in figures 2 and 3. Curves that are convex upward throughout (type I) are designated as 'favorable' to metal uptake in the organic phase; those which are concave upward throughout (type II) as 'unfavorable' to metal uptake (34). Several models for the representation of pure component and binary extraction isotherms in hydrometallurgical systems are:

1. Constant Separation Factor (34)

$$y = \frac{X}{r + X - rX} \qquad .....3.25$$

2. Langmuir Extraction Isotherm (17)

$$y = \frac{\theta_1 \cdot \theta_2 X}{1 + \theta_2 X} \qquad .....3.20$$

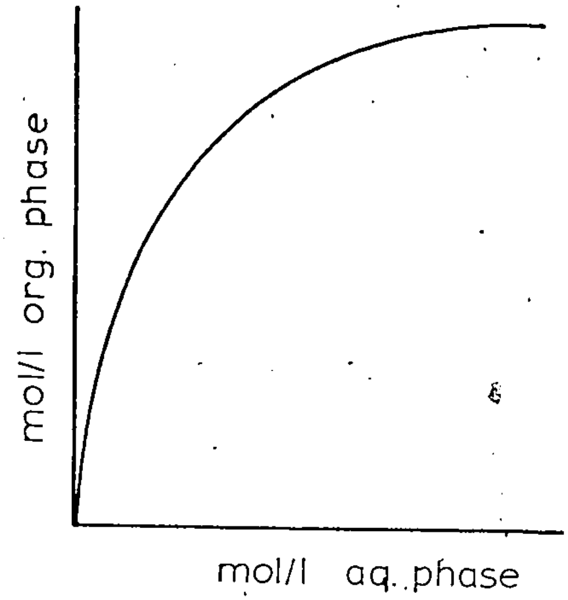


Fig. 2 Equilibrium isotherm type: favorable for the metal uptake

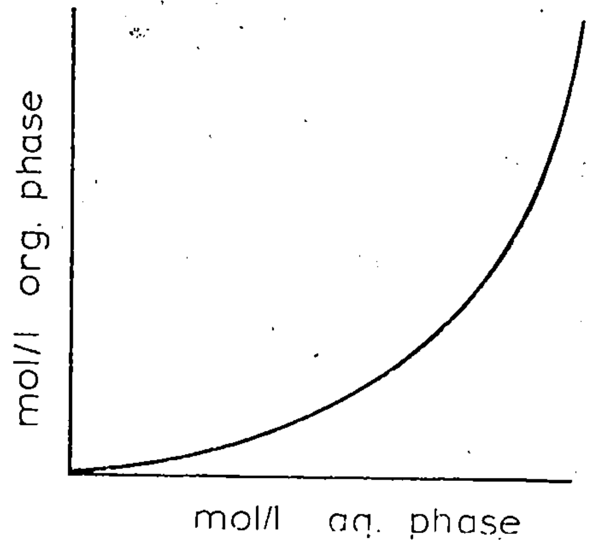


Fig. 3 Equilibrium isotherm type: unfavorable for the metal uptak

3. Freundlich Extraction Isotherm (17)

$$y = \theta_1 . x^{\theta_2} \quad .....3.21$$

4. Quadratic Extraction Isotherm (17)

$$y = a_1 x + a_2 x^2 \quad .....3.24$$

5. Cubic Extraction Isotherm (17)

$$y = a_1 x + a_2 x^2 + a_3 x^3 \quad .....3.23$$

Forrest and Hughes (17, 18) previously found that polynomial isotherms represented the extraction isotherms very well for copper and chromium extraction. Langmuir and Constant separation isotherms are similar.

3.3 PREDICTION OF BINARY/MULTICOMPONENT EQUILIBRIA FROM PURE COMPONENT ISOTHERMS

Smutz et. al. (44) suggested a method to predict multicomponent data from pure component data for the extraction of lanthanides in D2EHPA. Their method and approach were used in the present study and are outlined as follows.

The total metal concentration in the organic phase may be predicted with a series of linear terms and a series of terms which is a measure of the deviation from ideality (Ref. equation 3.30). The predicted term is obtained by multiplying the organic phase concentration of each element in the pure component state by its mole fraction in the aqueous phase ($y^{*}.\bar{x}$). It is termed as partial extractability of the element as an analogy to partial pressure. If total metal concentration is known at an initial level of equilibration of D2EHPA with ammonia, the information can be used to predict the equilibrium concentration of the binary mixture in terms of a deviation term Δy. The method is as follows:

1. Pure component and binary extraction equilibrium data are correlated numerically and the parameters of the model used for correlation are found for each system.

2. Δy is estimated using an analogy to Raoult's law

$$\Delta y = \underset{(\text{for mix})}{y_{\text{exptl.}}} - y^{*} \cdot \bar{x} \qquad \ldots\ldots 3.26$$

   where $y^{*}.\bar{x}$ is 'partial extractability' analogous to partial pressure.

   y^{*} = predicted ideal organic phase concentration for a given value of x.

   $\bar{x}$ = mole fraction of component in the mixture.

   Δy is termed as deviation from ideality.

3. Δy is correlated by an empirical correlation

$$e^{Dy} = \theta_1 . (x_1)^{\theta_2} . (1-x_1)^{\theta_3} . [H^+]^{\theta_4} \qquad \ldots\ldots 3.27$$

   where $Dy = \Delta y$

x_1 = mole fraction of cobalt in the mixture in the aqueous phase at equilibrium.

$[H^+]$ = concentration of hydrogen ions at equilibrium in the aqueous phase.

ϕ_1, ϕ_2, ϕ_3 and ϕ_4 are parameters.

4. Hydrogen ion concentration in the aqueous phase is correlated with metal ion concentration in the aqueous phase at equilibrium.

$$pH = a_1 + a_2 x + a_3 x^2 \qquad .....3.28$$

Note: Since correct mechanism of the extraction process is not known it is not possible to predict the pH as a function of initial ammonia concentration and metal concentration in the aqueous phase

5. Separation factor, K^{Co}_{Ni}, is calculated as

$$K^{Co}_{Ni} = \left\{\frac{y_{Co}}{x_{Co}}\right\} \left\{\frac{x_{Ni}}{y_{Ni}}\right\} \qquad .....3.29$$

6. Total organic concentration is defined as

$$y_T = y^*_{Co} \cdot \bar{x}_{Co} + y^*_{Ni} \cdot \bar{x}_{Ni} + \Delta y_{Co} + \Delta y_{Ni} \qquad .....3.30$$

also it is known from the experimental results that

$$y_T = y_{Co} + y_{Ni} \qquad .....3.31$$

7. Using equations 3.29 and 3.31

$$y_{Co} = \frac{y_T}{1 + \frac{1}{K_{Ni}^{Co}}\left(\frac{x_{Ni}}{x_{Co}}\right)} \qquad .....3.32$$

and $$y_{Ni} = y_T - y_{Co} \qquad .....3.31$$

8. Prediction of binary equilibria

   a) y_T is calculated from given $\bar{x}_{Co}$ and $\bar{x}_{Ni}$

   b) $\triangle y_{Co}$, $\triangle y_{Ni}$ and $[H^+]$ (required to calculate y_T) are estimated using correlations for a particular system considered.

   c) $\overset{*}{y}_{Co}$, $\overset{*}{y}_{Ni}$ are estimated for a given x , x (that is for a known value of x and x in the binary mixture). $\overset{*}{y}_{Co}$ and $\overset{*}{y}_{Ni}$ are the estimated organic phase metal concentrations, calculated as if it were a pure component.

9. y_{Co} and y_{Ni} are estimated using K_{Ni}^{Co}, the separation factor for the system.

The method has been suggested for the multicomponent solvent extraction equilibria.

3.4 SEPARATION FACTOR

Separation factor, K_{Ni}^{Co}, is calculated in the case of extraction of binary mixture of cobalt and nickel. It is defined as

$$K^{Co}_{Ni} = \left\{\frac{y_{Co}}{x_{Co}}\right\}\left\{\frac{x_{Ni}}{y_{Ni}}\right\} \qquad .....3.29$$

Separation factor is analogous to the term relative volatility in distillation, if the competitive cation-exchange process is described by the equations:

$$\overline{2E(NH_4)} + Co^{2+} \underset{\longleftarrow}{\xrightarrow{k_{Co}}} \overline{E_2-Co} + 2NH_4^+ \qquad .....3.33$$

$$\overline{2E(NH_4)} + Co^{2+} \underset{\longleftarrow}{\xrightarrow{k_{Ni}}} \overline{E_2-Co} + 2NH_4^+ \qquad .....3.34$$

it is difficult to calculate the individual equilibrium constants for each metal due to the presence of excess ammonia in the organic phase and the distribution of this species in the two phases is unknown (20). However, the ratio of the two equilibrium constants k_{Co} and k_{Ni} could be expressed as in equation 3.29, which is a separation factor for the Co-Ni pair.

3.5 THE SIGNIFICANCE OF INTERFACIAL TENSION AND VISCOSITY IN SOLVENT EXTRACTION

Solvent extraction reagents are the molecules which possess both hydrophilic and hydrophobic properties. Their polar hydrophilic groupings are necessary to interact with the metal ions or complexes in the aqueous phase to give species which will be soluble in the organic phase. The hydrophobic character provided by the organic part of the reagent molecule is required to maximise this solubility of the metal complex and also to reduce the aqueous solubility of the reagent itself thus minimising reagent losses to process raffinate.

Such compounds will clearly exhibit interfacial activity at the oil-water interface and the addition of these extraction reagents to an oil-water system will therefore modify these interfacial properties. For example, it facilitates the dispersion of the two phases by lowering interfacial tension. It is unlikely that interfacial properties of reagents will have a significant effect on the equilibrium parameters of an extraction process as they are dependent on bulk phase properties of the system. However, when rates of extraction processes are considered, these are dependent upon the concentration of the species at or close to the reaction site which may be the interface itself or a zone close to the interface in the organic or aqueous phase.

Replacing air by an oil phase increases the dimension of the adsorbed film. This increase occurs by a reduction of mutual interactions of the non-polar alkyl chains by solvation by the oil phase. Addition of inorganic salts to the aqueous phase causes a slight shift in the interfacial tension in addition to the change caused by pH. If the variation is in order of affinity of the metal ions for the alkylphosphoric acid, then the metal salts are more interfacially active than the parent acid. The measurement of interfacial tension indicates whether the metal complex is more (or less) interfacially active than the extractant.

Viscosity measurements of the organic phase with respect to metal loading in the organic phase may reveal whether there is any polymerisation in the organic phase. A rise in viscosity as metal loading increases may indicate that polymerisation does occur in the organic phase. If number of metal atoms in metal-D2EHPA-TBP polymer can be found, it may be related to the viscosity of the organic phase by the relationship

$$\eta = \beta . r_m^2 \qquad .....3.19$$

Chapter IV

EXPERIMENTAL PROCEDURES

The present work was carried out to do futher investigations in the extraction of cobalt and nickel by 20% and 40% D2EHPA (by volume). More recently, D2EHPA has replaced the carboxylic acids in metal extraction because of smaller extractant losses, higher metal loadings and faster mass transfer rates. TBP is used as a third phase modifier. It also reduces the solubility of diluent kerosene in water to a negligible extent. Kerosene is used as a diluent for the extractant D2EHPA and the modifier TBP.

The organic phase consisted of D2EHPA extractant, TBP phase modifier and kerosene diluent. Two levels of concentration of D2EHPA (20% and 40%) and 5% TBP were used. All concentrations were on a volume basis. An alkaline salt of D2EHPA was prepared by adding requisite amount of NH OH to the organic mixture. D2EHPA was equilibrated (saturated) stoichiometrically at different levels of saturation with NH such as 20%, 40%, 60%, 80%, 100%, and 110%; to see the effect of initial NH concentration on the solvent extraction.

The aqueous solution was synthetically prepared by dissolving $CoSO_4 .7H_2O$ and $NiSO_4.6H_2O$ in distilled water.

The initial metal ion concentration was kept at $\approx$ 10 g/l or 0.17 mol/l. The initial pH was adjusted to 4.0 in each case. Equilibrium can be obtained in two ways. The first employs variation of the phase ratio of the aqueous and organic phases, the second involves recontacting the organic phase with fresh aqueous phase until the saturation loading of the solvent is reached.

In the phase ratio variation method, the ratios usually employed were in the range of 0.5 to 10. For example, 100 ml. of an aqueous phase containing the metal, and 10 ml. of organic phase were contacted until equilibrium was reached. In the present work aqueous to organic phase ratio was varied from 0.5 to 10. Shakeout tests were carried out in separating funnels and the two phases were contacted for about two minutes. The equilibrium was reached within that time (22). After allowing the phases to disengage, they were separated and analysed for metal content in the aqueous phase. The analysis was carried out using an atomic absorption spectrophotometer (Fisher's Dial Atom Jerrel Ash III). Details of the procedure for analysis are given in appendix A. The experimental solution collected from aqueous phase, was diluted 1000 times for the analysis. The organic phase concentration was determined in most of the cases by material balance calculations. The organic phase was analysed in a few cases to check the material balance and it was found to agree within 5% error and a maximum difference of 6.5%.

All the equilibrium shake-out tests were carried out at atmospheric pressure and at an ambient temperature of 24-25 °C. Samples from aqueous phase were collected and pH was measured for all the samples using a pH meter. The pH meter was calibrated using standard buffer solutions. Samples from both the phases were also collected separately to measure the physical properties such as viscosity and interfacial tension. Viscosity of the organic phase was measured with the help of a rotating cylinder viscometer. The interfacial tension between the organic phase and the aqueous phase was measured by Fisher's Autotensiomat. The viscosity and interfacial tension were measured with respect to metal loading in the organic phase. Details of the method of viscosity and interfacial tension measurements are given in appendix B.

Models were fitted to the experimental data using linear and non-linear least square techniques. In the case of linear models, the program 'Linreg' was used to treat the data, while in the case of non-linear models a 'Gauss-Newton' method as well as a modified version of the Gauss-Newton method, and, a program (designated as) 'Nonlin', were used.

Chapter V

RESULTS

Equilibrium data have been collected for the system Co-Ni-D2EHPA. The data were obtained for the pure components, as well as, binary mixtures of two metals. Data on viscosity measurements and interfacial tension measurements were collected for pure component and binary mixtures. Variation of pH with metal loading in the organic phase is also noted.

The equilibrium data (x,y) is tabulated for the separate cases considered (depending on concentration of D2EHPA and its equilibration with NH_3 at various levels) in tables 1 through 10. Plots have been made to represent the equilibrium data for a constant cencentration of D2EHPA and its varying equilibration with NH_3 . These plots show the effect of ammonia concentration on the metal uptake in the organic phase. The data is represented for the extraction of cobalt and nickel as pure components and also in the mixture. Similar plots have been drawn for 10%, 20% and 40% D2EHPA (Ref. figures 4 to 13). The material balance calculations to determine organic phase concentration is displayed in appendix D.

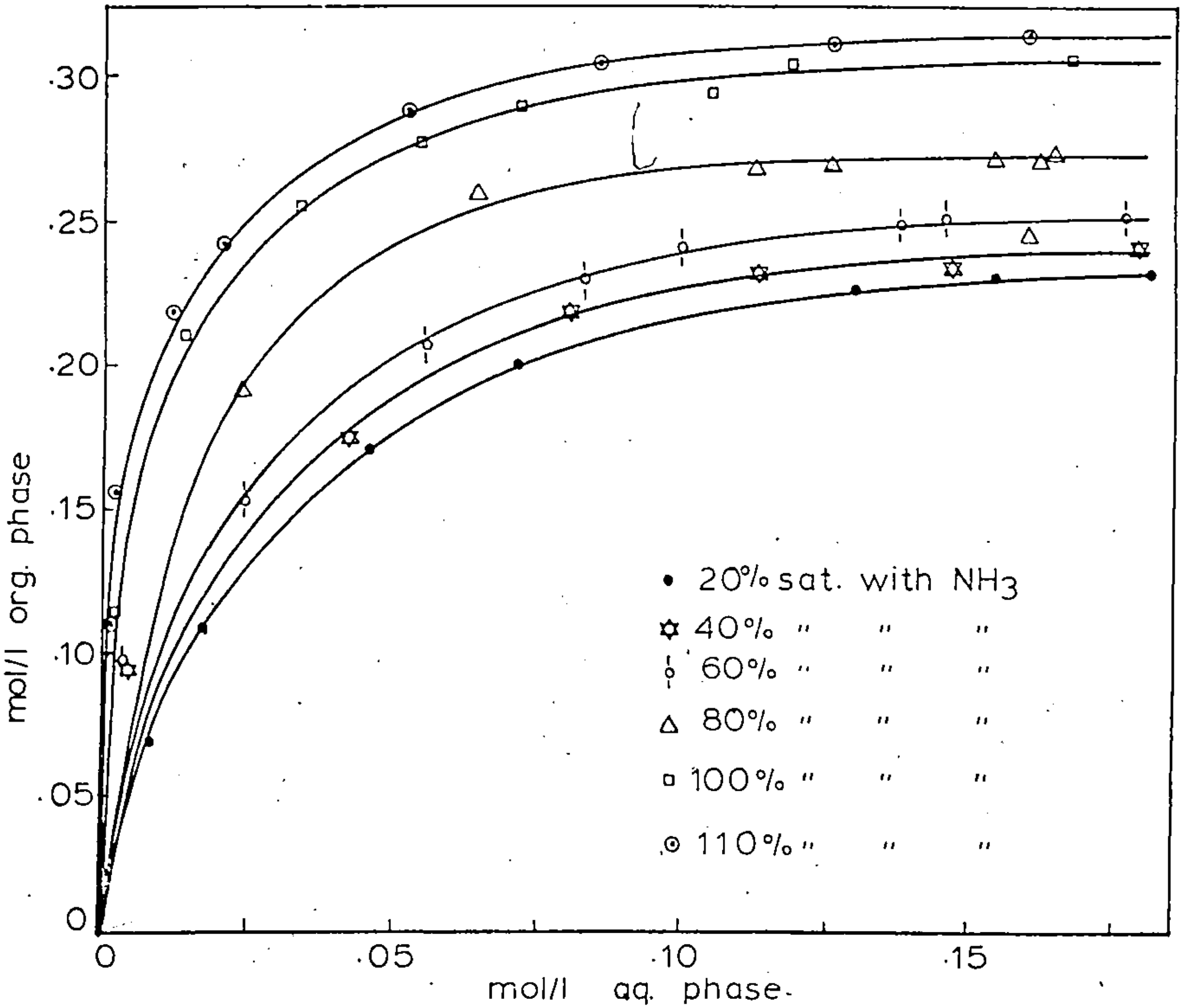


Fig. 4 Equilibrium isotherms for the system: pure component cobalt-10% D2EHPA-at the different levels of pre-equilibration of D2EHPA with ammonia

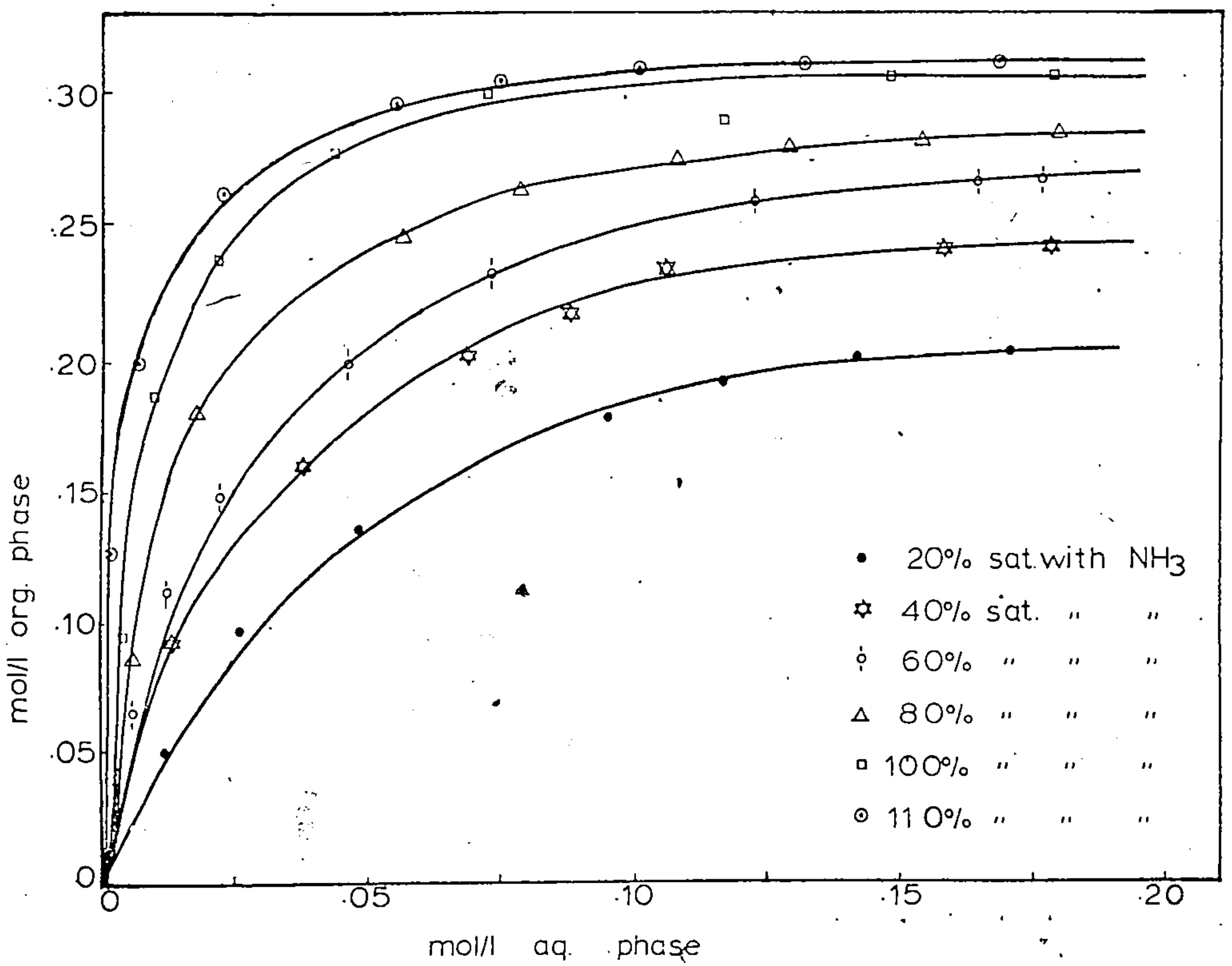


Fig. 5 Equilibrium isotherms for the system: pure component nickel-10% D2EHPA-at the different levels of pre-equilibration of D2EHPA with ammonia

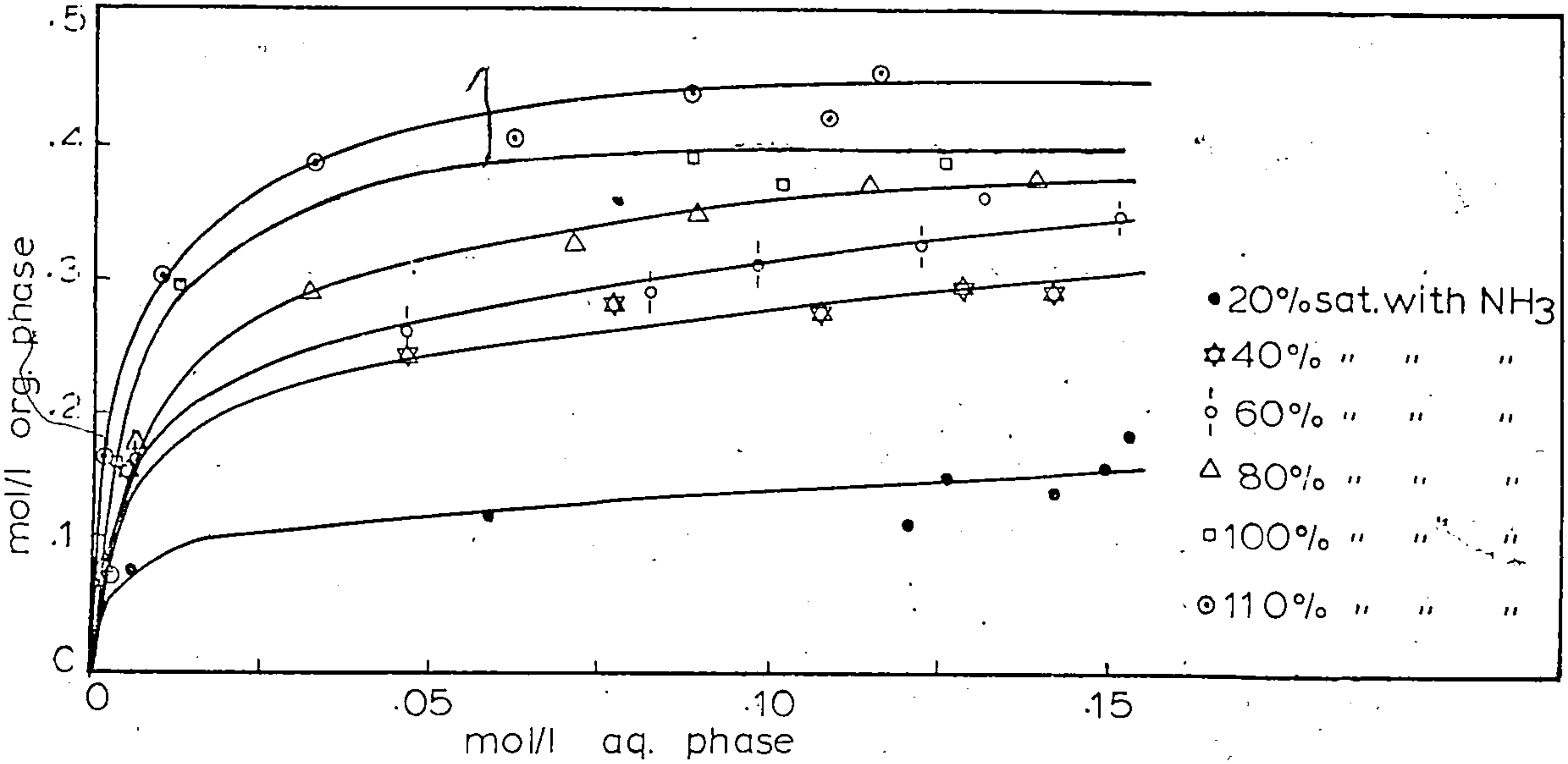


Fig. 6 Equilibrium isotherms for the system: pure component cobalt-20% D2EHPA-at different levels of pre-equilibration of D2EHPA with ammonia

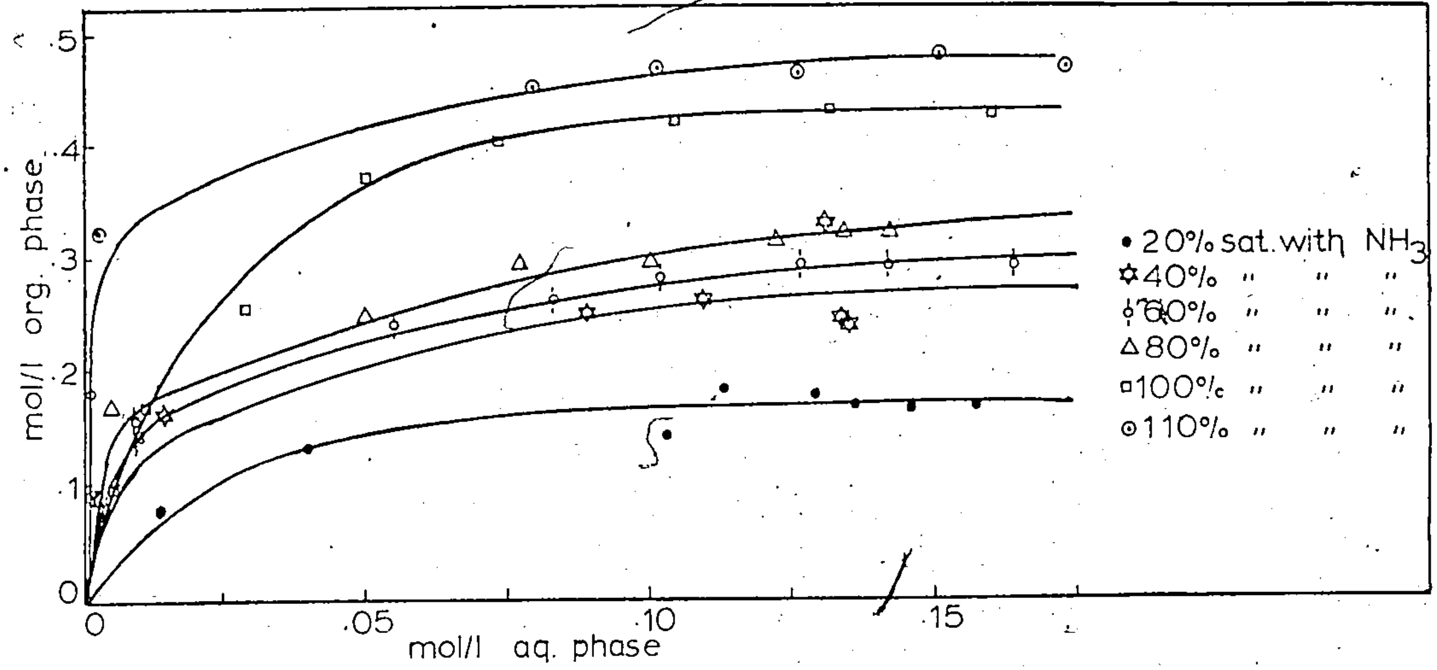


Fig. 7 Equilibrium isotherms for the system: pure component nickel-20% D2EHPA-at the different levels of pre-equilibration of D2EHPA with ammonia

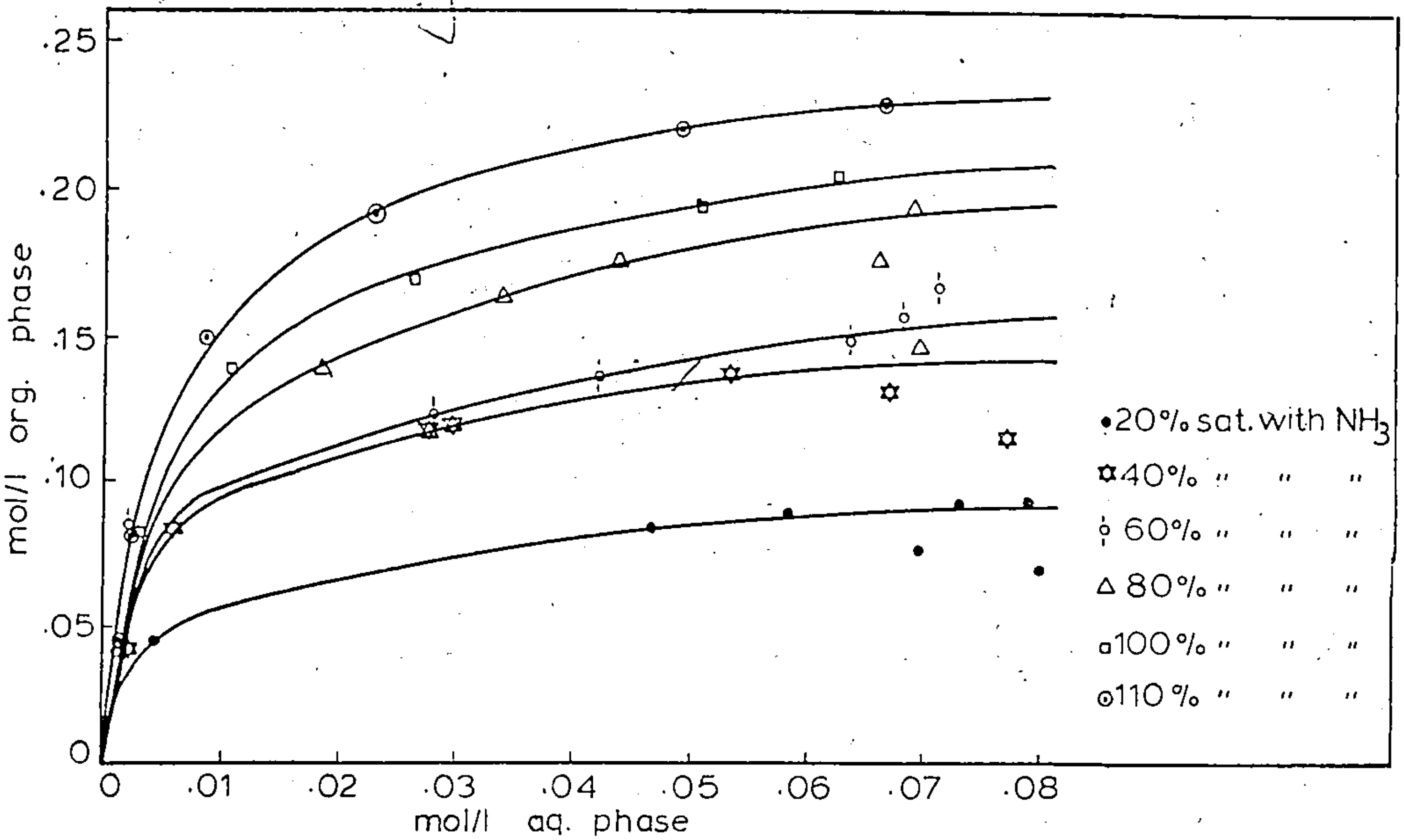


Fig. 8 Equilibrium isotherms for cobalt in the mixture of cobalt and nickel for the system: 20% D2EHPA-at the different levels of pre-equilibration of D2EHPA with ammonia

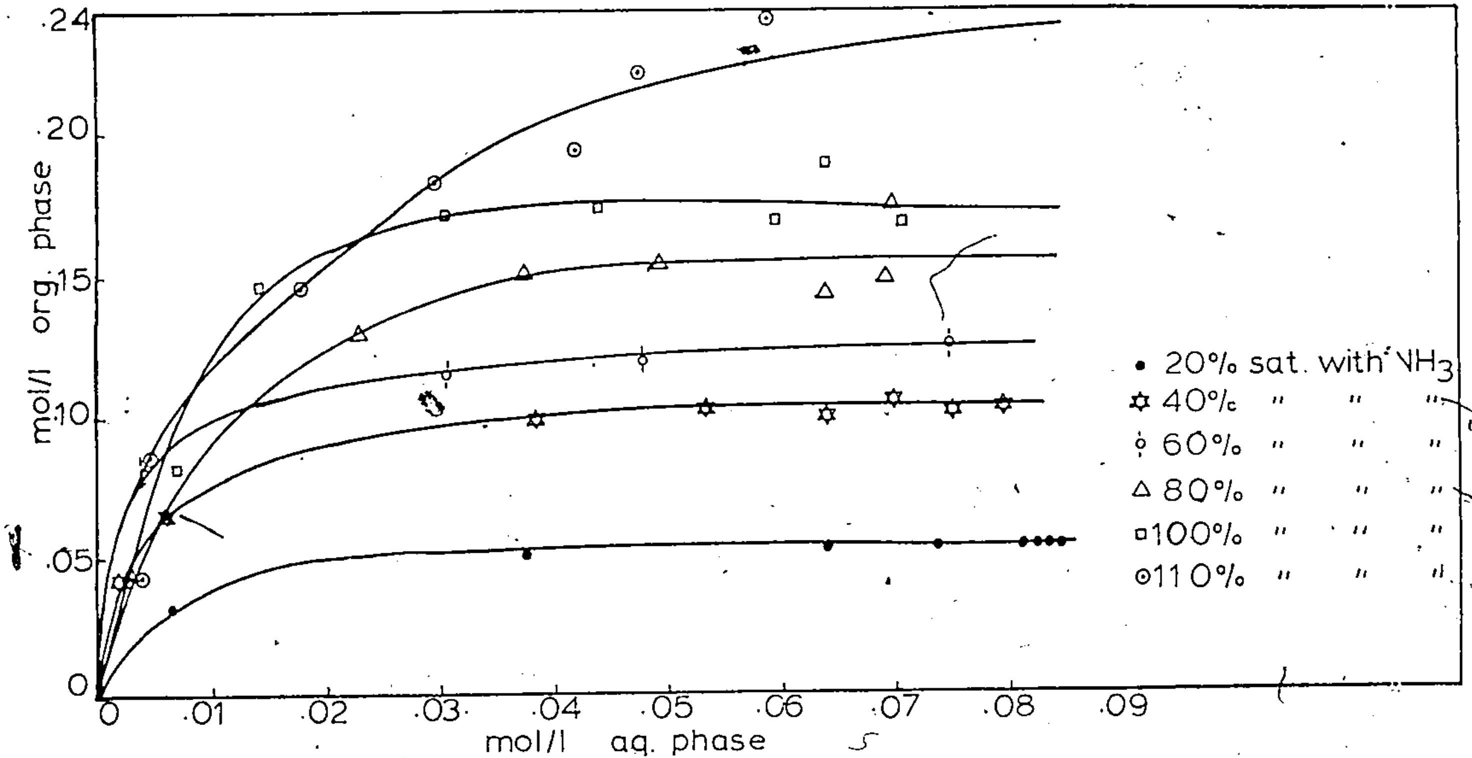


Fig. 9 Equilibrium isotherms for nickel in the mixture of cobalt and nickel for the system: 20% D2EHPA-at the different levels of pre-equilibration of D2EHPA with ammonia

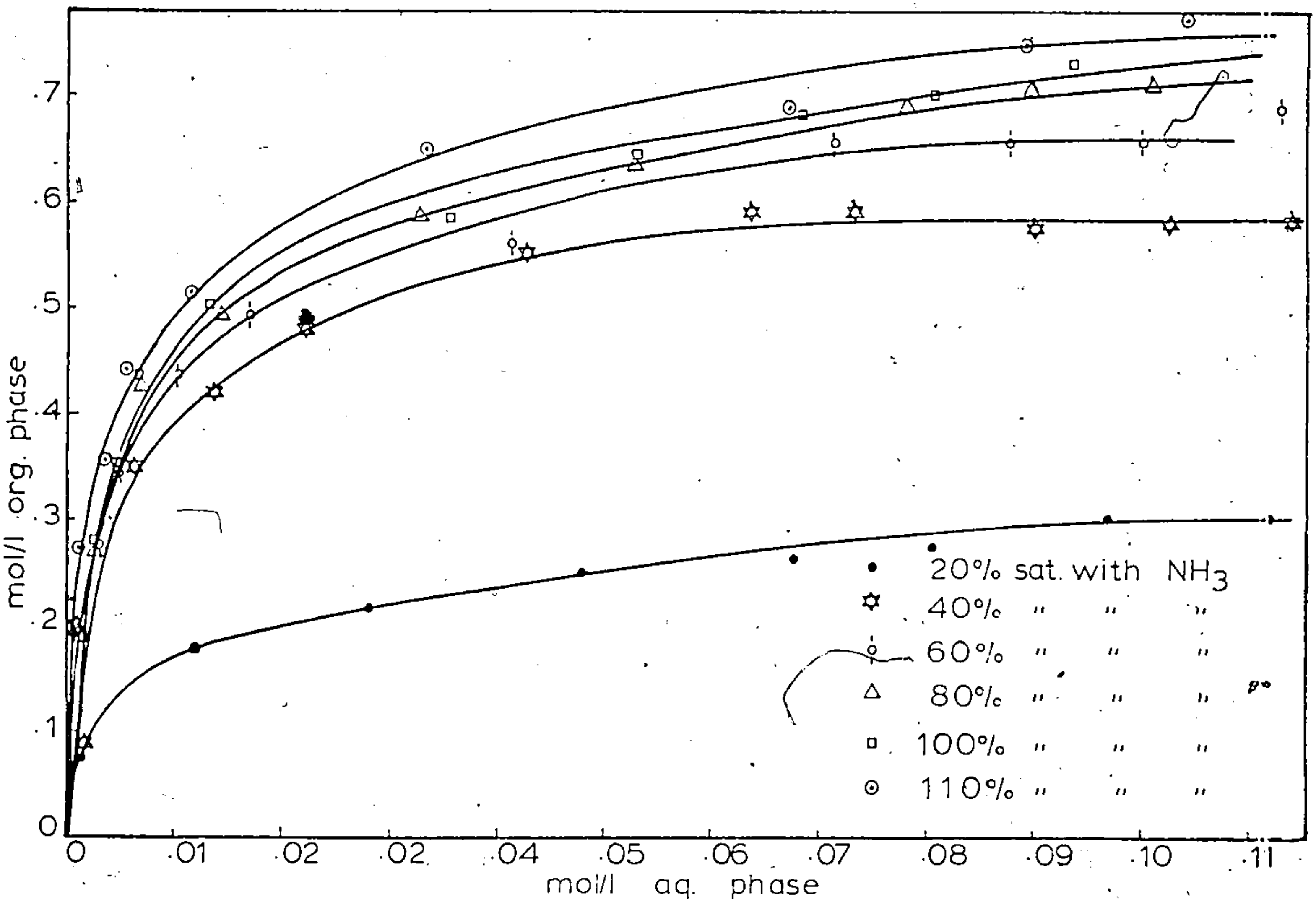


Fig. 10 Equilibrium isotherms for the system: pure component cobalt-40% D2EHPA-at the different levels of pre-equilibration of D2EHPA with ammonia

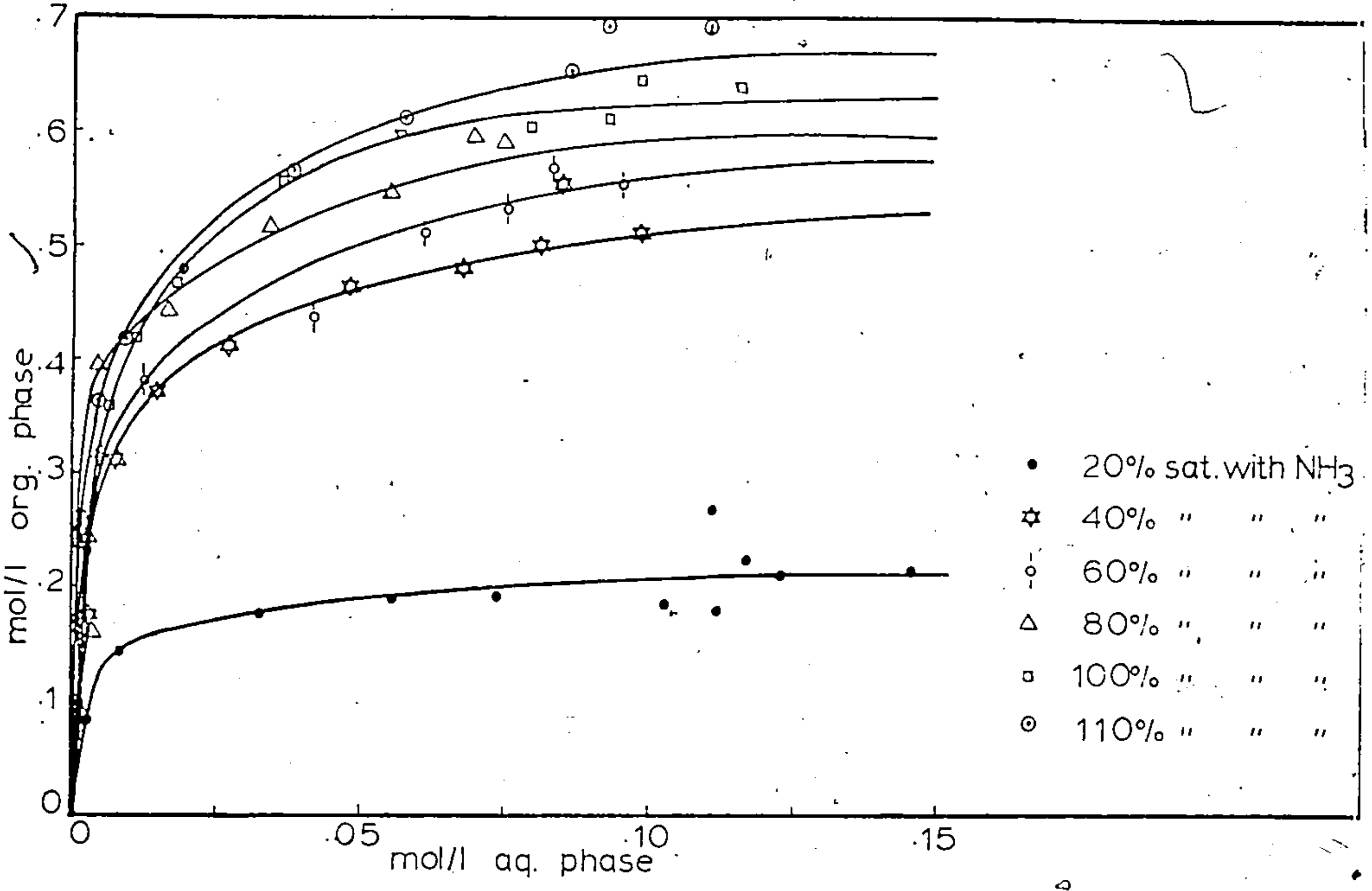


Fig. 11 Equilibrium isotherms for the system: pure component nickel-40% D2EHPA-at the different levels of pre-equilibration of D2EHPA with ammonia.

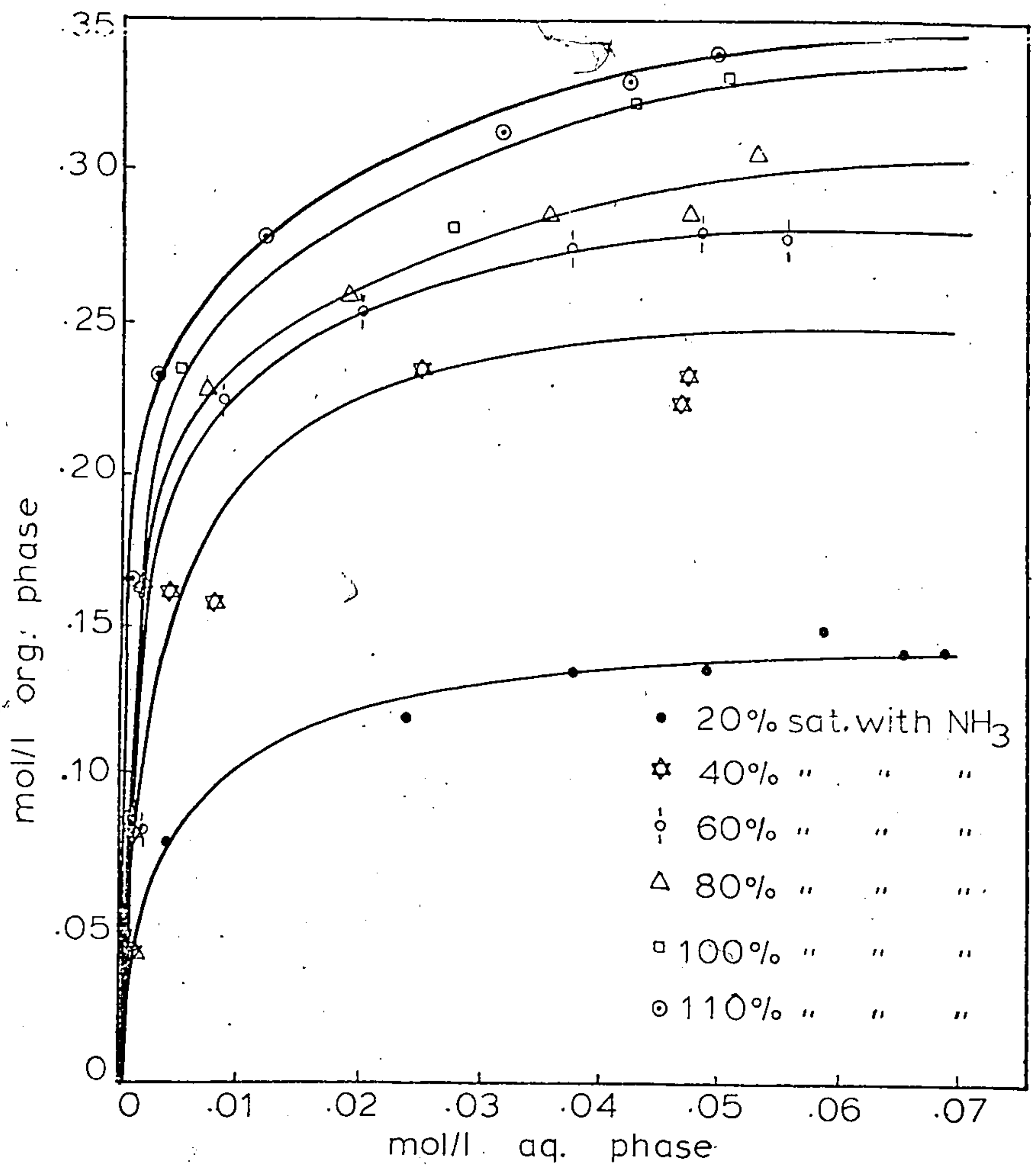


Fig. 12 Equilibrium isotherms for cobalt in the mixture of cobalt and nickel for the system: 40% D2EHPA-at the different levels of pre-equilibration of D2EHPA with ammonia

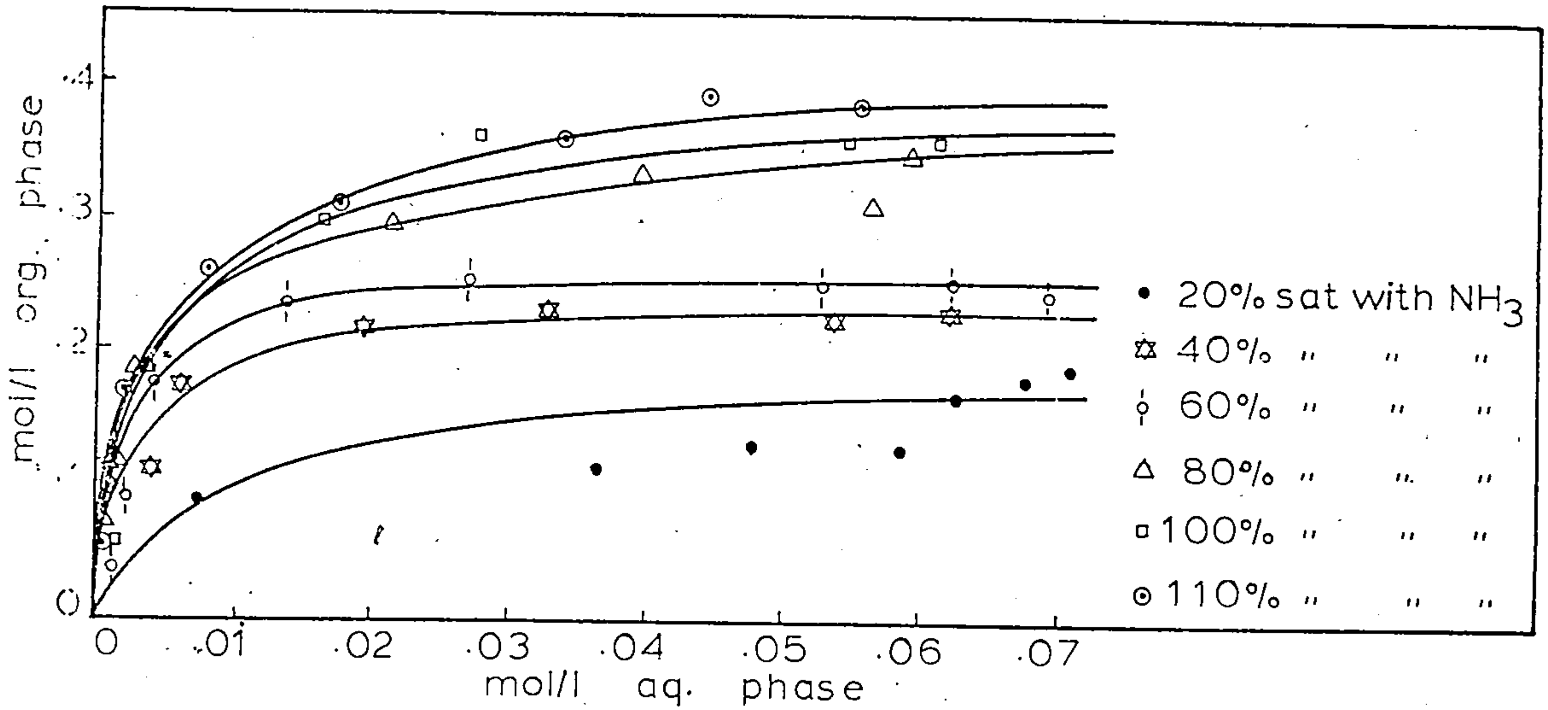


Fig. 13 Equilibrium isotherms for nickel in the mixture of cobalt and nickel for the system: 40% D2EHPA-at the different levels of pre-equilibration of D2EHPA with ammonia.

The equilibrium data have been correlated using semi-empirical and empirical correlations. The experimental curve as well as all the correlations are plotted together for a particular system. Comparisons are thus made to find the best fitting of the correlations tried. Figures 14 to 22 show some of the plots and comparisons of the correlations. Plots have been made to compare the correlations for pure component as well as binary mixture isotherms. The problem became more complicated when the binary mixture was considered. The presence of one metal affected the extraction of the other metal. Figures 23 and 24 show the isotherms drawn for the extraction of cobalt and nickel in the presence of each other, for 20% D2EHPA. The separation factor for a Co-Ni pair, as defined by equation 3.29, is calculated for the binary extraction of cobalt and nickel by 20% and 40% D2EHPA. The separation factors are tabulated in tables 18(A to F) according to the system.

The apparent equilibrium constant, k, was calculated as described by equation 3.15. The values for k were determined by fitting the data for a system using a least squares method. A graph can also be plotted as (V_O/V_A) $(C_O/C_A)^{1/2}$ versus $C_{ON_1}/2C_O$. Square of the slope of the graph gives the equilibrium constant, k.

Tables 17 (A through D) gives the values of k for extraction by 20% and 40% D2EHPA at various levels of saturation with ammonia and for pure components as well as binary

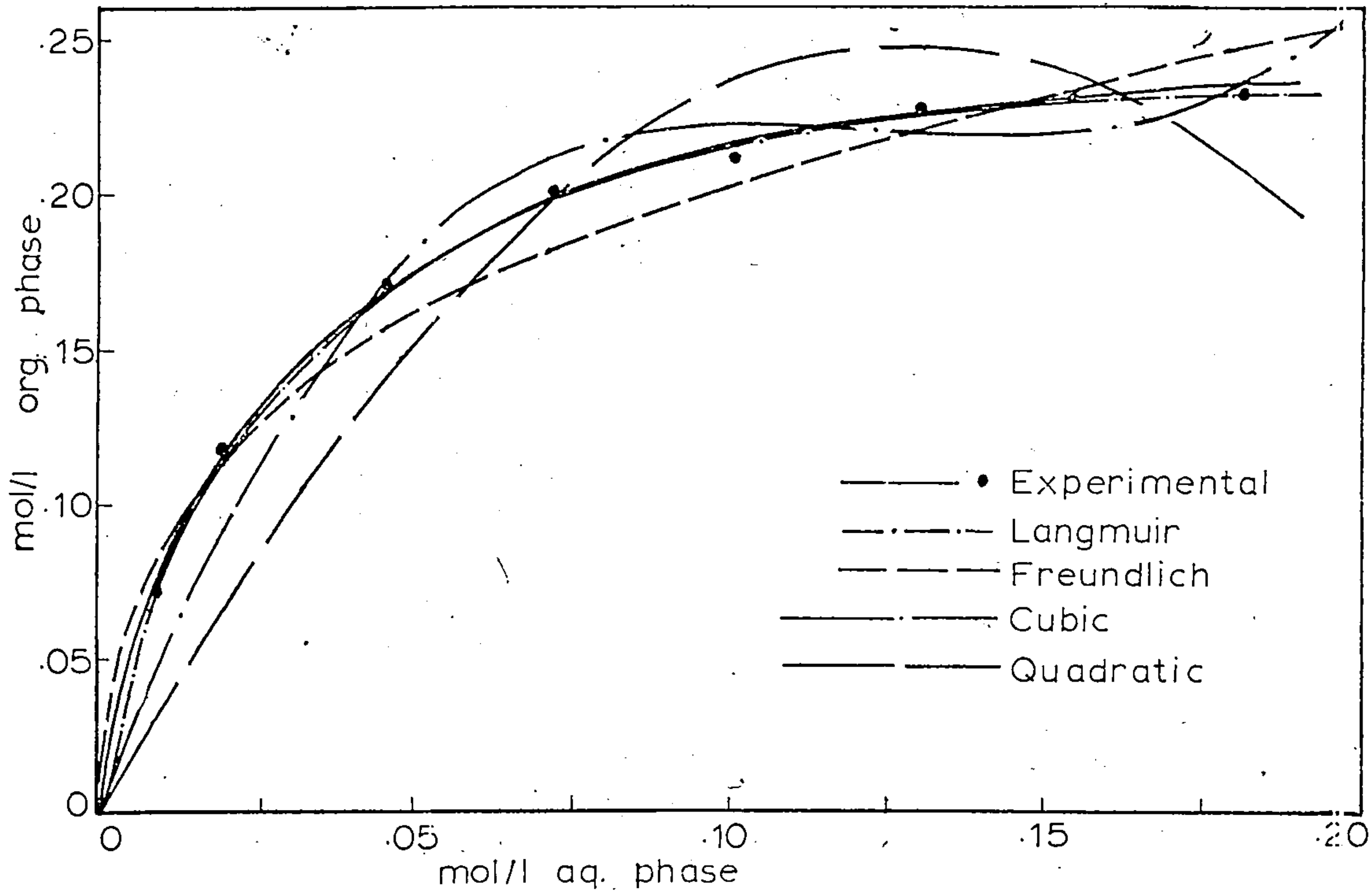


Fig. 14 Comparison of the different isotherm models for the system: pure component cobalt-10% D2EHPA-20% pre-equilibration of D2EHPA with ammonia

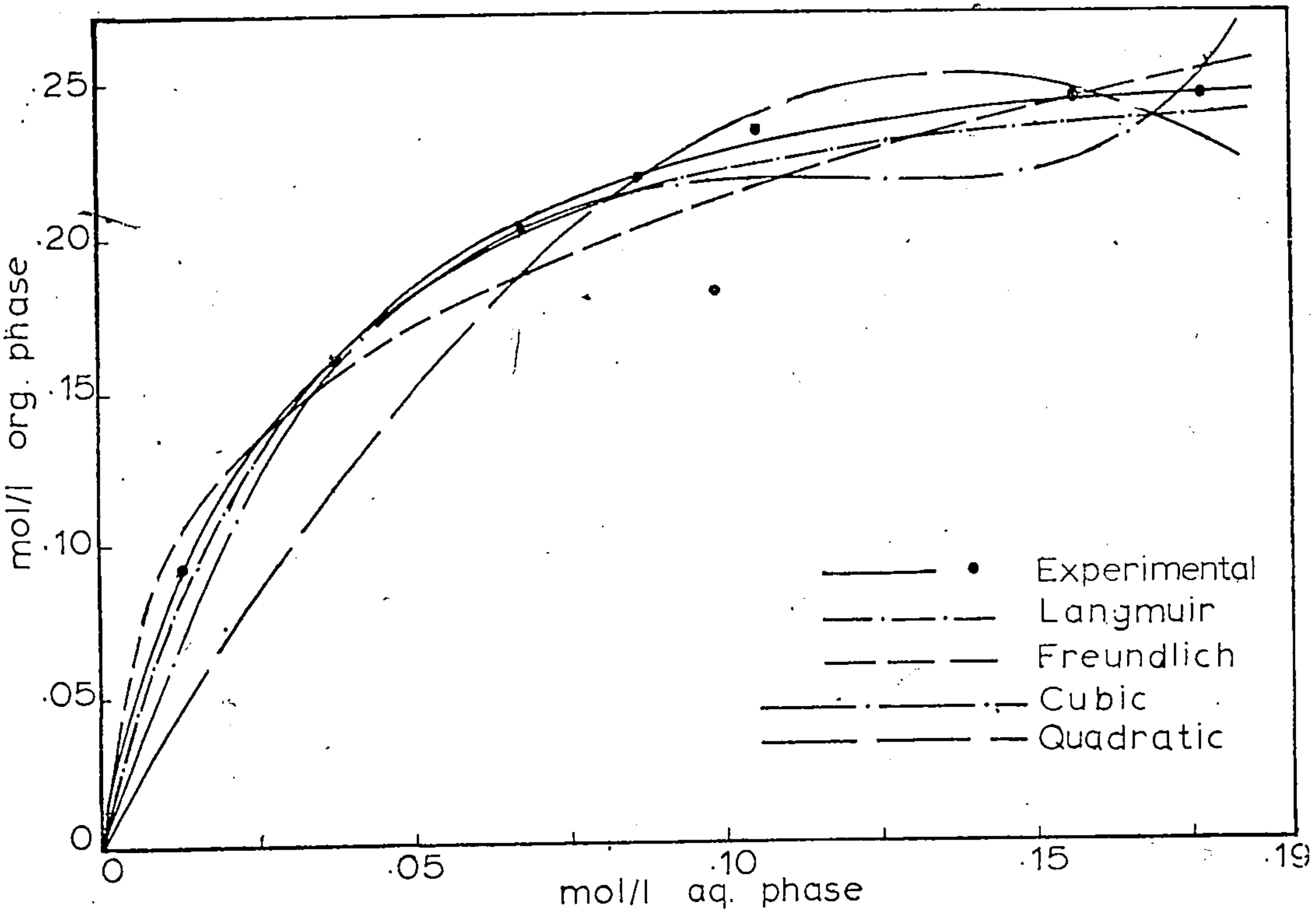


Fig. 15 Comparison of the different isotherm models for the system: pure component nickel-10% D2EHPA-40% pre-equilibration of D2EHPA with ammonia

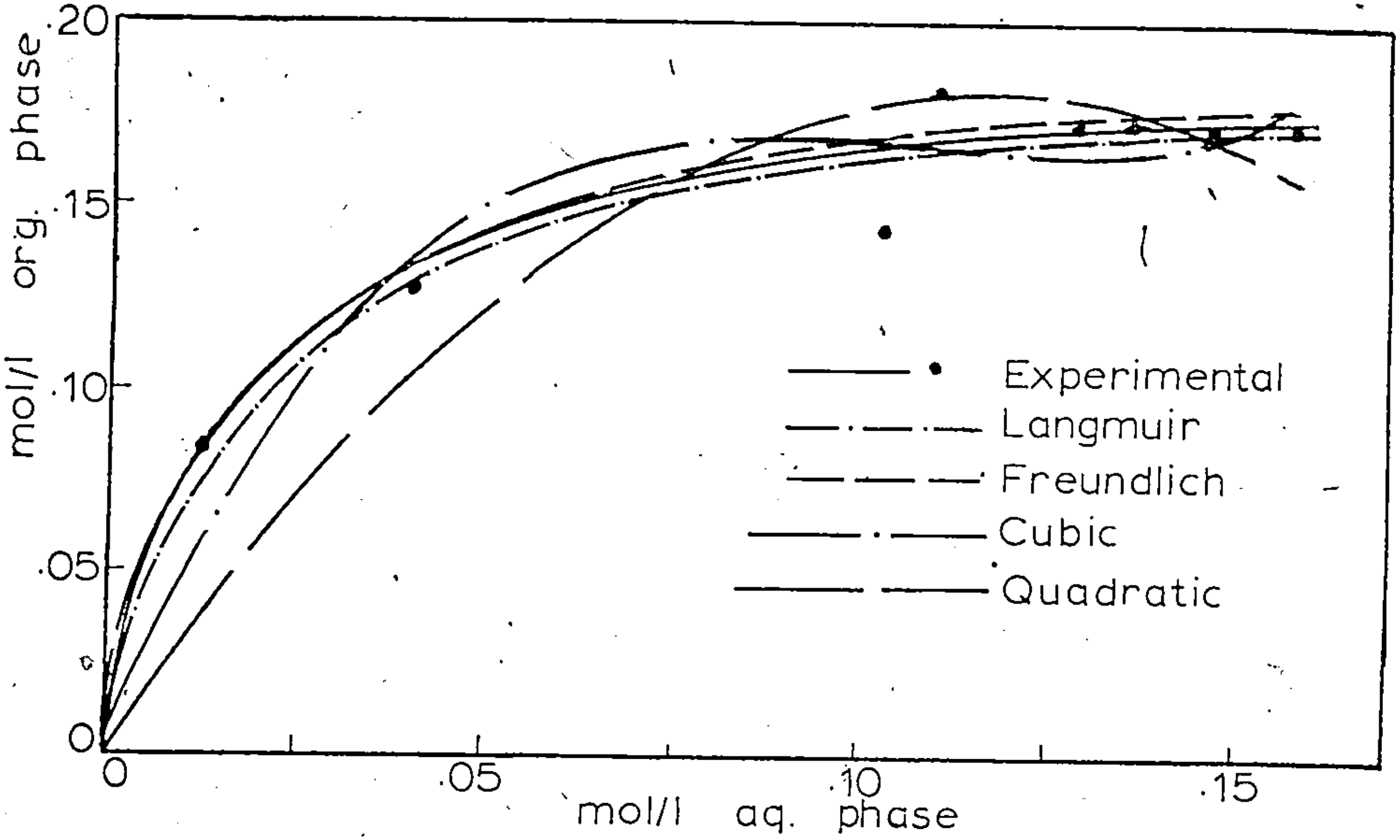


Fig. 16 Comparison of the different models for the system: pure component nickel-20% D2EHPA-20% pre-equilibration of D2EHPA with ammonia

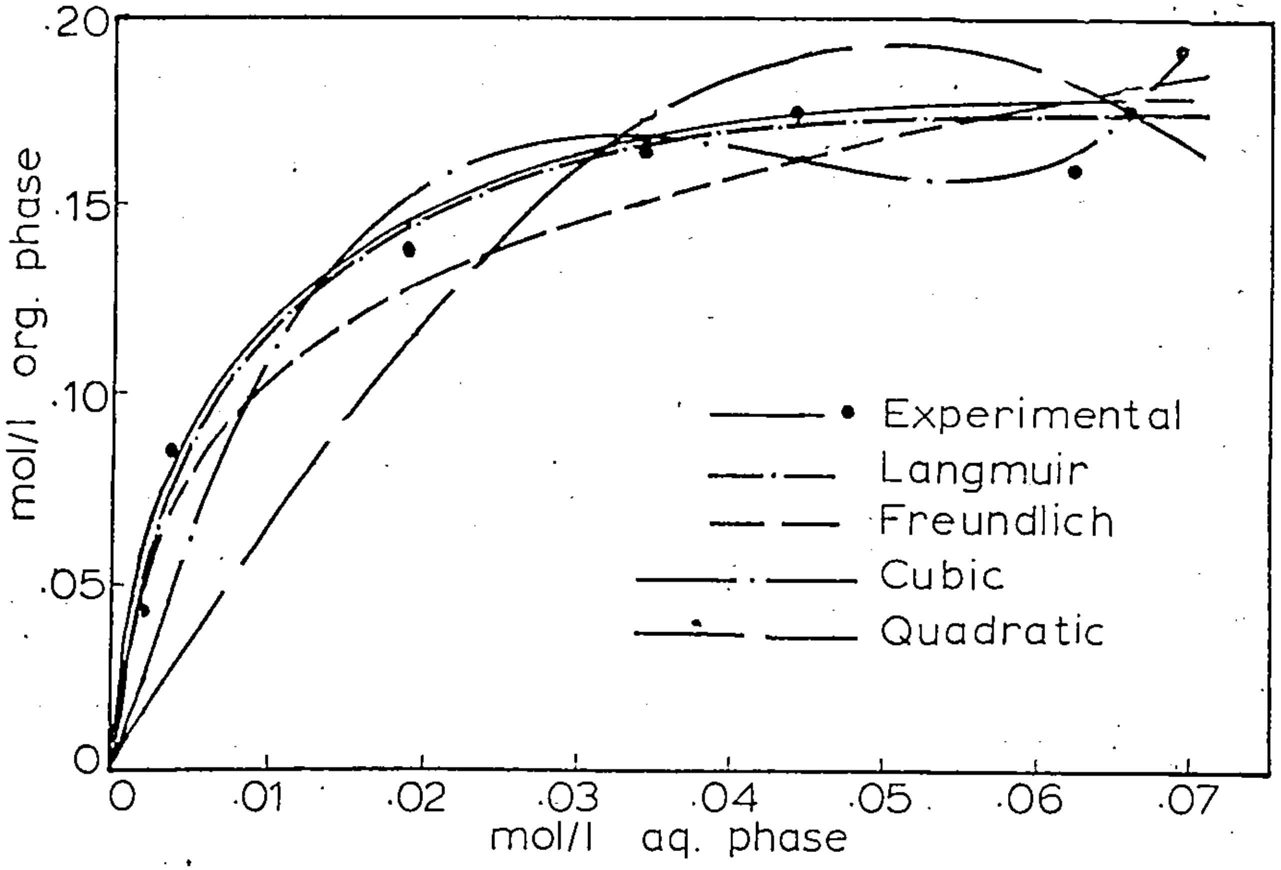


Fig. 17 Comparison of the different isotherm models for the system: cobalt in the mixture of cobalt and nickel-20% D2EHPA-80% pre-equilibration of D2EHPA with ammonia

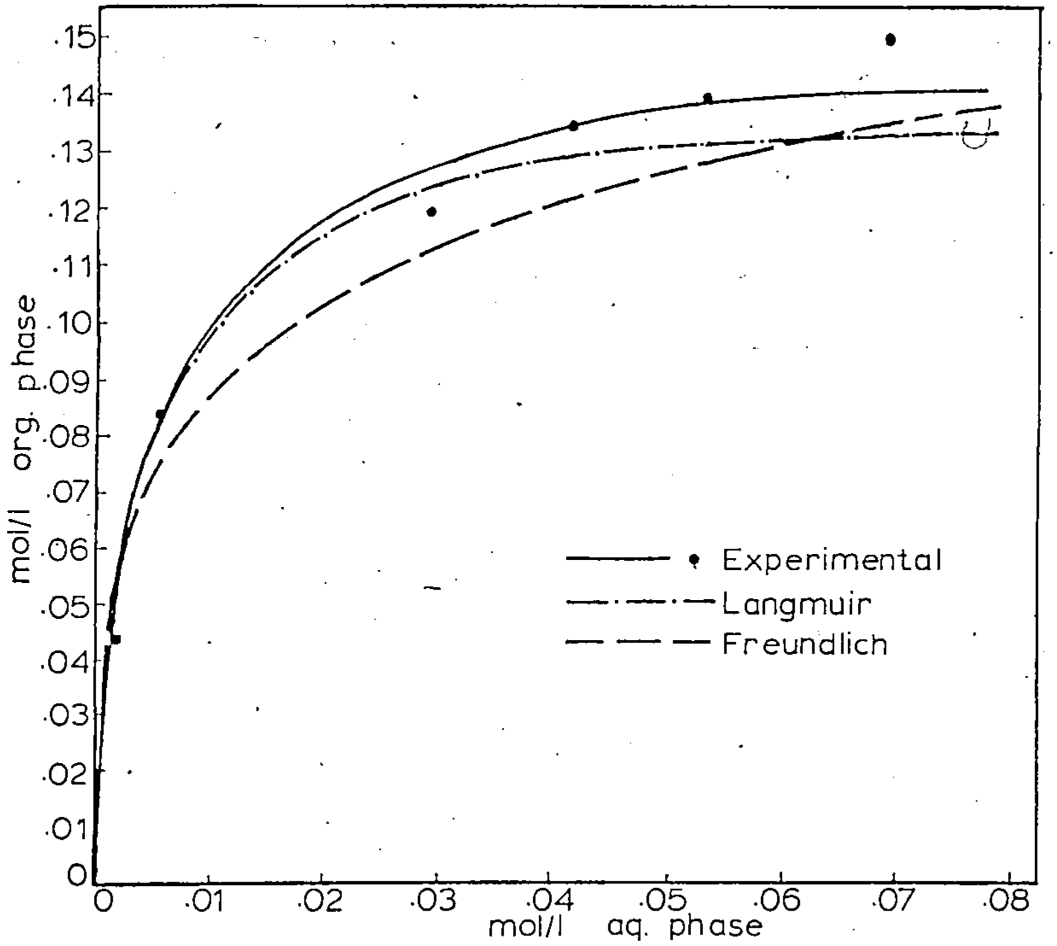


Fig. 18 Comparison of the Freundlich and Langmuir isotherms for the system: cobalt in the mixture of cobalt and nickel-20% D2EHPA-40% pre-equilibration of D2EHPA with ammonia

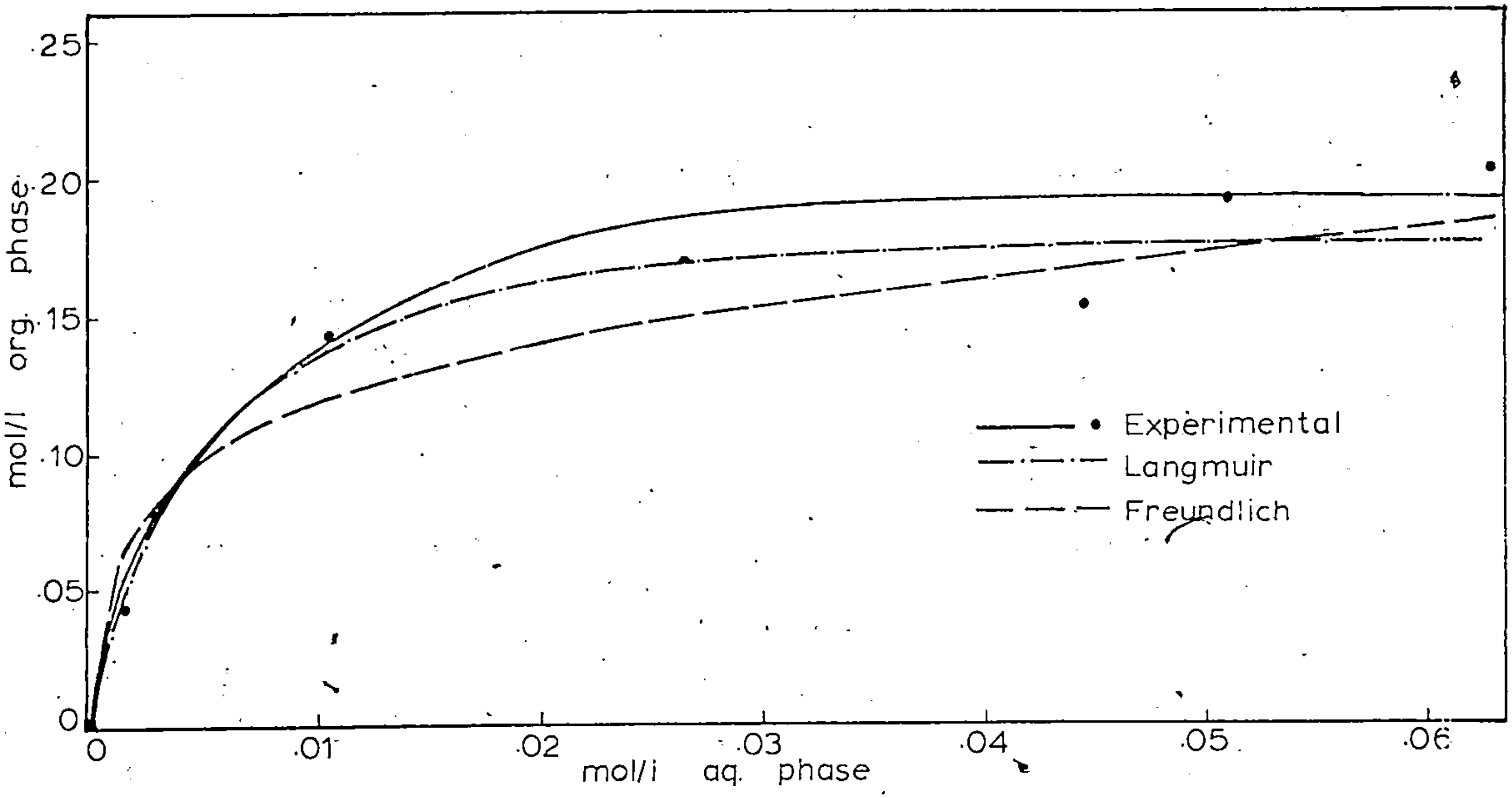


Fig. 19 Comparison of the Freundlich and Langmuir isotherms for the system: cobalt in the mixture of cobalt and nickel-20% D2EHPA-100% pre-equilibration of D2EHPA with ammonia

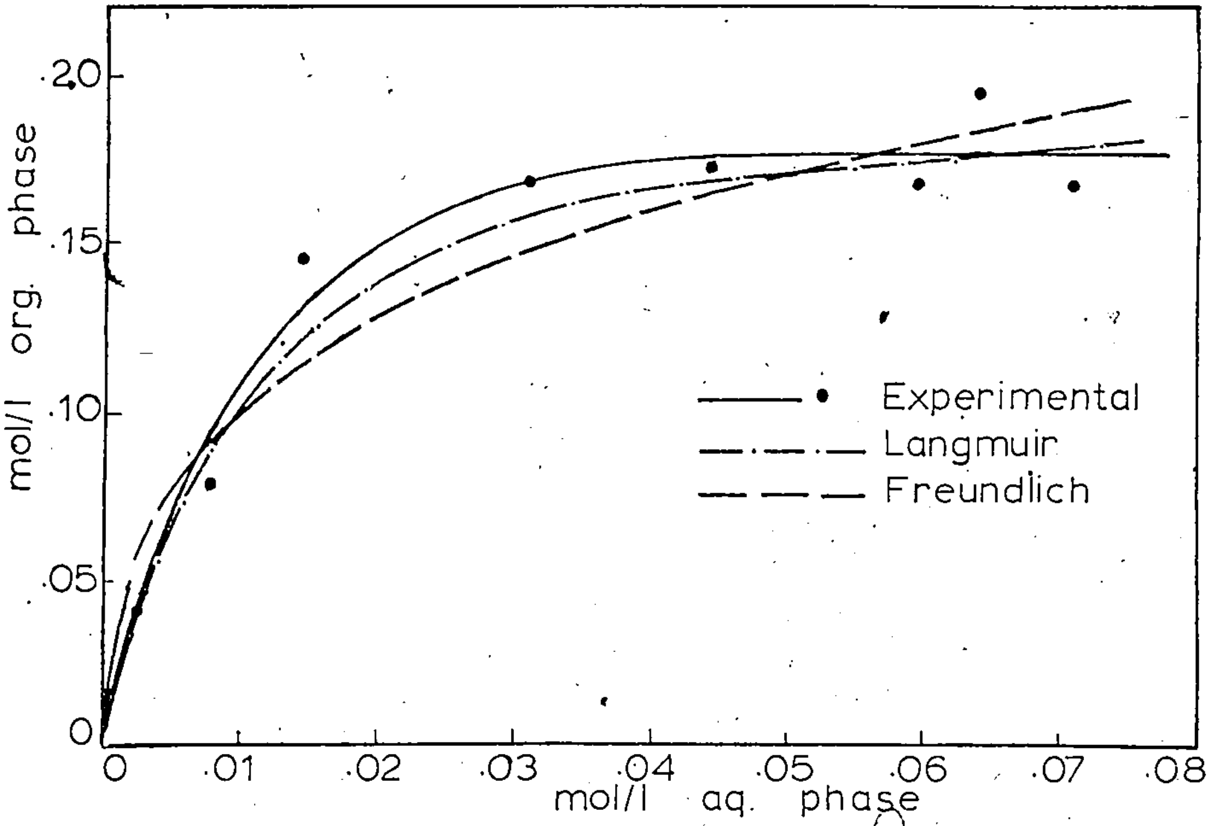


Fig. 20 Comparison of the Freundlich and Langmuir isotherms for the system: nickel the mixture of cobalt and nickel-20% D2EHPA-100% pre-equilibration of D2EHPA with ammonia

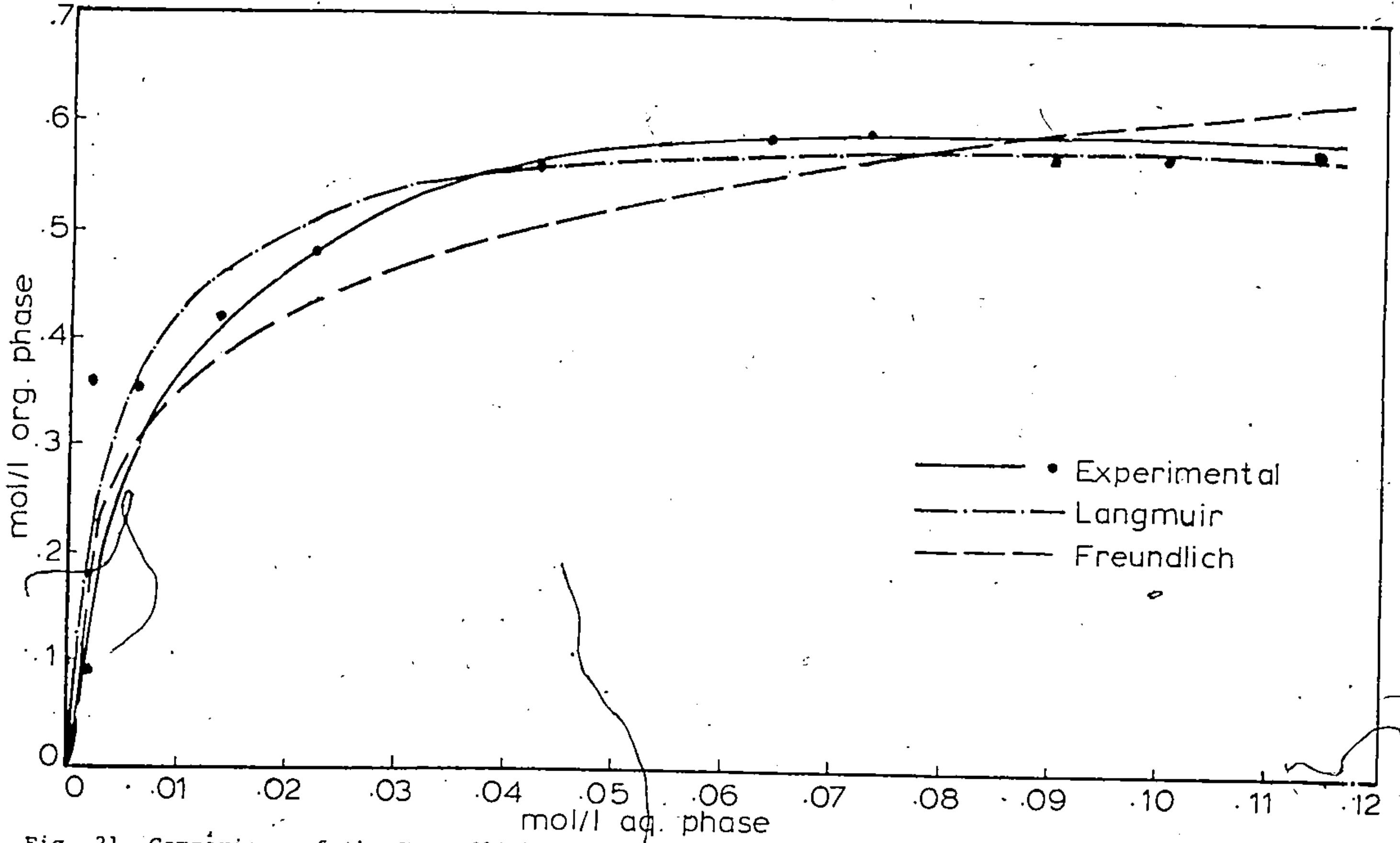


Fig. 21 Comparison of the Freundlich and Langmuir isotherms for the system: pure component cobalt-40% D2EHPA-40% pre-equilibration of D2EHPA with ammonia

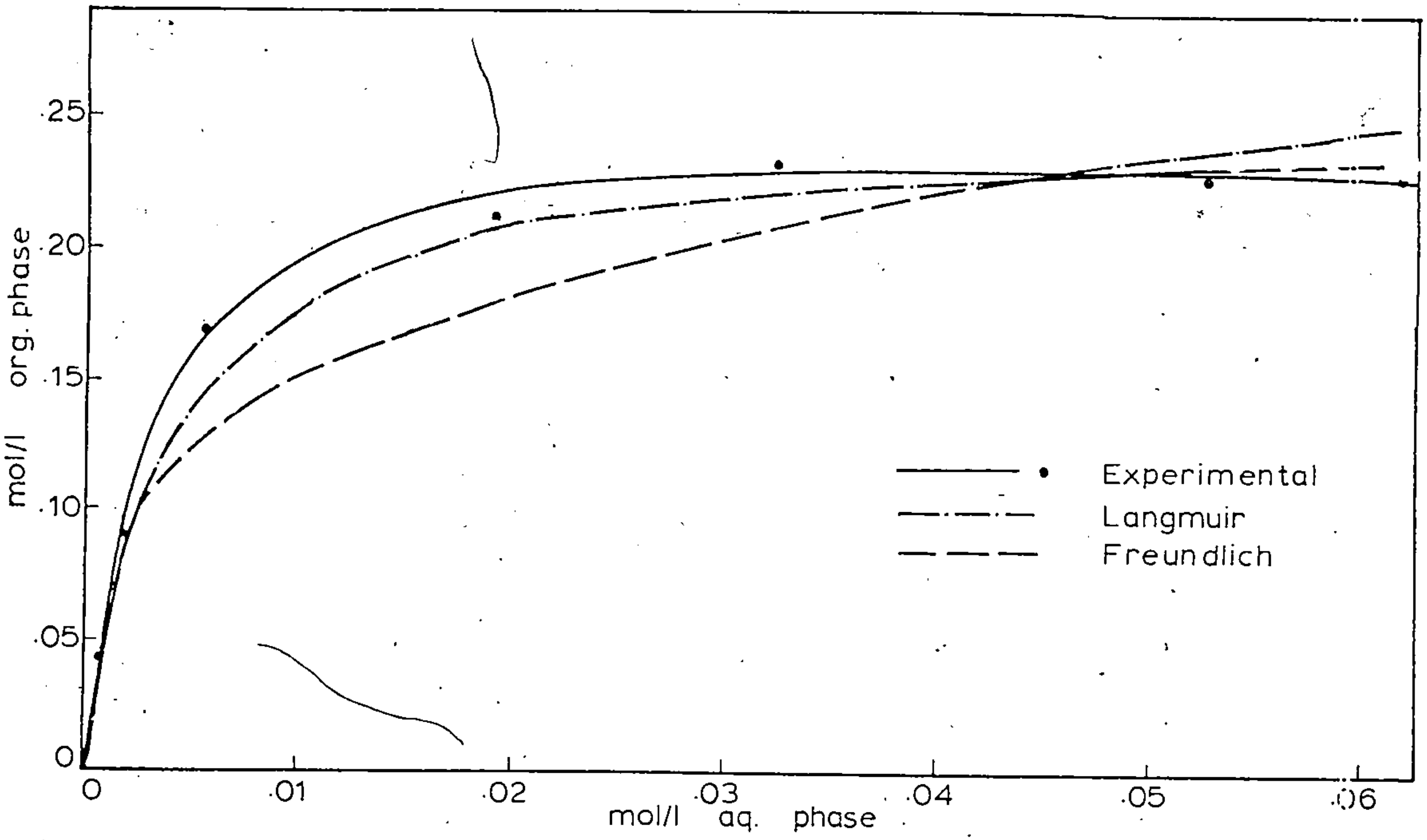


Fig. 22 Comparison of the Freundlich and Langmuir isotherms for the system: nickel in the mixture of cobalt and nickel-40% D2EHPA-40% pre-equilibration of D2EHPA with ammonia .

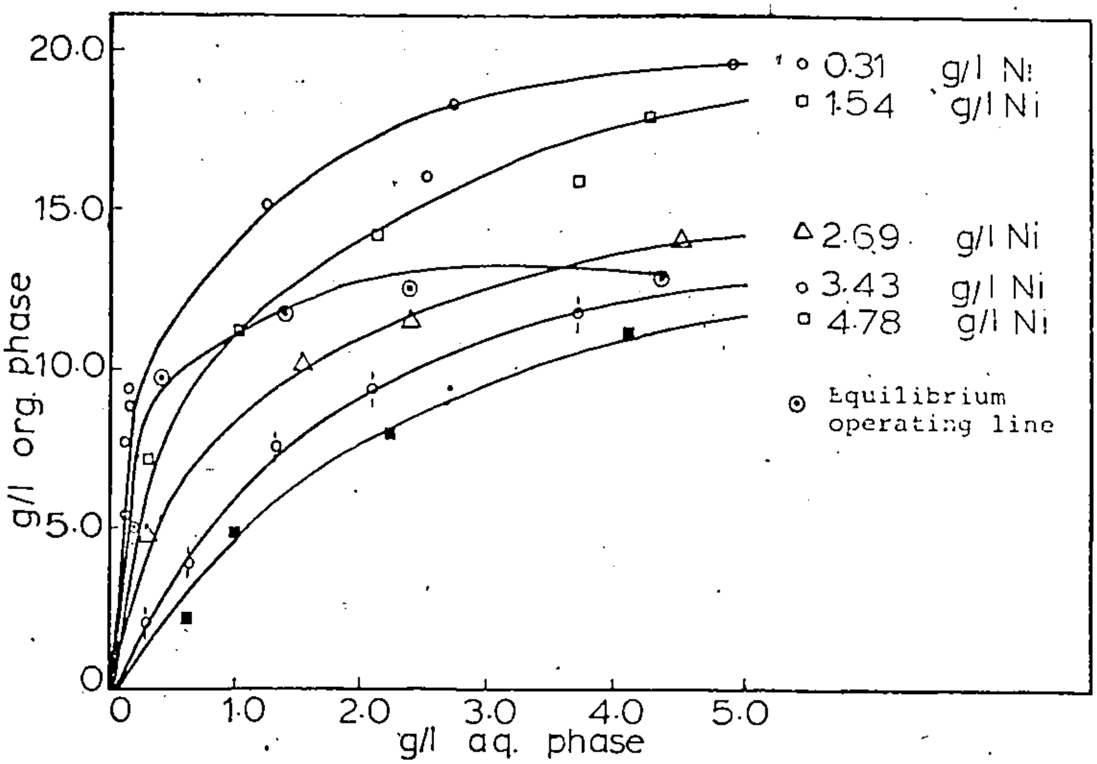


Fig. 23 Effect of the presence of nickel on the extraction of cobalt by 20% D2EHPA (100% pre-equilibrated with NH_3)

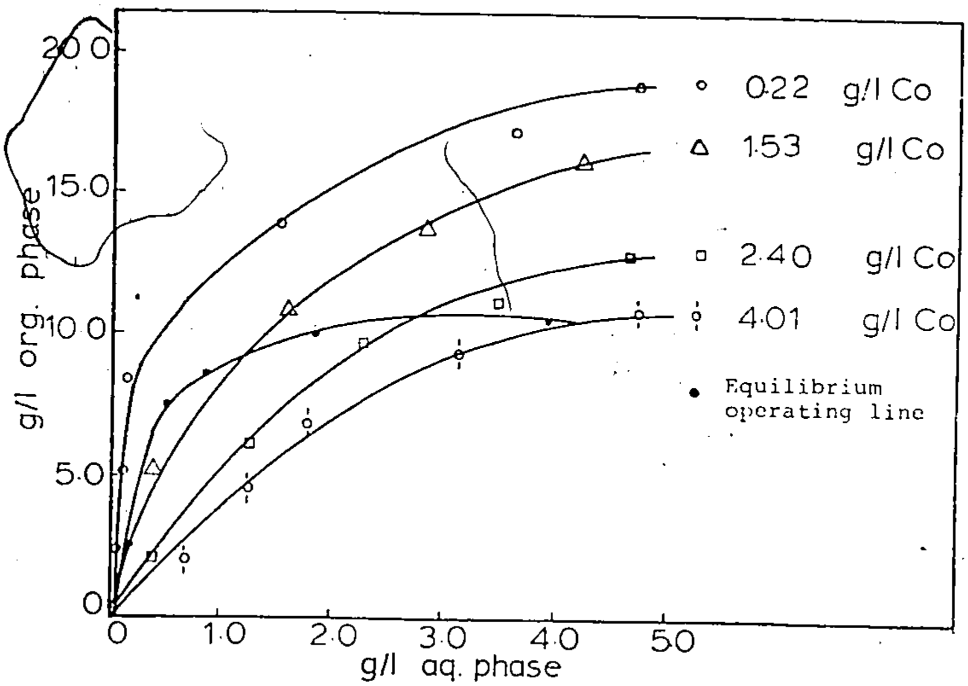


Fig. 24 Effect of presence of cobalt on the extraction of nickel by 20% D2EHPA (100% pre-equilibrated with NH_3)

mixtures. The sample calculations for k are given in the appendix D. Physical properties like viscosity and interfacial tension are determined for a particular system. The data collected on these properties are represented in the tables 19 and 20, with respect to metal loading in the organic phase. The measurements have been made for binary mixtures. Figures 25 and 26 show the increase in interfacial tension with respect to metal loading while figures 27 and 28 show the effect of metal loading in the organic phase on viscosity of the organic phase.

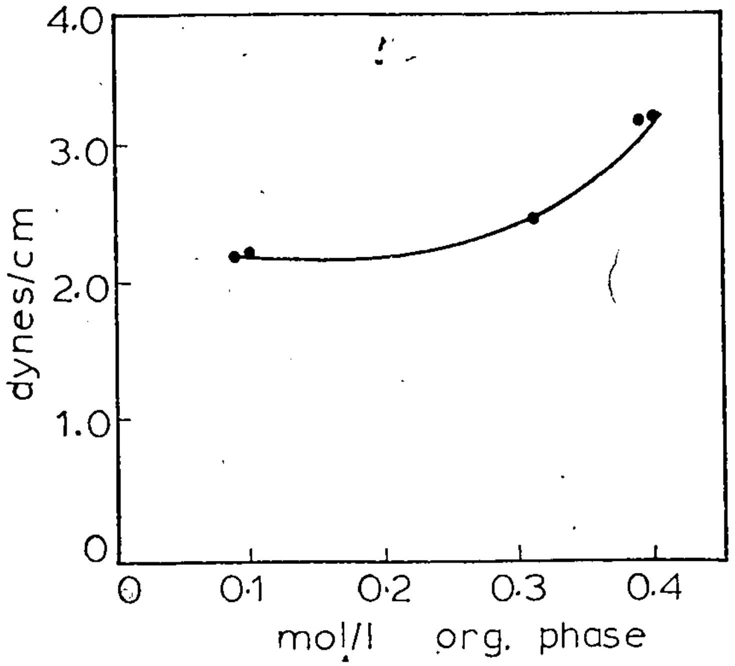


Fig. 25 Interfacial tension versus metal loading in the organic phase

System: 20% D2EHPA-100% pre-equilibration of D2EHPA with ammonia

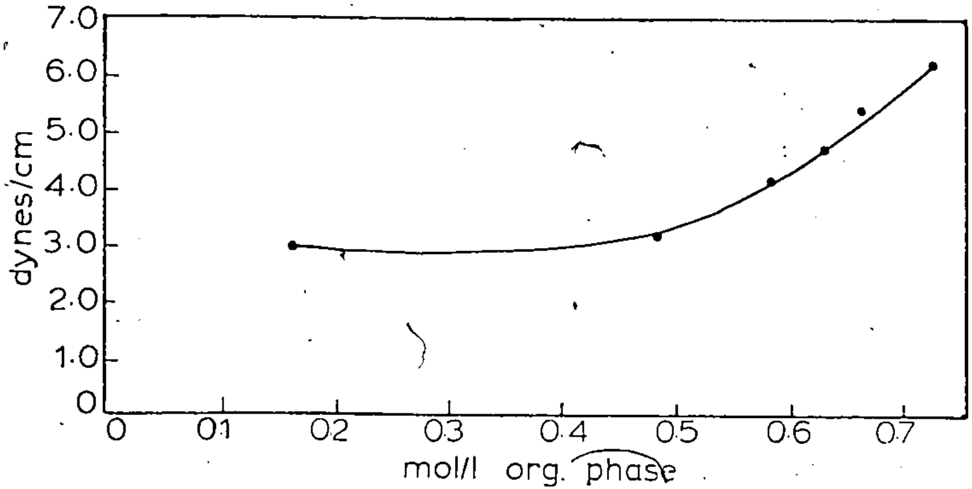


Fig. 26 Interfacial tension versus metal loading in the org. phase
System: 40% D2EHPA-100% pre-equilibration of D2EHPA with ammonia

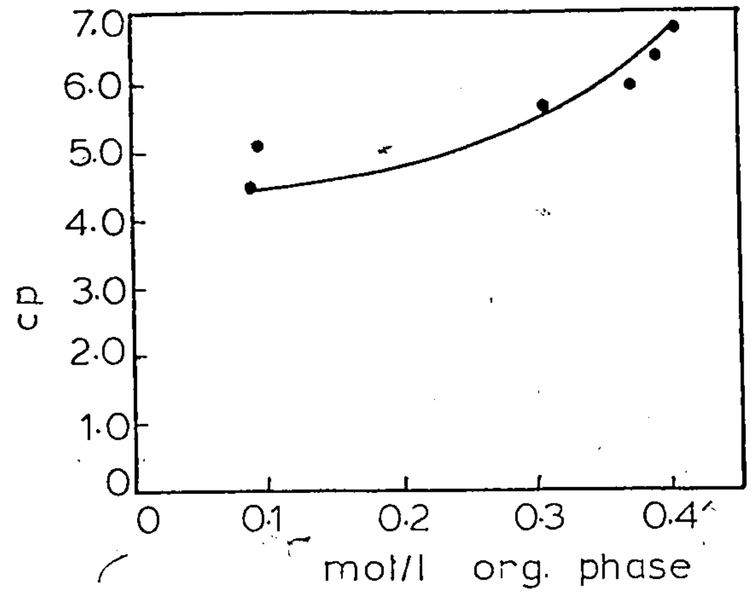


Fig. 27 Viscosity versus metal loading in the organic phase
System: 20% D2EHPA-100% pre-equilibration of D2EHPA with ammonia

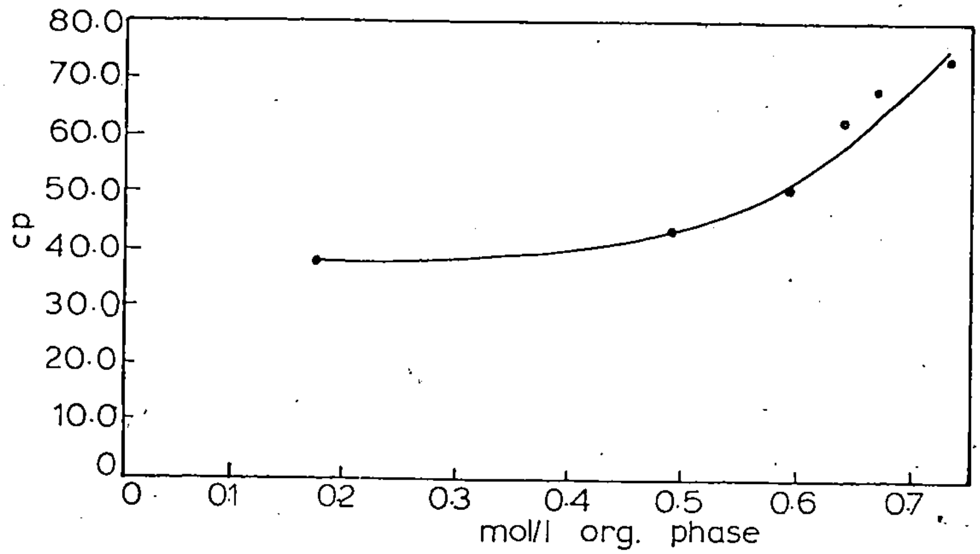


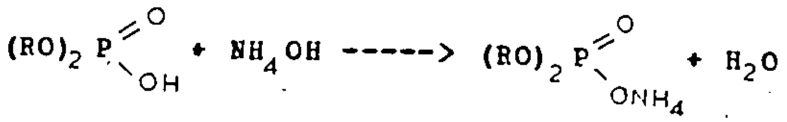
Fig. 28 Viscosity versus metal loading in the organic phase
System: 40% D2EHPA-100% pre-equilibration of D2EHPA with ammonia

Chapter VI

DISCUSSION OF RESULTS

6.1 EQUILIBRATION OF D2EHPA WITH AMMONIA

The equilibrium data for constant D2EHPA concentration have been plotted for the system Co-Ni-D2EHPA in kerosene. Various plots are shown in figures 4 to 13. It is seen from the plots that as the level of saturation of D2EHPA with ammonia was increased, the extraction of the metal became higher and higher. Hence, it was believed from these results that the extracting agent was an alkaline salt of D2EHPA, as discussed in the theory. An alkaline salt of D2EHPA was prepared by adding a concentrated solution of ammonium hydroxide to the mixture of D2EHPA and TBP in diluent kerosene.



$$(RO)_2P(=O)OH + NH_4OH \dashrightarrow (RO)_2P(=O)ONH_4 + H_2O \qquad .....3.1$$

Since, the extraction of metal increased, as the addition of ammonia in D2EHPA was increased, the alkaline salt was supposed to be responsible for the extraction of the metal. Similar trend was observed for the extraction of pure components and binary mixtures.

A family of extraction isotherms for each metal is shown in figures 23 and 24 at various equilibrium aqueous concentration ranges of the other metal. It was clearly seen that presence of one metal inhibited or lowered the extraction of the other metal. On comparing the extraction isotherms for both metals it was seen that cobalt was slightly more favorably extracted than nickel as could be expected from the data in the literature (20).

An operating equilibrium curve was also obtained for different initial concentrations of cobalt and nickel. It represented the equilibrium concentrations of the metal ions in aqueous and organic phases. Such lines are useful in devising counter current extraction systems and in determining the number of theoretical stages required to achieve a desired separation.

6.2 SEPARATION FACTOR

Treatment of data in tables 5,6,9 and 10 according to equation 3.29 provided a value for the separation factor, K_{Ni}^{Co}. Ritcey and Ashbrook (37) and Golding et. al. (20) reported a value of 1.6 and 1.47± 0.427 respectively for the separation factor using the same extractant. The values of the separation factor tabulated in table 18 indicated that cobalt was slightly more favorably extracted than nickel. Golding and Fouda (20) carried out shake-out tests keeping the initial concentration of one metal fixed and using variable initial concentrations of the other metal. The total initial metal ion concentration was kept constant. It appears, according to them (20) that the value of the separation factor was not affected by the metal concentration. A value of 0.56 for the separation factor of cobalt and nickel was reported for various concentrations using fatty acids as extractants (7).

The initial pH of aqueous solution was constant at 4.0 before extraction tests were carried out. The equilibration of the solvent with ammonia maintained the equilibrium pH higher than 4.5. However, in some cases, where D2EHPA was equilibrated with ammonia at 20% of the stoichiometric amount, the pH was lower than 4.5, and hence the extraction of metals was suppressed. Tables 3 to 10 give the value of pH in the equilibrated aqueous phase with respect to metal loading in the organic phase. Higher pH values were observed at low aqueous to organic phase volume ratio or lower pH at higher organic phase metal loading.

6.3 MECHANISM OF EXTRACTION

Sharma and Baird (43) have suggested a mechanism for metal extraction in their study of extraction of copper by D2EHPA. According to them, the process of extraction took place as suggested in equation 3.7. It was assumed that extraction by TBP is negligible, but Golding and Fouda (20) have reported that TBP was also an extractant. While the stoichiometric extraction corresponded to a maximum molar ratio of metal to extractant as 0.5:1, the maximum value observed was higher than that. It also appears to suggest that the extracted species may exist as a bridging ligand. The existence of a polymeric structure for divalent cobalt and nickel complexes with D2EHPA was previously reported by Brisk and McManamey (9, 10). Their proposed mechanism of polymer formation is described by equations 3.16-3.18.

There were several reasons to believe that a polymer has been formed during metal extraction, as discussed below:

1. The loading factor, L, decreased as the volume percentage of D2EHPA increased in the diluent kerosene. This may be explained by equations 3.16 to 3.18, that is, a dimer or higher ordered polymer was formed.

2. The existence of such polymer formation was demonstrated by viscosity measurements in the work by Baes et. al. (1). As the loading in the organic phase increased, the viscosity increased rapidly. If by some means mean value of number of metal atoms in metal-D2EHPA polymer, $\bar{r}$, is measured; then it may be related to the specific viscosity of the organic phase as,

$$\eta = \beta \bar{r}_m^2 \qquad \text{.....3.19}$$

where β is a constant.

3. Further visual qualitative evidence of polymer formation was provided by the appearance of the organic phase near saturation. The cobalt-D2EHPA complexes were blue in color at low to moderate organic phase metal loadings, but as saturation was approached the color deepened to violet. The solutions remained homogeneous with no evidence of the separation of a solid phase even at saturation. However, the addition of small quantities of acetone to the organic phase resulted in the precipitation of a blue solid, insoluble in water but soluble in excess acetone or kerosene. This solid may have been a long-chain polymer of the cobalt-D2EHPA complex, similar in form to the solid D2EHPA-lanthanides observed by Baes et. al. (1). Same type of complexes were also obtained by Brisk and McManamey (10) for extraction of cobalt and nickel by D2EHPA. They also observed the similar qualitative results.

6.4 APPARENT EQUILIBRIUM CONSTANT

The apparent equilibrium constant, k, was calculated using equation 3.15, as suggested by Sharma and Baird (43). The values of k are listed in Tables 17(A) to 17(D). k decreased as the equilibration level of D2EHPA with ammonia increased. The apparent equilibrium constant was calculated with the assumption that the activity coefficients in the equation 3.3 were unity and the change in equilibrium pH was not appreciable. Both the assumptions were not valid and, hence, a decrease in the value of k was observed as the pre-equilibration of D2EHPA with ammonia increased. The equilibrium pH was higher at higher level of equilibration of D2EHPA with ammonia. It is clear from equation 3.3 that the change in pH affects the value of k.

6.5 DATA FITTING

Figures 14 to 22 show various types of isotherms tried to fit the experimental data. The concentrations can be determined either numerically or graphically. In solvent extraction processes, stage concentrations are calculated from equilibrium relationship and conservation of mass expressions. However, these calculations are mainly dependent on two factors (i) the accuracy of the original data, and (ii) the precision with which they can be applied numerically.

It is seen that quadratic and cubic approximations of the curve did not fit the experimental data very well. It seemed that both the isotherms tried to approach the experimental value in an oscillating manner which was not the true representation of the expected behaviour. However, in the case of extraction of copper and chromium investigated by Forrest and Hughes (18) both the polynomials were found to fit the data very well. In fact, in their case the trinomial approximation was found to fit the best. The reason for better fit in their case might be the limited number of data collected from the experiments, so that the oscillations were not seen.

The Freundlich extraction isotherm gave a better fit than the polynomial approximations. However, it was observed from the plots that as the metal concentration in aqueous phase was increased, the organic phase metal loading also increased rapidly. This was also not the true representation of the experimental data as well as the expected behaviour. It is a simple model which can be used to represent the extraction isotherms favoring the metal uptake in organic phase. It was also observed that value of the parameter in the model showed a definite trend for a constant D2EHPA concentration and its various level of equilibrium with ammonia. Tables 13 (A to N) reveals this fact both for pure component as well as binary mixture isotherms.

From the values of the standard deviation calculated for certain systems and represented in Table 21 it was seen that Langmuir extraction isotherm fitted the experimental data better than Freundlich isotherm for pure component as well as binary mixture solvent extraction by 10%, 20% and 40% D2EHPA. Langmuir isotherm was also suitable for metal uptake. It reflected the predicted behaviour of an extraction isotherm. It was also observed that the parameter in the model represented the asymptotic metal concentration in the organic phase; while the parameter represented an equilibrium constant. Looking at the parameter values in tables 14 (A to N) for the Langmuir model, the value of the parameter showed a definite trend with the increase in the level of saturation with ammonia for a fixed D2EHPA concentration.

The models tried in this work offer varying advantages for the systems studied. Langmuir and Freundlich are semi-empirical isotherms and their model form is of mechanistic type. The polynomial forms of the isotherms are empirical models. Hence, while Langmuir and Freundlich isotherms can be used with some confidence for the prediction of the equilibrium data, the polynomial isotherms may be used with a little confidence. The models based on the chemistry of the system are highly specific in that a prior knowledge of the chemical reactions is required. The chemical approach becomes more sophisticated when activities are used instead of concentrations, but this knowledge requires a great deal of experimental effort and is perhaps not worthwhile when other simpler models can give just as good a fit. 't' and 'F' tests were applied to the polynomial isotherms to check up the form of the model, while the plots of residuals were examined for Freundlich and Langmuir isotherms to see the adequacy of the models. Both 't' and 'F' tests were found satisfactory and there was no definite trend observed in the plots of residuals.

6.6 PREDICTION OF BINARY EQUILIBRIA

Pure component and binary extraction equilibrium data have been used to find a method to predict the binary extraction equilibrium data from pure component isotherms. The detailed procedure is given in chapter 3. Some examples have been demonstrated in appendix F. Smutz et. al. (44) have tried the same method successfully for the extraction of lanthanides by D2EHPA. All the correlations used in this method were empirical and were not necessarily based on any physical or chemical basis. It was observed that the method was very simple in application and predicted the binary equilibrium data within 10% error. The pH has been correlated to metal ion concentration in the aqueous phase at equilibrium by simple polynomials. It would have been possible to correlate it or predict it by using a chemical method or extraction equation, had the correct extraction mechanism been known. Since the correlations used were mainly empirical, an interpolation can be done with some confidence but its application for extrapolation is very limited.

6.7 PHYSICAL PROPERTIES

Physical properties like interfacial tension and viscosity (of organic phase) displayed definite trend with respect to metal loading in the organic phase. It was reported by Sharma and Baird (43) and was also observed in the present work that the ammoniated D2EHPA had a low interfacial tension with respect to water. Sharma and Baird (43) also observed rapid break up of the organic phase when it entered the reciprocating plate extraction column, in the extraction of copper. Loading of the organic phase with metal, cobalt or nickel or both, appeared to increase the interfacial tension. This fact was revealed by the data on interfacial tension listed with respect to metal loading in organic phase in Table 20. Figures 25 and 26 show the increase in interfacial tension with the increase in the metal loading in the organic phase. The change in interfacial tension with respect to metal loading is an important factor, particularly when the extraction is carried out in a plate column. It helps in deciding the plate spacing at the entrance of extractant and at the exit. If proper spacing between the two plates is not provided at the entrance (of extractant) of the column, it might result in the flooding due to low interfacial tension between the unloaded organic phase and the aqueous phase. Near the exit (of organic phase) of the column, the organic phase is loaded with the metal and has a higher interfacial tension with the aqueous phase, so the close spacing of the plates may be kept. In this way, a more uniform dropsize throught the column could be obtained with higher throughputs before flooding occurred.

It was also observed from the data obtained for viscosity of the organic phase that the viscosity increased with respect to increase in metal loading in the organic phase (Ref. Table 19). Figures 27 and 28 reveal the fact that viscosity increased with the metal loading. This was quite consistent with the result obtained by Brisk and McMamey (10) for the extraction of cobalt by D2EHPA. A polymer reaction was believed to take place during metal extraction by which a polymeric complex of extracted metal and D2EHPA was formed. However, the degree of polymerisation was not known hence, a chemical reaction system suggesting exact mechanism of extraction could not be predicted.

Chapter VII

CONCLUSIONS

The following conclusions can be drawn from the results obtained in this study.

Di-(2-ethyl hexyl)-phosphoric acid extracted cobalt and nickel from an aqueous acidic solution of cobalt and nickel sulfates over a range of pH of 4.0 to 9.0. Comparing extraction isotherms for one metal in the presence of an another metal, it was observed that the presence of the other metal affected the extraction of the first metal. There existed two competitive extraction equilibria, the capacity of the organic phase being constant.

The pH was a significant factor in the metal extraction. It was seen that for a particular system, the equilibrium pH decreased as the metal uptake in the organic phase increased. Hence, in order to enable the extraction of metal in the organic phase, the D2EHPA solution must be pre-equilibrated with ammonia. The metal loading in the organic phase increased with an increase in the pre-equilibration level of D2EHPA with ammonia. Therefore, an alkaline salt of D2EHPA was responsible for the metal uptake in the organic phase.

The apparent equilibrium constant, k, as defined by Sharma and Baird (43) was a function of the equilibrium pH. The apparent equilibrium constant decreased as the equilibrium pH was increased, i.e. it decreased with the increase in the pre-equilibration level of D2EHPA with ammonia. At constant pH, k increased as the metal uptake in the organic phase was increased.

The separation factor for cobalt-nickel pair for the system cobalt-nickel-D2EHPA was found to vary with the concentration of D2EHPA. The separation factor decreased with an increase in the concentration of D2EHPA. A higher separation factor was expected in the lower pH range but a considerable scatter was observed. It was concluded by observing the values for the separation factor obtained in this study (1.72 and 1.402 for the extraction by 20% and 40% D2EHPA respectively) and also reported by Golding et. al. (20), that cobalt was more favorably extracted compared to nickel by D2EHPA.

Equilibrium data were fitted using four different numerical approximations: (i) Quadratic (ii) Cubic (iii) Freundlich and (iv) Langmuir isotherms. The best fits were the Freundlich and Langmuir isotherms, but the Langmuir isotherm gave a superior fit to the Freundlich isotherm. This was due to the violation of two basic assumptions in the Freundlich isotherm: (i) low solute concentrations and

(ii) small range of concentration of the solute in the organic phase. It can be concluded that the assumtion of an analogy between the Langmuir adsorption and extraction isotherms was fairly correct. The average standard deviation observed for the Langmuir isotherm was 1.36%. The parameter in the Langmuir isotherm gave an asymptotic equilibrium concentration of the metal in the organic phase.

Pure component data were successfully used to predict the binary extraction equilibria following the method suggested by Smutz et. al. (44). The deviation term, y, was found to be a function of metal ion concentrations at equilibrium and the equilibrium pH. The method predicted the binary equilibria with an average error of 8% and the maximum error of 10%.

It was observed that metal loading in the organic phase had an appreciable effect on the physical properties like interfacial tension and viscosity. For 20% D2EHPA the interfacial tension was found to vary from 0.5 to 3.5 dynes/cm, while for 40% D2EHPA it varied from 0.75 to 7.0 dynes/cm. The variation of the viscosity of the organic phase was from 2.2 to 6.92 cp for 20% D2EHPA, while for 40% D2EHPA it varied from 6.94 to 78.19 cp. An increase in both the properties was observed as the metal loading in the organic phase increased. An increase in the viscosity would be expected to reduce the mass transfer rates significantly due to reduced diffusion in the organic phase. In addition the change in interfacial tension could be expected to affect the drop coalescence and flooding characteristics in the pulsed sieve plate extraction columns.

Chapter VIII

RECOMMENDATIONS

The following recommendations are made with regard to pursuance of this study:

1. Experiments should be carried out for the extraction of cobalt and nickel using higher concentrations of D2EHPA. This will permit the correlation of equilibrium data for a particular level of equilibration of D2EHPA with ammonia. It will also help in estimating the equilibrium data using any percentage of D2EHPA in kerosene.

2. The structure of the extracted species is not clear. As observed by Brisk and McManamey (9, 10) and also in this study, a polymer formation is suspected during the extraction. Other methods like infrared spectrometry and molecular weight measurements could be used to indentify the extracted species and to study the extent of polymerisation. This will help

   a) to find out degree of polymerisation and the polymeric species.

b) to correlate physical properties like interfacial tension and viscosity with degree of polymerisation and metal loading in organic phase.

c) in applying rigorous chemical method to correlate the equilibrium data.

Chapter IX

NOMENCLATURE

a = Parameter in the polynomial isotherms

C = Concentration mol/l

D = symbol for difference

$\overline{EH}$ = Di-2-Ethyl-Hexyl-Phosphoric acid

$\overline{E_2Co}$ = complex of cobalt and D2EHPA

$\overline{ENH_4}$ = ammoniated D2EHPA

H^+ = hydrogen ion

k = apparent equilibrium constant

k_H = equilibrium constant in equation 3.4

k_N = equilibrium constant in equation 3.6

K^{Co}_{Ni} = separation factor for cobalt-nickel pair

L = ratio of metal concentration in the organic phase to initial concentration of D2EHPA

M = metal

R = alkyl group of D2EHPA

r = number of metal atoms in metal-D2EHPA polymer

V_A = volume of aqueous phase

V_O = volume of organic phase

x = concentration of metal in aqueous phase at equilibrium mol/l

x_1 = mole fraction of cobalt in aqueous phase at equilibrium

$\bar{x}$ = mole fraction of metals in aqueous phase at equilibrium

X = alkylphosphate radical

y = concentration of metal in organic phase at equilibrium mol/l

Subscripts

A = aqueous phase

AN = ammonia in aqueous phase

A_1 = metal in aqueous phase prior to shake-up equilibration

E = extractant in organic phase

H = for hydrogen ion

o = organic phase

ON = ammonia in organic phase

ON_1 = ammonia in organic phase prior to shake-up equilibration

T = total

w = aqueous phase

Superscripts

* = equilibrium for organic phase with respect to a pure component in aqueous phase

η = viscosity

β = constant

θ = parameter

Appendix A

ANALYSIS BY ATOMIC ABSORPTION SPECTROPHOTOMETER

Analysis of the experimental samples for metal content were done by Fisher's "Jarrel-Ash Dial-Atom III" Atomic Absorption Spectrophotometer.

The Dial-Atom III Atomic Absorption Spectrophotometer is designed for measuring metal content in either aqueous or organic solution by atomic absorption/flame emission techniques. The instrument consists of a hollow cathode as a light source, a flame as an absorption cell, a monochromator as a resonant wavelength isolator and a photomultiplier as a detector. The hollow cathode emits a spectrum of the element of interest. This light is passed through a high temperature flame and into a monochromator. The monochromator isolates the particular analytical line of the hollow cathode spectrum. The intensity of this line is measured at the exit slit of the monochromator by a detector.

The optimum operating current, slit-size, gases used for the flame and optimum range of concentration for analysis are tabulated in the instrument manual no. 82-760-D-1 (4-76). The solutions are prepared by dilution with distilled water so that the metal concentration analysis may be done within the optimum range specified.

When a solution containing the element to be analysed for is aspirated into the flame, ground state atoms of the element are produced. These are capable of absorbing light at the selected analytical wavelength. The decrease in intensity of the analytical line produced by the sample as compared to absorption produced by that of a standard gives a measure of concentration of the element of interest in the sample. The basic measurement is that of the transmittance of light through a sample. The electronic photometer system converts the transmittance measurement to absorbance or concentration units for direct read-out on the instrument's digital display.

There are three modes of operation, (i) Absorbance (ii) Emission and (iii) Concentration. Normally analysis is done in absorption mode. A standard plot of absorbance versus concentration is prepared for each element (metal) analysed. The experimental samples are then analysed for the absorbance and the metal concentration of each sample is determined from the calibration plot. The optimum settings for cobalt and Nickel are:

element	current (mA)	slit size μ	optimum range (ppm)	gases
cobalt	12	50	1 - 10	air-actl.
nickel	8	50	2 - 12	air-actl.

Appendix B

DETERMINATION OF PHYSICAL PROPERTIES

B.1 MEASUREMENT OF INTERFACIAL TENSION

Interfacial tension was measured with Fisher's 'Autotensiomet'. It uses a silicon strain gage to measure surface and interfacial tensions. The gage is a strain-sensitive wire fixed at one end to the balance beam and at the other to a transducer. When the measurement is done, the transducer provides a force-summing displacement signal that is proportional to the force or weight measured. There is a simple linear relationship between measured force and surface tension/interfacial tension.

A standard routine (as mentioned in the manual for Autotensiomet) for cleaning up the glass ware, platimum ring and interfacial tension measurement was followed. The interfacial tension was measured with the help of a chart-recorder.

B.2 MEASUREMENT OF VISCOSITY

Viscosity of selected samples was determined with the help of the Brookfield U.L. Adapter Viscometer. The measurement of low viscosity materials with extreme precision and accuracy may readily be made with Brookfield viscometer. The range of this viscometer is 0-200 cp, depending upon the selected speed of the viscometer cylinder. The equipment is suitable for both newtonian and non-newtonian fluids.

The instrument consists of a precision cylindrical spindle rotating inside an accurately machined tube. Alignment of these parts is accomplished by a special pivot housing and adapter body. A tube holding 20 cc. of the sample is slipped over the cylinder. The tube can be immersed in a temperature bath.

Appendix C

EXTRACTANTS AND MODIFIERS

Normally a metal ion exists in aqueous solution as a hydrated ion, with little or no tendency to transfer to an organic phase. Thus in order to achieve the required transfer the metal ion has to be modified. To convert a metal ion to an extractable species its charge requires neutralisation and some or all its water of hydration has to be replaced by some other molecules or ions. These requirements can be met by complexing the ion with an ion of opposite charge to form a neutral species, which at the same time replaces some or all of the water of hydration around the metal ion; by formation of ion-association complexes which also provide for the formation of a neutral species with the extractant; and by replacing the water of hydration with molecules of a solvent.

The nature of extractable metal species is therefore important in metal extraction systems. Accordingly, the systems are classified as

1. those which involve compound formation

2. those which involve ion association and

3. those which involve solvation of metal ion.

Some extractant may belong to more than one class depending on the experimental conditions.

C.1 EXTRACTANT CLASSIFICATION

There are mainly four classification for extractants: acidic, basic, neutral and chelating. The acidic and basic are also referred to as cationic and anionic extractants respectively.

C.2 ACIDIC EXTRACTANTS

The extractants, which are used considering cost and insolubility in water, are alkylphosphoric, sulphonic and aliphatic monocarboxylic acids.

D2EHPA is perhaps the most popular among the acidic extractants. The effect on extraction of metals using D2EHPA is expected to increase in the order $ClO_4^- < NO_3^- < Cl^- < CO_3^{--} < SO_4^{--}$. This is also similar for carboxylic acids. The other acidic extractants are aliphatic carboxylic acids. Their use is mainly in alkaline solutions. These extractants operate by a cation-exchange mechanism. Maximum extraction occurs just below the pH at which hydrolysis occurs, and therefore their use is highly pH-dependent.

C.3 BASIC EXTRACTANTS

These are mainly amine or anion-exchange extractants.

C.4 NEUTRAL EXTRACTANTS

The neutral extractants are best exemplified by TBP. It has mostly been used on the nuclear field. TBP can be used at 100% concentration, as well as at lower concentrations in a diluent.

C.5 CHELATING EXTRACTANTS

The commercial chelating extractants used are LIX 64, LIX 64N, KELEX 100 and LIX 63. Organic chelating extractants are those which contain donor groups capable of forming chelates with metal ions. They have been used successfully in the extraction of copper from acidic solutions as well as alkaline solutions.

For commercial operation of a solvent extraction process, the following criteria should be met in regards to reagent choice:

1. reagent availability and cost
2. high solubility in the organic diluent and low solubility in the aqueous phase

3. ease of formation of complex with metal and high solubility of the metal complex in the organic phase

4. ease of recovery of metal from the organic phase and regeneration of extractant for recycling.

C.6 DILUENTS

The diluent, or carrier solvent, is mainly required as a diluting medium to lower the viscosity of the organic phase and facilitate contact between the two phases. The additional important carrier properties are:

1. the ability to retain in solution both the complexed and uncomplexed extractant.

2. a low solubility in the aqueous phase

3. a high flash point and a consistent low rate of evaporation

4. high chemical stability over the range of conditions for plant operation.

The third point is important in plants erected in countries having high ambient temperatures, or where it is proposed to run the solvent extraction process at a high temperature. Although generally it is assumed that the diluent is inert and does not enter into the mechanism of extraction, certain diluents can assist and enhance the extraction.

C.7 MODIFIERS

Additional chemicals called modifiers are sometimes added to solvents to prevent third phase formation. The modifiers must also be inert to the system, soluble in the diluent, and insoluble in the aqueous phase. The main function of the modifier is to ensure that intermediates in the extraction reaction remain soluble in the diluent and do not cause a third phase or emulsion formation. Modifiers that have been most commonly used include TBP and alcohols such as 2-ethyl hexanol and isodecanol. Experience shows that (2) the alcohols have the disadvantage of being appreciably soluble in the aqueous phase and may contribute a severe environmental problem.

Bouboulis (8) has shown experimentally that when TBP is used as a modifier with D2EHPA extractant, a highly aromatic diluent such as Aromatic 150 or 180 (SOLVESSO 150 or 180) is preferred, otherwise the percentage extraction of cobalt/nickel is affected.

Appendix D

SAMPLE CALCULATIONS

D.1 SAMPLE CALCULATIONS FOR MATERIAL BALANCE

(i) system: pure component cobalt-20% D2EHPA-5% TBT and 80% equilibration with NH_3 .

data no. 6 of Table 3(D).

V_A/V_O = aqueous to organic volume ratio = 6

initial concentration of Co in aqueous phase

$= C_{aq.\,initial} = 10.4 \text{ g/l} = 0.1765 \text{ mol/l}$

after shake-out test,

equilibrium concentration of Co in aqueous phase

$= C_{aq.\,eq.} = 6.7 \text{ g/l} = 0.1137 \text{ mol/l}$

using material balance equation

$$C_{org.} = \frac{V_A}{V_O}\left(C_{aq.\,initial} - C_{aq.\,eq.}\right)$$

$$= 6(10.4 - 6.7) = 22.2 \text{ g/l}$$

$$= 0.3767 \text{ mol/l}$$

$$(x,y) = (0.1137.0.3767)$$

(ii) system: pure component nickel-40% D2EHPA-5% TBP ,

40% equilibration with NH_3

Ref: Table no. 8(B)

data no. 3

V_A/V_O = aqueous to oranic phase volume ratio = 1.5

initial concentration of Ni in aqueous phase

$= C_{aq._{initial}} = 9.6$ g/l = 0.1635 mol/l

after shake-out test,

equilibrium concentration of Ni in aqueous phase = 0.00426 mol/l

$$C_{org.} = (C_{aq._{initial}} - C_{aq._{eq.}})$$

$$= 1.5(0.1635 - 0.00043)$$

$$= 0.2446 \text{ mol/l}$$

$(x, y) = (0.00043, 0.2446)$

D.2 SAMPLE CALCULATIONS FOR APPARENT EQUILIBRIUM CONSTANT K

The apparent equilibrium constant k is defined by the equation 3.15,

$$(V_O/V_A)\ (C_O/C_A)^{1/2} = (k)^{\frac{1}{2}}\left[\frac{C_{ON_1}}{2C_O} - 1\right]$$

V_O/V_A = organic to aqueous phase volume ratio

C_O = concentration of the metal in the organic phase at equilibrium

C_A = concentration of the metal in the aqueous phase at equilibrium

C_{ON_1} = initial concentration of ammonia in the organic phase extractant mixture.

(i) system: pure component Co-40% D2EHPA-5% TBP

110% saturation with NH_3

Ref: Table no. 7(F)

No.	$(V_O/V_A)(C_O/C_A)^{1/2}$	$C_{ON_1}/2C_O$
1	14.5602	8.1833
2	10.2960	4.0917
3	11.9260	2.7127
4	5.1235	2.0671
5	3.7303	1.6693
6	2.1823	1.4467
7	1.0624	1.2378
8	0.7000	1.1419
9	0.5340	1.0717
10	0.4154	1.0587
11	0.3604	0.9953
12	0.2746	0.9442
mean	4.2838	2.2184

correlation = 0.88

k = 0.2143

(ii) system: mixture of cobalt and nickel.

Ni-20% D2EHPA-5% TBP-40% equilibration with NH

Ref. Table no. 6(B)

No.	$(V_O/V_A)(C_O/C_A)^{1/2}$	$C_{ON_1}/2C_O$
1	10.020	3.150
2	3.690	1.660
3	0.800	1.380
4	0.460	1.330
5	0.303	1.440

6	0.203	1.300
7	0.144	1.363
8	0.101	1.660
mean	1.965	1.660

correlation = 0.958

k = 28.87

Appendix E

LEAST SQUARE ESTIMATION FOR A SINGLE RESPONSE

The least square estimates of the parameter θ in the model $\eta = f(\xi, \theta)$, fitted to the data (x, y) are those values of θ for which

$$S(\theta) = \Sigma(y_i - f(x_i - \theta))^2$$

is minimised.

Gauss-Newton method of fitting non-linear model.

It is also known as linearisation method. Let the general non-linear model be,

$$y_i = f(x_i, \theta) + \varepsilon_i \qquad i = 1, n$$

where x_i are independent variables

y_i are dependent variables

θ is a parameter vector

n is number of data points

let initial estimates (guesses) of the parameters be,

$$\underline{\theta}_0 = (\theta_{10}, \theta_{20}, \qquad \theta_{p0})^T$$

p is number of parameters

expanding $f(x_i, \theta)$ in a Taylor series, about θ_0 and neglecting 2nd and higher order terms,

$$f(x_i, \theta) = f(x_i, \theta_0) + \sum_{j=1}^{p} (\theta_j - \theta_{j0}) \times \left\{ \frac{\partial f(x_i, \theta)}{\partial \theta_j} \right\}_{\theta = \theta_0}$$

$$\therefore \quad y_i = f(x_i, \theta_0) + \sum_{j=1}^{p} (\theta_j - \theta_{j0}) \times \left\{ \frac{\partial f(x_i, \theta)}{\partial \theta_j} \right\}_{\theta = \theta_0} + \varepsilon_i$$

which is a linear model of the form

$$Z_i = \sum_{j=1}^{p} \beta_{j0} X_{j0} + \varepsilon_i$$

where $$Z_i = y_i - f(x_i, \theta_0)$$

$$\beta_{j0} = \theta_j - \theta_{j0}$$

$$X_{j0} = \left\{\frac{\partial f(x_i,\theta)}{\partial \theta_j}\right\}_{\theta = \theta_0}$$

Least square estimates of the β's can be obtained by linear least square method and thus provides estimate of the $\theta_j - \theta_{jo}$.

Thus, given data (x_i, y_i), $i=1,n$

$$Z = \underline{X}_0 \underline{\beta}_0 + \underline{e}$$

where

$$\underline{Z} = \begin{bmatrix} y_1 - f(x_1,\theta_1) \\ y_2 - f(x_2,\theta_2) \\ \\ \\ y_n - f(x_n,\theta_n) \end{bmatrix}$$

$$\underline{\beta}_0 = \begin{bmatrix} \theta_1 - \theta_{10} \\ \theta_2 - \theta_{20} \\ \\ \theta_p - \theta_{p0} \end{bmatrix}$$

$$\underline{X}_0 = \begin{bmatrix} \frac{\partial f(x_1,\theta)}{\partial\theta_1}\Big|_{\underline{\theta}=\underline{\theta}_0} & \cdots\cdots & \frac{\partial f(x_1,\theta)}{\partial\theta_p}\Big|_{\underline{\theta}=\underline{\theta}_0} \\ \vdots & & \vdots \\ \frac{\partial f(x_n,\theta)}{\partial\theta_1}\Big|_{\underline{\theta}=\underline{\theta}_0} & \cdots\cdots & \frac{\partial f(x_n,\theta)}{\partial\theta_p}\Big|_{\underline{\theta}=\underline{\theta}_0} \end{bmatrix}$$

$$\underline{\beta}_0 = (\underline{X}_0^T\underline{X}_0)^{-1}\ \underline{X}^T\underline{Z}$$

Thus the new estimate of $\underline{\theta}$ is given by $\underline{\theta}_1 = \underline{\theta}_0 + \underline{\beta}_0$

The above procedure is repeated using $\underline{\theta}_1$ in place of $\underline{\theta}_0$ until both $S(\underline{\theta})$ and $\underline{\theta}$ converge.

Box modified Gauss-Newton method uses a scaled advance

$$\underline{\theta} = \underline{\theta}_0 + \underline{\beta}$$

where

$$\underline{\beta} = \frac{1}{1+\lambda}\ \{(\underline{X}_0^T\underline{X})^{-1}\underline{X}_0^T\underline{Z}\}$$

This algorithm is used in the WATFIV program 'NONLIN'.

The program to fit Langmuir isotherm is given on the next page.

```
//          JOB   (SPabcdef,
//  ),'SANAT',MSGLEVEL=(1,1),CLASS=K
//  EXEC  WATFIV
//WATFIV.SYSIN  DD  *
$JOB   SPabcdef,WATFIV,PAGES=15,TIME=15
C      THIS IS FOR 40% D2EHPA,  CO 40%, CN4040
       CALL NONLIN(0)
       STOP
       END
       SUBROUTINE DERIV(Z,THETA,X,P,DELT,TPD,D)
       COMMON/DIM/NVAR,NPAR,NDATA,NVND,NPNP,NPND
       DIMENSION Z(NVND),D(NPND),X(NVAR),P(NPAR),THETA(NPAR),DELT(NPAR
      1   TPD(NPAR)
       COMMON/WEIGHT/W(100),IWATE
       M1 = -NVAR
       M3 = -NPAR
       DO 100 KK = 1,NDATA
       M1 = M1 + NVAR
       M3 = M3 + NPAR
       DO 101 J = 1,NVAR
       M2 = M1 + J
       X(J) = Z(M2)
  101  CONTINUE
C      INSERT DERIVATIVES HERE IN FORM
C PARTIAL DERIVATIVE WITH RESPECT THETA1 IS P(1)
C PARTIAL DERIVATIVE WITH RESPECT THETA2 IS P(2)
       P(1) = (THETA(2)*X(1))/(1.0+THETA(2)*X(1))
       P(2) = ((THETA(1)*X(1))*(1.0+THETA(2)*X(1))-(X(1)*THETA(2)*
      1THETA(1)*X(1)))/((1.0+THETA(2)*X(1))**2)
       DO 102 J = 1,NPAR
       M4 = M3 + J
       D(M4) = P(J)*W(KK)
  102  CONTINUE
  100  CONTINUE
       RETURN
       END
       SUBROUTINE RESID (Z,THETA,Y,NOP,X,DELY,SS)
       COMMON/WEIGHT/W(100),IWATE
       COMMON/DIM/NVAR,NPAR,NDATA,NVND,NPNP,NPND
       DIMENSION Z(NVND),Y(NDATA),DELY(NDATA),THETA(NPAR),X(NVAR)
    1  FORMAT (5X,I5,5X,3E20.5)
    2  FORMAT ('1',20X,'RESIDUALS ANALYSIS',/,6X,'RUN NUMBER',13X,
      1'PRIDICTED',12X,'ACTUAL',13X,'RESIDUAL',/)
       IF (NOP.EQ.3) WRITE (6,2)
       M1 = -NVAR
       SS = 0.0
       DO 100 I= 1,NDATA
       IF (IWATE.EQ.0) W(I) = 1.0
       M1 = M1 + NVAR
       DO 101 J = 1,NVAR
       M2 = M1 + J
       X(J) = Z(M2)
  101  CONTINUE
C INSERT MODEL IN FORM
```

```
      F = (THETA(1)*THETA(2)*X(1))/(1.0+THETA(2)*X(1))
      DELY(I) = Y(I)-F
      IF (NOP.EQ.3) WRITE (6,1) I,F,Y(I),DELY(I)
C     DATA AND RESIDUALS MAY BE PUNCHED OUT HERE
      DELY(I) = DELY(I)*W(I)
      SS =  SS + (DELY(I)**2)
  100 CONTINUE
      RETURN
      END
$ENTRY
NON LINEAR REGRESSION ANALYSIS
      (2F15.8)
         8         2         1        50         1    0.001       1.0
  0.9    100.0
      0.001273       0.0411
      0.0017         0.08145
      0.004242       0.15781
      0.008739       0.15272
      0.01315        0.2101
      0.024604       0.2342
      0.04667        0.2189
      0.0467         0.2172
$STOP
```

Appendix F

SAMPLE CALCULATIONS

1. To calculate the equilibrium organic phase concentrations in a binary system Co-Ni-D2EHPA in kerosene containing $CoSO_4$ and $NiSO_4$ solutes.

The equilibrated aqueous conditions are:

$\overline{x}_{Co} = 0.5$, $x_{Co} = 3$ g/l = 0.05091 mol/l

system: 20% D2EHPA + 5% TBP in kerosene

110% equilibration with NH_3

initial total metal concentration = 0.17 mol/l

(a) calculations for cobalt

estimated pH for the system = 7.373 (Ref. Table no. 16(C))

estimation of y,

$$e^{Dy} = \theta_1 \times x_1^{\theta_2} \times (1-x_1)^{\theta_3} \times H^{+\theta_4}$$

x_1 = mole fraction of cobalt = 0.5

H^+ = Hydrogen ion concentration at equilibrium

= 4.2394×10^{-8} mol/l

from Table 15(A): $\theta_1=2.636$, $\theta_2=0.2883$, $\theta_3=0.77962$, $\theta_4=0.01476$

$\therefore$ Dy = Δy = -0.02157 mol/l

$$y = \frac{\theta_1 \theta_2 \ x}{1 + \theta_2 \ x} \quad \text{where } x = 0.05091 \text{ mol/l}$$

θ_1 and θ_2 are selected using Langmuir isotherm for the system Co-D2EHPA in kerosene for 20% D2EHPA, 110% equilibrated with NH_3. (Ref. Table no. 14(C))

$\theta_1=0.4563$, $\theta_2=183.70$

y = 0.4025 mol/l

$$\therefore y_{Co(estimated)} = y \cdot x_1 + \Delta y$$

$$= 0.4025(0.5) + (-0.02157)$$

$= 0.1797$ mol/l

$y_{Co(experimental)} = 0.177$ mol/l

error $= 1.53\%$

(b) Calculations for nickel

$\bar{x}_{Ni} = 0.5$, $x_{Ni} = 2.9889$ g/l $= 0.05091$ mol/l

estimated pH = 7.27 (Ref. Table no. 16(D))

estimation of Δy,

from Table no. 15(B): $\theta_1=0.9316$, $\theta_2=-0.1103$, $\theta_3=-0.2964$, $\theta_4=0.00739$

$H^+ = 5.3692 \times 10^{-8}$ mol/l

$$e^{Dy} = 0.9316(0.5)^{-0.1103} \times (0.5)^{-0.27964} \times (5.3692 \times 10^{-8})^{0.00739}$$

$$= 1.0787$$

$Dy = \Delta y = 0.07573$ mol/l

$$y = \frac{\theta_i \theta_2 \; x}{1 + \theta_2 \; x}$$

$\theta_1 = 0.58$, $\theta_2 = 29.634$ (Ref. Table no. 14(D))

$y = 0.3488$ mol/l

$y_{Ni(estimated)} = 0.3488(0.5) + 0.07573$

$= 0.25013$ mol/l

$y_{Ni(experimental)} = 0.256$ mol/l

error $= 2.34\%$

2. To find equilibrium organic phase concentrations in a binary system Co-Ni-D2EHPA in kerosene containing $CoSO_4$ and $NiSO_4$ solutes.

The equilibrated aqueous conditions are:

$\bar{x}_{Co} = 0.345$, $x_{Co} = 0.00382$ mol/l

system: 40% D2EHPA + 5% TBP in kerosene

20% equilibration with NH_3

(a) calculations for cobalt

estimated equilibrium pH = 3.91 (Ref. Table no. 16(G))

estimation of Δy (Ref. Table no. 15(C))

$\theta_1 = 0.56074$, $\theta_2 = -0.3076$, $\theta_3 = -0.3344$, $\theta_4 = -0.0175$

$H^+ = 1.2313 \times 10^{-4}$ mol/l

$e^{Dy} = 1.04905$

$\therefore Dy = \Delta y = 0.047884$ mol/l

$$y = \frac{\theta_1 \theta_2 \; x}{1 + \theta_2 x} \qquad \theta_1 = 0.3365, \; \theta_2 = 100.66$$

(Ref. Table no. 14(c))

$y = 0.09345$ mol/l

$y_{Co(estimated)} = 0.09345(0.345) + 0.04788$

$= 0.08012$ mol/l

$y_{Co(experimental)} = 0.078$ mol/l

error = 2.72%

(b) calculation for nickel

$\bar{x}_{Ni} = 0.655$, $x_{Ni} = 0.007253$ mol/l

estimated equilibrium pH = 3.849 (Ref. Table no. 16(H))

estimation of Δy, (Ref. Table no. 15(D))

$\theta_1 = 0.29553$, $\theta_2 = -1.4596$, $\theta_3 = -0.9172$, $\theta_4 = 0.04363$

$H^+ = 1.415 \times 10^{-4}$ mol/l

$e^{Dy} = \theta_1 \times (x_1)^{\theta_2} \times (1-x_1)^{\theta_3} \times H^{+\theta_4}$

$\therefore Dy = \Delta y = -0.011972$ mol/l

$y = \dfrac{\theta_1 \theta_2 \; x}{1+\theta_2 \; x}$ $\quad \theta_1 = 0.212; \; \theta_2 = 332.80$

(Ref. Table no. 14(H))

$y = 0.1499$ mol/l

$y_{Ni\,(estimated)} = 0.1499(0.645) + (-0.011972)$

$= 0.08621$ mol/l

$y_{Ni\,(experimental)} = 0.081$ mol/l

error = 6.43%

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TABLE 1(A) PURE COMPONENT COBALT-10%D2EHPA-20%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase
1	0.5	0.00848	0.06787
2	1.0	0.01951	0.11539
3	2.0	0.04582	0.16968
4	3.0	0.07127	0.19853
5	4.0	0.10011	0.21804
6	6.0	0.12981	0.22738
7	8.0	0.15441	0.23077
8	10.0	0.18071	0.23162

TABLE 1(B) PURE COMPONENT COBALT-10%D2EHPA-40%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase
1	0.5	0.00424	0.09502
2	1.0	0.04242	0.17477
3	2.0	0.08060	0.21890
4	3.0	0.11284	0.23247
5	4.0	0.13914	0.10011
6	6.0	0.14678	0.23416
7	8.0	0.15950	0.24604
8	10.0	0.17902	0.24265

TABLE 1(C) PURE COMPONENT COBALT-10%D2EHPA-60%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase
1	0.5	0.00255	0.09672
2	1.0	0.02460	0.15272
3	2.0	0.05600	0.20701
4	3.0	0.08315	0.22907
5	4.0	0.10011	0.24095
6	6.0	0.13829	0.24774
7	8.0	0.17817	0.25113
8	10.0	0.14593	0.25113

TABLE 1(D) PURE COMPONENT COBALT-10%D2EHPA-80%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase
1	0.5	0.02376	0.19174
2	1.0	0.00170	0.09672
3	2.0	0.06448	0.25962
4	3.0	0.11284	0.26810
5	4.0	0.12641	0.26980
6	6.0	0.15441	0.27149
7	8.0	0.16205	0.27149
8	10.0	0.16544	0.27319

TABLE 1(E) PURE COMPONENT COBALT-10%D2EHPA-100%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase
1	0.5	0.00212	0.11454
2	1.0	0.01358	0.21211
3	2.0	0.03394	0.25453
4	3.0	0.05430	0.27658
5	4.0	0.07212	0.28846
6	6.0	0.10520	0.29355
7	8.0	0.11878	0.30373
8	10.0	0.16799	0.30543

TABLE 1(F) PURE COMPONENT COBALT-10%D2EHPA-110%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase
1	0.5	0.00127	0.10860
2	1.0	0.00212	0.15611
3	2.0	0.01103	0.21890
4	3.0	0.01951	0.24265
5	4.0	0.05260	0.28846
6	6.0	0.08484	0.30374
7	8.0	0.12557	0.31052
8	10.0	0.16035	0.31392

TABLE 2(A) PURE COMPONENT NICKEL-10%D2EHPA-20%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase
1	0.5	0.01278	0.05451
2	1.0	0.02555	0.09709
3	2.0	0.04769	0.13626
4	3.0	0.06813	0.16011
5	4.0	0.09453	0.17885
6	6.0	0.11582	0.19332
7	8.0	0.14137	0.20270
8	10.0	0.17033	0.20610

TABLE 2(B) PURE COMPONENT NICKEL-10%D2EHPA-40%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase
1	0.5	0.01278	0.09368
2	1.0	0.03747	0.16011
3	2.0	0.06813	0.20269
4	3.0	0.09879	0.18055
5	4.0	0.08687	0.21802
6	6.0	0.10475	0.23505
7	8.0	0.15670	0.24357
8	10.0	0.17714	0.24357

TABLE 2(C) PURE COMPONENT NICKEL-10%D2EHPA-60%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase
1	0.5	0.00596	0.06473
2	1.0	0.01278	0.11071
3	2.0	0.02214	0.14819
4	3.0	0.04599	0.19929
5	4.0	0.07239	0.23335
6	6.0	0.12179	0.25975
7	8.0	0.16437	0.26912
8	10.0	0.17629	0.26997

TABLE 2(D) PURE COMPONENT NICKEL-10%D2EHPA-80%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase
1	0.50	0.00596	0.08516
2	1.0	0.01703	0.18140
3	2.0	0.05536	0.24698
4	3.0	0.07750	0.26401
5	4.0	0.10731	0.27593
6	6.0	0.12775	0.28104
7	8.0	0.15330	0.28275
8	10.0	0.17885	0.28615

TABLE 2(E) PURE COMPONENT NICKEL-10%D2EHPA-100%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase
1	0.5	0.00426	0.09368
2	1.0	0.00937	0.18736
3	2.0	0.02129	0.23846
4	3.0	0.04258	0.28104
5	4.0	0.07154	0.30148
6	6.0	0.11582	0.28956
7	8.0	0.14733	0.30659
8	10.0	0.17799	0.30830

TABLE 2(F) PURE COMPONENT NICKEL-10%D2EHPA-110%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase
1	0.5	0.00170	0.12604
2	1.0	0.00596	0.19758
3	2.0	0.02214	0.26231
4	3.0	0.05425	0.29637
5	4.0	0.07410	0.30490
6	6.0	0.10050	0.31000
7	8.0	0.13115	0.31170
8	10.0	0.16777	0.31341

TABLE 3(A) PURE COMPONENT COBALT-20%D2EHPA-20%NH$_3$

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00424	0.08611	4.91
2	1.0	0.05939	0.11708	4.30
3	2.0	0.12132	0.11369	4.10
4	3.0	0.12560	0.15271	4.10
5	4.0	0.14170	0.13914	4.05
6	6.0	0.14932	0.16290	4.00
7	8.0	0.15340	0.18411	3.97
8	10.0	0.16500	0.11880	4.00

TABLE 3(B) PURE COMPONENT COBALT-20%D2EHPA-40%NH$_3$

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00127	0.08761	6.10
2	1.0	0.00510	0.17138	5.82
3	2.0	0.04751	0.25792	5.67
4	3.0	0.07636	0.30034	5.58
5	4.0	0.10690	0.27828	5.34
6	6.0	0.12780	0.29270	5.27
7	8.0	0.14084	0.28507	5.15
8	10.0	0.14253	0.33940	5.05

TABLE 3(C) PURE COMPONENT COBALT-20%D2EHPA-60%NH$_3$

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00127	0.08761	7.15
2	1.0	0.00594	0.17053	7.00
3	2.0	0.04670	0.25962	6.85
4	3.0	0.08150	0.28507	6.75
5	4.0	0.09842	0.31222	6.70
6	6.0	0.12220	0.32579	6.65
7	8.0	0.13066	0.36652	6.42
8	10.0	0.15102	0.25453	6.31

TABLE 3(D) PURE COMPONENT COBALT-20%D2EHPA-80% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00042	0.08807	7.45
2	1.0	0.00594	0.17562	7.00
3	2.0	0.03224	0.28846	6.90
4	3.0	0.07127	0.31561	6.75
5	4.0	0.08910	0.34955	6.75
6	6.0	0.11369	0.37330	6.65
7	8.0	0.13660	0.31900	6.45
8	10.0	0.13914	0.37330	6.15

TABLE 3(E) PURE COMPONENT COBALT-20%D2EHPA-100% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00255	0.07933	8.05
2	1.0	0.00212	0.15908	7.60
3	2.0	0.00764	0.30713	7.29
4	3.0	0.03309	0.38433	7.18
5	4.0	0.06193	0.39706	7.10
6	6.0	0.08824	0.43778	7.07
7	8.0	0.10860	0.42081	6.95
8	10.0	0.11540	0.45814	6.89

TABLE 3(F) PURE COMPONENT COBALT-20%D2EHPA-110% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00255	0.07933	8.65
2	1.0	0.00170	0.15950	8.10
3	2.0	0.01018	0.30204	7.80
4	3.0	0.03903	0.36651	7.50
5	4.0	0.06193	0.39706	7.40
6	6.0	0.10096	0.36143	7.30
7	8.0	0.08781	0.38710	7.22
8	10.0	0.12560	0.35633	7.20

TABLE 4(A) PURE COMPONENT NICKEL-20%D2EHPA-20% NH$_3$

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.01278	0.08091	5.22
2	1.0	0.04020	0.12945	5.10
3	2.0	0.10305	0.14308	5.05
4	3.0	0.11327	0.18396	5.03
5	4.0	0.12945	0.18055	5.02
6	6.0	0.14648	0.16863	5.01
7	8.0	0.15755	0.17033	5.00
8	10.0	0.13626	0.17033	5.00

TABLE 4(B) PURE COMPONENT NICKEL-20%D2EHPA-40% NH$_3$

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00170	0.08644	6.00
2	1.0	0.01278	0.16182	5.90
3	2.0	0.06302	0.22313	5.90
4	3.0	0.08942	0.25550	5.90
5	4.0	0.10901	0.26231	5.90
6	6.0	0.13286	0.33384	5.82
7	8.0	0.13541	0.23505	5.82
8	10.0	0.13371	0.23676	5.81

TABLE 4(C) PURE COMPONENT NICKEL-20%D2EHPA-60% NH$_3$

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00170	0.08516	6.90
2	1.0	0.00852	0.16522	6.85
3	2.0	0.05536	0.23846	6.70
4	3.0	0.08534	0.26571	6.45
5	4.0	0.10237	0.28450	6.35
6	6.0	0.12690	0.29467	6.15
7	8.0	0.14222	0.29637	6.15
8	10.0	0.16352	0.29467	5.95

TABLE 4(D) PURE COMPONENT NICKEL-20%D2EHPA-80% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00170	0.08644	7.45
2	1.0	0.00511	0.16948	7.40
3	2.0	0.05025	0.24868	7.39
4	3.0	0.07665	0.29382	7.39
5	4.0	0.10050	0.29637	7.38
6	6.0	0.12180	0.31681	7.37
7	8.0	0.13371	0.32703	7.35
8	10.0	0.14222	0.32363	7.31

TABLE 4(E) PURE COMPONENT NICKEL-20%D2EHPA-100% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00596	0.08516	7.96
2	1.0	0.01192	0.16352	7.82
3	2.0	0.02896	0.25550	7.70
4	3.0	0.05025	0.37302	7.56
5	4.0	0.07324	0.40538	7.31
6	6.0	0.10390	0.42412	6.92
7	8.0	0.13158	0.43092	6.83
8	10.0	0.159683	0.430932	6.71

TABLE 4(F) PURE COMPONENT NICKEL-20%D2EHPA-110% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00085	0.17714	8.50
2	1.0	0.02555	0.32363	8.31
3	2.0	0.05110	0.18494	8.20
4	3.0	0.07963	0.45307	7.58
5	4.0	0.10135	0.47011	7.30
6	6.0	0.12604	0.46670	7.05
7	8.0	0.15117	0.48544	6.93
8	10.0	0.17288	0.47181	6.80

TABLE 5(A) COBALT IN MIXTURE, CO-20%D2EHPA-20% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00340	0.04242	4.60
2	1.0	0.00221	0.06620	4.30
3	2.0	0.04670	0.08315	4.20
4	3.0	0.05850	0.08904	4.10
5	4.0	0.06957	0.07466	4.05
6	6.0	0.07300	0.09163	4.05
7	8.0	0.08000	0.06787	4.05
8	10.0	0.07890	0.09333	4.00

TABLE 5(B) COBALT IN MIXTURE, CO-20%D2EHPA-40% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00170	0.04330	6.10
2	1.0	0.00509	0.08315	5.82
3	2.0	0.02890	0.11880	5.67
4	3.0	0.04160	0.14000	5.58
5	4.0	0.05350	0.13710	5.34
6	6.0	0.06700	0.12730	5.27
7	8.0	0.06957	0.14932	5.15
8	10.0	0.07721	0.11030	5.05

TABLE 5(C) COBALT IN MIXTURE, CO-20%D2EHPA-60% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00170	0.04330	6.90
2	1.0	0.00255	0.08570	6.63
3	2.0	0.02800	0.12050	6.30
4	3.0	0.04242	0.13744	6.22
5	4.0	0.05350	0.13800	6.15
6	6.0	0.06363	0.14762	6.10
7	8.0	0.06872	0.15611	6.05
8	10.0	0.07130	0.16980	6.00

TABLE 5(D) COBALT IN MIXTURE, CO-20%D2EHPA-80% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00170	0.04327	8.20
2	1.0	0.00340	0.08484	7.60
3	2.0	0.01870	0.13914	7.18
4	3.0	0.03400	0.16290	7.00
5	4.0	0.04412	0.17650	6.95
6	6.0	0.06190	0.16120	6.89
7	8.0	0.06618	0.17647	6.85
8	10.0	0.06900	0.19514	6.80

TABLE 5(E) COBALT IN MIXTURE, CO-20%D2EHPA-100% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00170	0.04330	8.98
2	1.0	0.00255	0.08600	8.35
3	2.0	0.00764	0.16118	7.70
4	3.0	0.02291	0.19598	7.40
5	4.0	0.03903	0.19683	7.23
6	6.0	0.04921	0.23416	7.10
7	8.0	0.06278	0.20400	7.05
8	10.0	0.06957	0.18700	7.00

TABLE 5(F) COBALT IN MIXTURE, CO-20%D2EHPA-110% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00127	0.04095	9.50
2	1.0	0.00255	0.08060	9.00
3	2.0	0.01061	0.14508	8.15
4	3.0	0.02673	0.16935	7.60
5	4.0	0.04454	0.15441	7.45
6	6.0	0.05091	0.19344	7.25
7	8.0	0.06448	0.14932	7.20
8	10.0	0.06278	0.20362	7.10

TABLE 6(A) NICKEL IN MIXTURE, NI-20%D2EHPA-20% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00511	0.02725	4.60
2	1.0	0.03750	0.04982	4.30
3	2.0	0.06387	0.05114	4.20
4	3.0	0.07240	0.05200	4.10
5	4.0	0.08010	0.05212	4.05
6	6.0	0.08261	0.05246	4.05
7	8.0	0.08520	0.05280	4.05
8	10.0	0.08431	0.05230	4.00

TABLE 6(B) NICKEL IN MIXTURE, NI-20%D2EHPA-40% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00170	0.04275	6.10
2	1.0	0.00596	0.06430	5.82
3	2.0	0.03832	0.09800	5.67
4	3.0	0.05365	0.10092	5.58
5	4.0	0.06387	0.09710	5.34
6	6.0	0.06984	0.10390	5.27
7	8.0	0.07495	0.10050	5.15
8	10.0	0.07920	0.10135	5.05

TABLE 6(C) NICKEL IN MIXTURE, NI-20%D2EHPA-60% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00256	0.04241	6.90
2	1.0	0.00426	0.08304	6.63
3	2.0	0.03066	0.11330	6.30
4	3.0	0.04812	0.11753	6.22
5	4.0	0.06473	0.09030	6.15
6	6.0	0.07154	0.09450	6.10
7	8.0	0.07835	0.07154	6.05
8	10.0	0.07495	0.12350	6.00

TABLE 6(D) NICKEL IN MIXTURE, NI-20%D2EHPA-80% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00255	0.04241	8.20
2	1.0	0.02640	0.06090	7.60
3	2.0	0.02299	0.12860	7.18
4	3.0	0.03747	0.14950	7.00
5	4.0	0.04940	0.15160	6.95
6	6.0	0.06387	0.14050	6.89
7	8.0	0.06898	0.14650	6.85
8	10.0	0.06984	0.17460	6.80

TABLE 6(E) NICKEL IN MIXTURE, NI-20%D2EHPA-100% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00256	0.04241	8.98
2	1.0	0.00767	0.07963	8.35
3	2.0	0.01448	0.14563	7.70
4	3.0	0.03066	0.17000	7.40
5	4.0	0.04430	0.17203	7.23
6	6.0	0.05962	0.16610	7.10
7	8.0	0.06387	0.18740	7.05
8	10.0	0.07069	0.16610	7.00

TABLE 6(F) NICKEL IN MIXTURE, NI-20%D2EHPA-110% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00400	0.04310	9.00
2	1.0	0.00470	0.08560	9.00
3	2.0	0.01811	0.14430	8.15
4	3.0	0.02981	0.18140	7.60
5	4.0	0.04216	0.19250	7.45
6	6.0	0.04812	0.25300	7.25
7	8.0	0.05876	0.25210	7.20
8	10.0	0.05834	0.32000	7.10

TABLE 7(A) PURE COMPONENT COBALT-40%D2EHPA-20%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00170	0.08500	4.65
2	1.0	0.00680	0.16500	4.25
3	1.5	0.02800	0.21520	4.00
4	2.0	0.04800	0.24690	3.93
5	2.5	0.06790	0.25900	3.85
6	3.0	0.08060	0.27230	3.85
7	4.0	0.09672	0.29900	3.85
8	5.0	0.11200	0.29900	3.75
9	6.0	0.12130	0.30000	3.73
10	7.0	0.12900	0.29900	3.75
11	8.0	0.12300	0.38700	3.73
12	10.0	0.13400	0.37330	3.70

TABLE 7(B) PURE COMPONENT COBALT-40%D2EHPA-40%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00170	0.08990	6.55
2	1.0	0.00170	0.18000	6.50
3	1.5	0.00170	0.36000	6.45
4	2.0	0.00594	0.35120	6.35
5	2.5	0.01360	0.42000	6.22
6	3.0	0.02210	0.47900	6.17
7	4.0	0.04242	0.55700	6.10
8	5.0	0.06363	0.59000	6.05
9	6.0	0.07300	0.59000	5.50
10	7.0	0.09000	0.57010	5.70
11	8.0	0.10000	0.57010	5.65
12	10.0	0.11370	0.57700	5.60

TABLE 7(C) PURE COMPONENT COBALT-40%D2EHPA-60%NH$_3$

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00255	0.09000	6.75
2	1.0	0.00127	0.18030	6.75
3	1.5	0.00255	0.26900	6.70
4	2.0	0.00424	0.35500	6.65
5	2.5	0.00933	0.43070	6.50
6	3.0	0.01696	0.49400	6.41
7	4.0	0.04160	0.56000	6.20
8	5.0	0.05430	0.51000	6.30
9	6.0	0.07127	0.66200	6.20
10	7.0	0.08740	0.66000	5.61
11	8.0	0.10000	0.65840	5.60
12	10.0	0.11300	0.68720	5.45

TABLE 7(D) PURE COMPONENT COBALT-40%D2EHPA-80%NH$_3$

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00085	0.09040	7.80
2	1.0	0.00127	0.18030	7.00
3	1.5	0.00170	0.27000	7.35
4	2.0	0.00340	0.35630	7.20
5	2.5	0.00600	0.43910	7.06
6	3.0	0.01270	0.50650	7.00
7	4.0	0.03224	0.59730	6.81
8	5.0	0.05260	0.64500	6.80
9	6.0	0.06790	0.68210	6.71
10	7.0	0.07720	0.73050	6.71
11	8.0	0.08910	0.74000	6.70
12	10.0	0.10950	0.72100	6.70

TABLE 7(E) PURE COMPONENT COBALT-40%D2EHPA-100%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00085	0.09000	8.30
2	1.0	0.00085	0.18070	8.25
3	1.5	0.00255	0.26900	8.00
4	2.0	0.00340	0.35630	7.78
5	2.5	0.00594	0.43910	7.65
6	3.0	0.01272	0.50650	7.50
7	4.0	0.03521	0.58530	7.35
8	5.0	0.05260	0.64480	7.31
9	6.0	0.06787	0.68210	7.40
10	7.0	0.08060	0.70670	7.31
11	8.0	0.09080	0.72630	7.30
12	10.0	0.10000	0.82300	7.30

TABLE 7(F) PURE COMPONENT COBALT-40%D2EHPA-110%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00170	0.09000	9.00
2	1.0	0.00170	0.18000	8.50
3	1.5	0.00085	0.27150	8.25
4	2.0	0.00339	0.35630	7.97
5	2.5	0.00509	0.44120	7.81
6	3.0	0.01190	0.50910	7.71
7	4.0	0.03292	0.59500	7.56
8	5.0	0.05260	0.64500	7.48
9	6.0	0.06700	0.68720	7.42
10	7.0	0.08230	0.69570	7.38
11	8.0	0.08910	0.74000	7.39
12	10.0	0.10350	0.78000	7.31

TABLE 8(A) PURE COMPONENT NICKEL-40%D2EHPA-20%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00085	0.07410	4.50
2	1.0	0.00852	0.14050	4.20
3	1.5	0.03280	0.17440	4.05
4	2.0	0.05540	0.18730	4.00
5	2.5	0.07370	0.18840	3.95
6	3.0	0.08133	0.20320	3.90
7	4.0	0.10310	0.18400	3.78
8	5.0	0.11240	0.18310	~~3.85~~
9	6.0	0.11070	0.26830	3.85
10	7.0	0.11670	0.22650	3.90
11	8.0	0.12260	0.21120	3.85
12	10.0	0.14560	0.22140	3.85

TABLE 8(B) PURE COMPONENT NICKEL-40%D2EHPA-40%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00256	0.08050	5.10
2	1.0	0.00085	0.16270	4.95
3	1.5	0.00426	0.24460	4.81
4	2.0	0.00852	0.31000	4.73
5	2.5	0.01450	0.37300	4.64
6	3.0	0.02730	0.40900	4.58
7	4.0	0.04770	0.46330	4.53
8	5.0	0.06730	0.48120	4.42
9	6.0	0.08010	0.50100	4.38
10	7.0	0.08390	0.55750	4.24
11	8.0	0.09900	0.51800	4.20
12	10.0	0.10390	0.59620	4.15

TABLE 8(C) PURE COMPONENT NICKEL-40%D2EHPA-60%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00085	0.08130	6.20
2	1.0	0.00170	0.16180	6.20
3	1.5	0.00170	0.24270	6.10
4	2.0	0.00511	0.31680	6.00
5	2.5	0.01235	0.37800	5.87
6	3.0	0.04430	0.42600	5.80
7	4.0	0.06220	0.47700	5.75
8	5.0	0.06217	0.50700	5.70
9	6.0	0.07500	0.53140	5.70
10	7.0	0.08300	0.56600	5.65
11	8.0	0.09500	0.55190	5.65
12	10.0	0.10400	0.59620	5.61

TABLE 8(D) PURE COMPONENT NICKEL-40%D2EHPA-80%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00256	0.08050	6.80
2	1.0	0.00340	0.16010	6.61
3	1.5	0.00340	0.24020	6.52
4	2.0	0.00680	0.31340	6.39
5	2.5	0.00340	0.40000	6.30
6	3.0	0.01703	0.44000	6.20
7	4.0	0.03410	0.51800	6.15
8	5.0	0.05450	0.54500	6.10
9	6.0	0.06890	0.60000	6.08
10	7.0	0.08500	0.61100	6.05
11	8.0	0.09300	0.64730	6.02
12	10.0	0.11000	0.63900	6.00

TABLE 8(E) PURE COMPONENT NICKEL-40%D2EHPA-100%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00100	0.08340	7.20
2	1.0	0.00150	0.16900	7.00
3	1.5	0.00210	0.25340	6.90
4	2.0	0.00530	0.35030	6.75
5	2.5	0.01000	0.41900	6.62
6	3.0	0.01810	0.46300	6.55
7	4.0	0.03620	0.55700	6.51
8	5.0	0.05630	0.59300	6.49
9	6.0	0.06890	0.65100	6.40
10	7.0	0.08500	0.67100	6.35
11	8.0	0.09300	0.68300	6.35
12	10.0	0.11000	0.69000	6.30

TABLE 8(F) PURE COMPONENT NICKEL-40%D2EHPA-110%NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00043	0.08921	7.80
2	1.0	0.00085	0.17800	7.40
3	1.5	0.00128	0.26640	7.15
4	2.0	0.00426	0.35000	7.00
5	2.5	0.00980	0.42300	6.85
6	3.0	0.01960	0.47800	6.75
7	4.0	0.03830	0.56210	6.60
8	5.0	0.05750	0.60680	6.50
9	6.0	0.07410	0.62850	6.40
10	7.0	0.08602	0.65000	6.32
11	8.0	0.09240	0.69200	6.32
12	10.0	0.10990	0.69000	6.32

TABLE 9(A) COBALT IN MIXTURE, CO-40%D2EHPA-20% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00085	0.04123	4.00
2	1.0	0.00382	0.07933	3.90
3	2.0	0.02376	0.11880	3.70
4	3.0	0.03776	0.13620	3.70
5	4.0	0.04878	0.13744	3.65
6	6.0	0.05812	0.15020	3.60
7	8.0	0.06533	0.14253	3.35
8	10.0	0.06872	0.14423	3.25

TABLE 9(B) COBALT IN MIXTURE, CO-40%D2EHPA-40% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00127	0.04110	5.10
2	1.0	0.00170	0.08145	5.10
3	2.0	0.00424	0.15781	5.05
4	3.0	0.00874	0.15272	5.05
5	4.0	0.01315	0.21010	5.00
6	6.0	0.02460	0.23420	4.85
7	8.0	0.04667	0.21890	4.80
8	10.0	0.04670	0.21720	3.50

TABLE 9(C) COBALT IN MIXTURE, CO-40%D2EHPA-60% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00170	0.04072	6.30
2	1.0	0.00255	0.08298	6.15
3	2.0	0.00170	0.16290	5.90
4	3.0	0.00804	0.22534	5.60
5	4.0	0.01951	0.25453	5.35
6	6.0	0.03733	0.27490	5.35
7	8.0	0.04794	0.28170	5.35
8	10.0	0.05532	0.27830	5.20

TABLE 9(D) COBALT IN MIXTURE, CO-40%D2EHPA-80% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00042	0.04140	6.15
2	1.0	0.00042	0.08272	5.95
3	2.0	0.00127	0.16375	5.75
4	3.0	0.00721	0.22780	5.15
5	4.0	0.01867	0.25792	5.25
6	6.0	0.03563	0.28507	5.25
7	8.0	0.04794	0.28168	5.15
8	10.0	0.05220	0.30967	5.00

TABLE 9(E) COBALT IN MIXTURE, CO-40%D2EHPA-100% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00064	0.04127	6.40
2	1.0	0.00170	0.08145	6.20
3	2.0	0.00170	0.16290	6.00
4	3.0	0.00424	0.23671	5.90
5	4.0	0.02750	0.27830	5.70
6	6.0	0.02757	0.33343	5.50
7	8.0	0.04285	0.32240	5.40
8	10.0	0.05010	0.33090	5.00

TABLE 9(F) COBALT IN MIXTURE, CO-40%D2EHPA-110% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00106	0.04105	7.25
2	10	0.00042	0.08272	7.25
3	2.0	0.00170	0.16290	6.85
4	3.0	0.00552	0.23290	6.60
5	4.0	0.01358	0.27830	6.55
6	6.0	0.03139	0.31052	6.00
7	8.0	0.04200	0.32920	5.60
8	10.0	0.04921	0.33940	5.25

TABLE 10(A) NICKEL IN MIXTURE, NI-40%D2EHPA-20% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00085	0.04480	4.00
2	1.0	0.00724	0.08312	3.90
3	2.0	0.03662	0.10731	3.70
4	3.0	0.04770	0.12780	3.70
5	4.0	0.05920	0.12440	3.65
6	6.0	0.06260	0.16611	3.60
7	8.0	0.06730	0.18396	3.35
8	10.0	0.07070	0.19588	3.25

TABLE 10(B) NICKEL IN MIXTURE, NI-40%D2EHPA-40% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00085	0.04480	5.10
2	1.0	0.00170	0.08860	5.10
3	2.0	0.00409	0.09880	3.50
4	3.0	0.00554	0.16950	5.05
5	4.0	0.01916	0.21334	5.05
6	6.0	0.03236	0.23165	5.00
7	8.0	0.05280	0.22483	4.85
8	10.0	0.06174	0.22824	4.80

TABLE 10(C) NICKEL IN MIXTURE, NI-40%D2EHPA-60% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00170	0.04072	6.30
2	1.0	0.00255	0.08298	6.15
3	2.0	0.00170	0.16290	5.0
4	3.0	0.00804	0.22534	5.60
5	4.0	0.01951	0.25453	5.35
6	6.0	0.03733	0.27490	5.35
7	8.0	0.04794	0.28170	5.35
8	10.0	0.05532	0.27830	5.20

TABLE 10(D) NICKEL IN MIXTURE, NI-40%D2EHPA-80% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00085	0.04621	6.15
2	1.0	0.00128	0.09198	5.95
3	2.0	0.00170	0.18310	5.75
4	3.0	0.00852	0.25430	5.25
5	4.0	0.02129	0.28786	5.25
6	6.0	0.03918	0.32450	5.15
7	8.0	0.05540	0.30320	5.15
8	10.0	0.05834	0.34917	5.00

TABLE 10(E) NICKEL IN MIXTURE, NI-40%D2EHPA-100% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00170	0.04582	6.40
2	1.0	0.00341	0.08993	6.20
3	2.0	0.00341	0.17970	6.00
4	3.0	0.00852	0.25430	5.90
5	4.0	0.01618	0.30830	5.70
6	6.0	0.02683	0.39860	5.50
7	8.0	0.05408	0.31341	5.40
8	10.0	0.05970	0.33560	5.00

TABLE 10(F) NICKEL IN MIXTURE, NI-40%D2EHPA-110% NH_3

No.	A/O	mol/l aq. phase	mol/l org. phase	pH
1	0.5	0.00107	0.04616	7.25
2	1.0	0.00256	0.09070	7.25
3	2.0	0.00298	0.18055	6.85
4	3.0	0.00767	0.25677	6.60
5	4.0	0.01703	0.30490	6.55
6	6.0	0.03364	0.35770	6.00
7	8.0	0.04430	0.39100	5.60
8	10.0	0.05536	0.37898	5.25

TABLE 11(A) PURE COMPONENT COBALT-10%D2EHPA

sat. with NH_3	parameter a1	parameter a2
20%	3.8668	-14.9780
40%	3.4789	-13.1639
60%	4.2842	-16.9506
80%	5.2645	-22.6468
100%	6.2709	-28.0112
110%	7.2910	-35.0760

TABLE 11(B) PURE COMPONENT NICKEL-10%D2EHPA

sat. with NH_3	parameter a1	parameter a2
20%	3.1489	-11.8176
40%	3.6801	-13.4733
60%	4.8851	-19.7248
80%	5.0502	-20.3613
100%	6.6103	-29.2078
110%	6.6814	-30.3192

TABLE 11(C) PURE COMPONENT COBALT-20%D2EHPA

sat. with NH_3	parameter a1	parameter a2
20%	2.3369	-09.0402
40%	6.1999	-29.2656
60%	6.5516	-31.5997
80%	7.7566	-38.7100
100%	12.2387	-75.8022
110%	12.6766	-80.5548

TABLE 11(D) PURE COMPONENT NICKEL-20%D2EHPA

sat. with NH_3	parameter a1	parameter a2
20%	3.1353	-13.5942
40%	5.3350	-25.3074
60%	5.0984	-20.9584
80%	5.9800	-26.9101
100%	8.5611	-38.3299
110%	7.3704	-27.3493

TABLE 11(E) COBALT IN MIXTURE, CO-20%D2EHPA

sat. with NH_3	parameter a1	parameter a2
20%	3.2856	-29.1959
40%	5.8842	-57.4718
60%	5.1716	-42.4367
80%	7.6380	-75.1046
100%	10.9753	-122.7200
110%	9.2264	-104.7240

TABLE 11(F) NICKEL IN MIXTURE, NI-20%D2EHPA

sat. with NH_3	parameter a1	parameter a2
20%	1.8146	-14.4410
40%	3.8970	-34.4950
60%	5.2717	-54.3414
80%	5.1474	-42.0874
100%	8.4713	-89.5722
110%	7.7476	-51.8751

TABLE 11(G) PURE COMPONENT COBALT-40%D2EHPA

sat. with NH_3	parameter a1	parameter a2
20%	5.9499	-026.5548
40%	18.8129	-129.6390
60%	18.5716	-111.3480
80%	21.6870	-146.8370
100%	21.9994	-151.7530
110%	22.0473	-152.4940

TABLE 11(H) PURE COMPONENT NICKEL-40%D2EHPA

sat. with NH_3	parameter a1	parameter a2
20%	4.2190	-019.7637
40%	15.5847	-104.1850
60%	14.1086	-086.7290
80%	18.4930	-123.3950
100%	19.8120	-131.7500
110%	19.4664	-129.0670

TABLE 11(M) COBALT IN MIXTURE, CO-40%D2EHPA

sat. with NH_3	parameter a1	parameter a2
20%	6.0608	-059.5884
40%	17.8142	-276.2230
60%	18.5901	-257.8470
80%	19.4283	-274.2930
100%	19.9859	-280.0430
110%	23.6159	-359.6670

TABLE 11(N) NICKEL IN MIXTURE, NI-40%D2EHPA

sat. with NH_3	parameter a1	parameter a2
20%	3.4251	-012.5845
40%	14.2495	-179.0010
60%	14.9820	-174.7680
80%	19.6422	-248.4590
100%	25.1198	-339.8440
110%	22.7831	-300.8700

TABLE 12(A) PURE COMPONENT COBALT-10%D2EHPA

sat. with NH_3	parm. a1	parm. a2	parm. a3
20%	5.7450	-48.19	131.17
40%	7.3419	-77.36	247.76
60%	6.6059	-57.50	160.57
80%	9.2132	-93.09	288.02
100%	11.0480	-119.47	385.84
110%	13.9539	-169.40	594.54

TABLE 12(B) PURE COMPONENT NICKEL-10%D2EHPA

sat. with NH_3	parm. a1	parm. a2	parm. a3
20%	4.2373	-32.39	86.45
40%	6.0867	-56.33	169.89
60%	7.3719	-68.30	169.89
80%	8.6172	-81.79	240.26
100%	11.8010	-125.24	389.30
110%	12.6403	-142.94	473.01

TABLE 12(C) PURE COMPONENT COBALT-20%D2EHPA

sat. with NH_3	parm. a1	parm. a2	parm. a3
20%	3.5575	-29.86	84.11
40%	12.0706	-151.28	578.59
60%	8.5834	-70.89	177.10
80%	13.6331	-163.16	602.48
100%	24.8693	-410.83	2000.77
110%	17.7758	-203.64	677.77

TABLE 12(D) PURE COMPONENT NICKEL-20%D2EHPA

sat. with NH_3	parm. a1	parm. a2	parm. a3
20%	5.0916	-49.11	151.90
40%	10.5643	-133.45	520.07
60%	8.7097	-85.74	269.68
80%	10.6129	-122.62	456.50
100%	12.2086	-113.10	336.98
110%	8.9912	-56.63	119.35

TABLE 12(E) COBALT IN MIXTURE, CO-20%D2EHPA

sat. with NH_3	parm. a1	parm. a2	parm. a3
20%	10.6737	-260.71	1840.09
40%	9.0000	-177.07	1059.02
60%	11.7058	-304.96	2452.46
80%	14.2334	-371.29	2978.50
100%	18.6114	-459.67	3363.79
110%	16.6981	-451.72	3669.24

TABLE 12(F) NICKEL IN MIXTURE, NI-20%D2EHPA

sat. with NH_3	parm. a1	parm. a2	parm. a3
20%	3.4210	-67.28	406.18
40%	8.8677	-207.85	1432.60
60%	10.2230	-240.34	1609.28
80%	6.3906	-97.61	551.07
100%	12.9642	-293.94	2068.37
110%	13.4262	-343.23	3385.20

TABLE 12(G) PURE COMPONENT COBALT-40%D2EHPA

sat. with NH_3	parm. a1	parm. a2	parm. a3
20%	11.3451	-149.50	639.08
40%	33.7162	-542.22	2582.19
60%	36.2525	-610.50	3088.57
80%	41.6357	-700.54	3519.76
100%	47.6487	-940.60	5523.62
110%	45.3067	-841.52	4670.60

TABLE 12(H) PURE COMPONENT NICKEL-40%D2EHPA

sat. with NH_3	parm. a1	parm. a2	parm. a3
20%	6.7426	-71.13	245.83
40%	28.5848	-493.13	2635.76
60%	32.9431	-605.21	3350.04
80%	33.7200	-557.85	2808.25
100%	35.5100	-580.16	2900.34
110%	35.3225	-578.26	2899.45

TABLE 12(M) COBALT IN MIXTURE, CO-40%D2EHPA

sat. with NH_3	parm. a1	parm. a2	parm. a3
20%	10.5511	-251.38	1890.33
40%	30.8812	-1244.93	14645.40
60%	31.9204	-1034.89	10017.20
80%	36.5171	-1326.61	14267.30
100%	55.3756	-2313.50	27026.00
110%	42.5505	-1580.41	17574.70

TABLE 12(N) NICKEL IN MIXTURE, NI-40%D2EHPA

sat. with NH_3	parm. a1	parm. a2	parm. a3
20%	12.1955	-356.12	3184.16
40%	25.5071	-789.49	7133.00
60%	24.0886	-623.39	4757.13
80%	37.0601	-1217.22	11733.60
100%	36.2068	-1060.41	9191.90
110%	36.7656	-1110.47	10384.50

TABLE 13(A) PURE COMPONENT COBALT-10%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.43991	0.33476	0.0014
40%	0.31852	0.20598	0.0159
60%	0.39195	0.23579	0.0006
80%	0.40724	0.20440	0.0012
100%	0.45636	0.19075	0.0018
110%	0.45674	0.17838	0.0021

TABLE 13(B) PURE COMPONENT NICKEL-10%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.46739	0.42751	0.0008
40%	0.43900	0.31952	0.0022
60%	0.50742	0.33622	0.0020
80%	0.48262	0.26453	0.0033
100%	0.47820	0.20756	0.0070
110%	0.44817	0.16576	0.0026

TABLE 13(C) PURE COMPONENT COBALT-20%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.19794	0.16194	0.0036
40%	0.47344	0.21386	0.0037
60%	0.50091	0.22527	0.0090
80%	0.56748	0.22227	0.0038
100%	0.80611	0.25654	0.0185
110%	0.76617	0.24720	0.0567

TABLE 13(D) PURE COMPONENT NICKEL-20%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.30217	0.28306	0.0010
40%	0.44061	0.24118	0.0068
60%	0.47626	0.24100	0.0008
80%	0.53100	0.24633	0.0014
100%	0.94207	0.36953	0.0122
110%	0.74592	0.24659	0.0390

TABLE 13(E) COBALT IN MIXTURE, CO-20%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.11524	0.12362	0.0009
405	0.24500	0.22148	0.0019
60%	0.31067	0.26162	0.0009
80%	0.40846	0.29134	0.0014
100%	0.44014	0.25605	0.0042
110%	0.37755	0.25579	0.0042

TABLE 13(F) NICKEL IN MIXTURE, NI-20%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.09031	0.21286	0.0000
40%	0.17640	0.20476	0.0001
60%	0.14563	0.13502	0.0032
80%	0.46235	0.39957	0.0043
100%	0.42398	0.30751	0.0031
110%	1.47800	0.59190	0.0046

TABLE 13(G) PURE COMPONENT COBALT-40%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.59169	0.28850	0.0102
40%	1.0096	0.22158	0.0548
60%	1.25950	0.26855	0.0498
80%	1.38960	0.26066	0.0365
100%	1.46570	0.27400	0.0327
110%	1.41760	0.26534	0.0560

TABLE 13(H) PURE COMPONENT NICKEL-40%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.46739	0.42751	0.0008
20%	0.32498	0.19201	0.0052
40%	0.98794	0.25273	0.0359
60%	1.04610	0.26257	0.0184
80%	1.27700	0.29081	0.0728
100%	1.35520	0.28420	0.0297
110%	1.22180	0.24971	0.0143

TABLE 13(M) COBALT IN MIXTURE, CO-40%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.29044	0.24773	0.0003
40%	0.54650	0.26989	0.0079
60%	0.68163	0.28456	0.0140
80%	0.63402	0.24134	0.0674
100%	0.83693	0.29165	0.0134
110%	0.83605	0.28485	0.0100

TABLE 13(N) NICKEL IN MIXTURE, NI-40%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.44476	0.37036	0.0034
40%	0.52584	0.26885	0.0053
60%	0.53085	0.25836	0.0161
80%	0.74461	0.26748	0.0121
100%	0.89041	0.30424	0.0320
110%	1.14380	0.35189	0.0120

ss = sum of square of errors

TABLE 14(A) PURE COMPONENT COBALT-10%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.26941	038.84	0.0001
40%	0.22019	162.20	0.0159
60%	0.25478	115.74	0.0033
80%	0.27437	222.19	0.0021
100%	0.30461	218.01	0.0010
110%	0.30377	391.35	0.0028

TABLE 14(B) PURE COMPONENT NICKEL-10%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.26579	021.98	0.0001
40%	0.27643	037.49	0.0017
60%	0.30644	042.99	0.0001
80%	0.30961	073.69	0.0002
100%	0.32452	125.27	0.0009
110%	0.31500	321.65	0.0006

TABLE 14(C) PURE COMPONENT COBALT-20%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.14530	316.51	0.0041
40%	0.30436	266.52	0.0030
60%	0.31585	218.37	0.0085
80%	0.36209	173.38	0.0071
100%	0.44690	178.11	0.0445
110%	0.45627	183.70	0.0083

TABLE 14(D) PURE COMPONENT NICKEL-20%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.19366	053.23	0.0008
40%	0.27308	153.25	0.0085
60%	0.29645	163.72	0.0018
80%	0.31812	205.71	0.0263
100%	0.52378	038.51	0.0022
110%	0.58000	029.63	0.0630

TABLE 14(E) COBALT IN MIXTURE, CO-20%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.08451	708.27	0.0845
40%	0.13887	282.68	0.0010
60%	0.15490	320.20	0.0014
80%	0.19060	194.00	0.0008
100%	0.22446	239.59	0.0022
110%	0.18852	274.82	0.0023

TABLE 14(F) NICKEL IN MIXTURE NI-20%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.05583	188.98	0.0000
40%	0.10500	331.79	0.0000
60%	0.10577	457.89	0.0025
80%	0.20450	046.88	0.0047
100%	0.20158	119.12	0.0012
110%	0.46425	023.92	0.0062

TABLE 14(G) PURE COMPONENT COBALT-40%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.33647	100.66	0.0159
40%	0.59346	277.23	0.0044
60%	0.67312	184.52	0.0413
80%	0.72798	251.12	0.0141
100%	0.74251	227.47	0.0281
110%	0.74048	226.99	0.0522

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TABLE 14(H) PURE COMPONENT NICKEL-40%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.21200	332.80	0.0729
40%	0.56231	142.92	0.0700
60%	0.54840	265.66	0.0223
80%	0.70340	125.86	0.0603
100%	0.65530	146.86	0.0520
110%	0.68910	178.19	0.0160

TABLE 14(M) COBALT IN MIXTURE, CO-40%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.14790	329.43	0.0004
40%	0.24586	284.91	0.0025
60%	0.30510	251.79	0.0095
80%	0.29310	732.59	0.0026
100%	0.34510	350.12	0.0064
110%	0.34767	356.94	0.0059

TABLE 14(N) NICKEL IN MIXTURE NI-40%D2EHPA

sat. with NH_3	parm. theta1	parm. theta2	ss
20%	0.18410	089.721	0.0058
40%	0.24790	270.83	0.0017
60%	0.2771	195.13	0.0108
80%	0.33940	374.53	0.0055
100%	0.39818	168.88	0.0150
110%	0.42806	167.28	0.0039

ss = sum of square of errors

TABLE 15(A) COBALT IN MIXTURE, CO-20%D2EHPA

NH_3 level	theta1	theta2	theta3	theta4
20%	1.0053	-0.02001	0.00458	0.000047
40%	1.7084	0.05662	0.42510	0.020870
60%	0.1320	-1.60100	-1.80800	0.022900
80%	3.7367	0.27636	0.90511	0.030300
100%	1.4750	-0.01670	0.26200	0.013600
110%	2.6360	0.28830	0.77962	0.014762

TABLE 15(B) NICKEL IN MIXTURE, NI-20%D2EHPA

NH_3 level	theta1	theta2	theta3	theta4
20%	1.4874	0.15233	0.53820	-0.002600
40%	0.5659	0.00236	-0.39615	-0.023890
60%	-7.0580	-3.96860	-5.43000	-0.040400
80%	0.7974	0.04040	-0.24020	-0.006170
100%	1.1061	0.09771	0.17920	-0.004561
110%	0.9316	-0.11030	-0.27964	0.007390

TABLE 15(C) COBALT IN MIXTURE, CO-40%D2EHPA

NH_3 level	theta1	theta2	theta3	theta4
20%	0.5607	-0.39760	-0.33440	-0.017500
40%	1.1351	0.00820	0.17625	0.001704
60%	0.5600	-0.76320	-0.86350	0.042350
80%	1.2696	-0.02000	0.28040	0.007020
100%	2.3330	0.38712	0.74281	0.004544
110%	2.2391	0.22516	0.75857	0.010860

TABLE 15(D) NICKEL IN MIXTURE, NI-40%D2EHPA

NH_3 level	theta1	theta2	theta3	theta4
20%	0.2955	-1.45962	-0.91723	0.043630
40%	1.0364	0.00119	0.14030	-0.005584
60%	3.6270	0.53060	0.98108	0.026570
80%	0.7640	0.18825	-0.01820	-0.037040
100%	1.1089	0.28734	-0.00224	-0.012500
110%	1.7077	0.14931	0.11190	0.022800

TABLE 16(A) PURE COMPONENT COBALT-20%D2EHPA

sat. with NH_3	parameter a1	parameter a2	parameter a3
20%	4.934	-11.652	36.790
40%	6.815	-8.562	18.184
60%	7.073	-2.727	-13.873
80%	7.351	-7.502	1.542
100%	7.704	-15.242	76.413
110%	8.288	-22.269	113.279

TABLE 16(B) PURE COMPONENT NICKEL-20%D2EHPA

sat. with NH_3	parameter a1	parameter a2	parameter a3
20%	5.237	-2.963	9.531
40%	5.956	-0.294	-5.070
60%	6.908	-4.343	-9.320
80%	7.423	-0.183	-3.230
100%	8.017	-11.760	21.120
110%	8.618	-13.714	16.342

TABLE 16(C) COBALT IN MIXTURE, CO-20%D2EHPA

sat. with NH_3	parameter a1	parameter a2	parameter a3
20%	4.467	-6.59	11.781
40%	6.003	-10.502	-20.470
60%	6.800	-19.280	121.880
80%	7.[illegible]81	-42.492	384.660
100%	8.267	-41.800	350.793
110%	9.270	-79.467	744.803

TABLE 16(D) NICKEL IN MIXTURE, NI-20%D2EHPA

sat. with NH_3	parameter a1	parameter a2	parameter a3
20%	4.636	-8.866	20.624
40%	5.981	-3.280	-102.900
60%	6.822	-18.632	113.600
80%	8.289	-45.627	358.740
100%	8.895	-67.790	605.186
110%	9.596	-89.163	821.411

TABLE 16(E) PURE COMPONENT COBALT-40%D2EHPA

sat. with NH_3	parameter a1	parameter a2	parameter a3
20%	4.463	-13.069	58.342
40%	6.485	-13.263	47.596
60%	6.685	-7.679	-30.329
80%	7.409	-19.755	128.152
100%	8.026	-23.505	172.781
110%	8.256	-22.525	137.345

TABLE 16(F) PURE COMPONENT NICKEL-40%D2EHPA

sat. with NH_3	parameter a1	parameter a2	parameter a3
20%	4.387	-9.601	42.151
40%	4.914	-10.590	35.300
60%	6.123	-9.676	48.469
80%	6.552	-13.083	78.036
100%	6.934	-13.794	77.770
110%	7.315	-24.164	143.912

TABLE 16(G) COBALT IN MIXTURE, CO-40%D2EHPA

sat. with NH_3	parameter a1	parameter a2	parameter a3
20%	3.937	-3.701	-84.810
40%	4.944	35.92	-974.772
60%	6.140	-45.941	565.491
80%	5.879	-44.411	581.685
100%	6.174	-19.558	-39.211
110%	7.093	-40.950	100.382

TABLE 16(H) NICKEL IN MIXTURE, NI-40%D2EHPA

sat. with NH_3	parameter a1	parameter a2	parameter a3
20%	3.946	0.731	-129.613
40%	4.681	15.982	-228.678
60%	6.206	-39.632	392.432
80%	5.928	-43.706	512.910
100%	6.279	-37.970	326.610
110%	7.153	-40.234	115.140

TABLE 17(A) APPARENT EQUILIBRIUM CONSTANT-20%D2EHPA

sat. with NH_3	pure component cobalt	pure component nickel
20%	362.98	172.31
40%	229.00	114.07
60%	141.03	69.63
80%	95.52	31.26
100%	10.79	5.37
110%	9.64	4.69

TABLE 17(B) APPARENT EQUILIBRIUM CONSTANT-20%D2EHPA

sat. with NH_3	cobalt in mixture	nickel in mixture
20%	62.15	11.10
40%	21.60	28.87
60%	9.51	5.92
80%	4.53	2.03
100%	2.60	1.63
110%	2.51	1.02

TABLE 17(C) APPARENT EQUILIBRIUM CONSTANT-40%D2EHPA

sat. with NH_3	pure component cobalt	pure component nickel
20%	151.38	229.46
40%	34.50	23.43
60%	11.86	21.68
80%	16.71	3.70
100%	11.23	7.08
110%	4.65	16.92

TABLE 17(D) APPARENT EQUILIBRIUM CONSTANT-40%D2EHPA

sat. with NH_3	cobalt in mixture	nickel in mixture
20%	34.89	40.29
40%	4.41	7.95
60%	1.21	0.79
80%	3.46	2.12
100%	1.16	0.58
110%	0.78	0.80

TABLE 18 (A) SEPARATION FACTOR FOR CO-NI PAIR-40%D2EHPA

No.	A/O	20% sat. with NH K	40% sat. with NH_3 K
1	0.5	0.924	0.613
2	1.0	1.810	0.923
3	2.0	1.706	1.332
4	3.0	1.344	0.571
5	4.0	1.341	1.435
6	6.0	0.974	1.330
7	8.0	0.800	1.102
8	10.0	0.757	1.050

TABLE 18 (B) SEPARATION FACTOR FOR CO-NI PAIR-40%D2EHPA

No.	A/O	60% sat. with NH K	80% sat. with NH_3 K
1	0.5	1.882	1.800
2	1.0	1.278	2.708
3	2.0	1.882	1.197
4	3.0	1.623	1.058
5	4.0	1.379	1.022
6	6.0	1.582	0.966
7	8.0	1.462	1.073
8	10.0	1.437	0.992

TABLE 18 (C) SEPARATION FACTOR FOR CO-NI PAIR-40%D2EHPA

No.	A/O	100% sat. with NH K	110% sat. with NH_3 K
1	0.5	6.725	0.883
2	1.0	0.550	5.493
3	2.0	0.550	1.585
4	3.0	0.540	1.261
5	4.0	1.882	1.145
6	6.0	1.223	0.930
7	8.0	0.770	0.886
8	10.0	0.850	1.007

TABLE 18 (D) SEPARATION FACTOR FOR CO-NI PAIR-20%D2EHPA

No.	A/O	20% sat. with NH K	40% sat. with NH_3 K
1	0.5	1.556	1.016
2	1.0	2.256	1.197
3	2.0	2.429	1.611
4	3.0	2.464	1.790
5	4.0	2.967	1.775
6	6.0	3.691	1.276
7	8.0	4.225	1.628
8	10.0	3.346	1.399

TABLE 18(E) SEPARATION FACTOR FOR CO-NI PAIR-20%D2EHPA

No.	A/O	40% sat. with NH K	60% sat. with NH_3 K
1	0.5	1.536	1.536
2	1.0	1.727	1.840
3	2.0	1.165	1.333
4	3.0	1.327	1.203
5	4.0	1.866	1.303
6	6.0	1.772	1.183
7	8.0	2.488	1.256
8	10.0	1.445	1.136

TABLE 18(F) SEPARATION FACTOR FOR CO-NI PAIR-20%D2EHPA

No.	A/O	100% sat. with NH K	110% sat. with NH_3 K
1	0.5	1.536	2.988
2	1.0	3.241	1.733
3	2.0	2.100	1.716
4	3.0	1.544	1.044
5	4.0	1.300	0.760
6	6.0	1.710	0.723
7	8.0	1.106	0.540
8	10.0	1.142	0.592

TABLE 19(A) VISCOSITY OF THE ORGANIC PHASE-20%D2EHPA

20% equilibration with NH_3

No.	metal loading in organic phase	viscosity (cp)
1	0.05942	2.20
2	0.09430	2.62
3	0.09687	2.65
4	0.12525	2.80
5	0.13379	2.86
6	0.13847	3.01

TABLE 19(B) VISCOSITY OF THE ORGANIC PHASE-20%D2EHPA

40% equilibration with NH_3

No.	metal loading in organic phase	viscosity (cp)
1	0.04500	4.51
2	0.08911	4.64
3	0.15712	4.96
4	0.19497	5.21
5	0.19714	5.27
6	0.22427	5.30

TABLE 19(C) VISCOSITY OF THE ORGANIC PHASE-20%D2EHPA

60% equilibration with NH_3

No.	metal loading in organic phase	viscosity (cp)
1	0.08571	4.51
2	0.15724	4.59
3	0.20354	4.93
4	0.23364	4.85
5	0.26092	5.12
6	0.27634	5.21

TABLE 19(D) VISCOSITY OF THE ORGANIC PHASE-20%D2EHPA

80% equilibration with NH_3

No.	metal loading in organic phase	viscosity (cp)
1	0.08568	4.61
2	0.14574	5.01
3	0.26774	5.34
4	0.30170	5.39
5	0.32297	5.63
6	0.32818	6.78

TABLE 19(E) VISCOSITY OF THE ORGANIC PHASE-20%D2EHPA

100% equilibration with NH_3

No.	metal loading in organic phase	viscosity (cp)
1	0.08571	4.44
2	0.08823	5.11
3	0.30681	5.62
4	0.36886	5.90
5	0.39140	6.36
6	0.40026	6.83

TABLE 19(F) VISCOSITY OF THE ORGANIC PHASE-20%D2EHPA

110% equilibration with NH_3

No.	metal loading in organic phase	viscosity (cp)
1	0.08405	4.47
2	0.16620	3.67
3	0.28938	5.60
4	0.34691	5.63
5	0.44644	6.07
6	0.52362	6.92

TABLE 19(G) VISCOSITY OF THE ORGANIC PHASE-40%D2EHPA

20% equilibration with NH_3

No.	metal loading in organic phase	viscosity (cp)
1	0.16245	6.94
2	0.26400	7.10
3	0.26184	7.16
4	0.31630	12.16
5	0.32649	16.87
6	0.34011	20.14

TABLE 19(H) VISCOSITY OF THE ORGANIC PHASE-40%D2EHPA

40% equilibration with NH_3

No.	metal loading in organic phase	viscosity (cp)
1	0.17005	18.15
2	0.32723	23.63
3	0.42344	27.53
4	0.44373	30.61
5	0.44544	34.55
6	0.46585	40.65

TABLE 19(M) VISCOSITY OF THE ORGANIC PHASE-40%D2EHPA

60% equilibration with NH_3

No.	metal loading in organic phase	viscosity (cp)
1	0.16985	26.80
2	0.45614	36.81
3	0.50833	44.16
4	0.51930	49.23
5	0.52020	51.44
6	0.53723	57.71

TABLE 19(N) VISCOSITY OF THE ORGANIC PHASE-40%D2EHPA

80% equilibration with NH_3

No.	metal loading in organic phase	viscosity (cp)
1	0.17470	31.90
2	0.48210	43.00
3	0.54518	48.54
4	0.58490	53.33
5	0.60957	61.19
6	0.65889	67.75

TABLE 19(P) VISCOSITY OF THE ORGANIC PHASE-40%D2EHPA

100% equilibration with NH_3

No.	metal loading in organic phase	viscosity (cp)
1	0.17138	37.80
2	0.49101	44.32
3	0.58660	50.61
4	0.63581	63.32
5	0.66650	68.54
6	0.73203	73.34

TABLE 19(Q) VISCOSITY OF THE ORGANIC PHASE-40%D2EHPA

110% equilibration with NH_3

No.	metal loading in organic phase	viscosity (cp)
1	0.17342	41.66
2	0.48967	47.38
3	0.58320	54.87
4	0.66822	66.76
5	0.72100	69.38
6	0.71838	78.19

Viscosity of unloaded organic phase

20% D2EHPA	2.12 cp
40% DEEHPA	6.38 cp

TABLE 20(A) INTERFACIAL TENSION-20%D2EHPA

20% equilibration with NH_3

No.	metal loading in organic phase	interfacial tension (dynes/cm)
1	0.05942	0.500
2	0.09687	0.950
3	0.12525	1.625
4	0.13379	2.000
5	0.13842	2.000

TABLE 20(B) INTERFACIAL TENSION-20%D2EHPA

40% equilibration with NH_3

No.	metal loading in organic phase	interfacial tension (dynes/cm)
1	0.04500	0.250
2	0.08911	0.750
3	0.15712	1.500
4	0.19714	2.250
5	0.22427	2.500

TABLE 20(C) INTERFACIAL TENSION-20%D2EHPA

60% equilibration with NH_3

No.	metal loading in organic phase	interfacial tension (dynes/cm)
1	0.08571	0.875
2	0.15724	2.000
3	0.23364	2.250
4	0.26092	2.260
5	0.27634	2.500

TABLE 20(D) INTERFACIAL TENSION-20%D2EHPA

80% equilibration with NH_3

No.	metal loading in organic phase	interfacial tension (dynes/cm)
1	0.08568	0.500
2	0.26774	1.500
3	0.30170	2.500
4	0.32297	2.500
5	0.32818	2.500

TABLE 20(E) INTERFACIAL TENSION-20%D2EHPA

100% equilibration with NH_3

No.	metal loading in organic phase	interfacial tension (dynes/cm)
1	0.08571	2.250
2	0.08823	2.250
3	0.30681	2.500
4	0.39140	3.250
5	0.40026	3.250

TABLE 20(F) INTERFACIAL TENSION-20%D2EHPA

110% equilibration with NH_3

No.	metal loading in organic phase	interfacial tension (dynes/cm)
1	0.08405	1.500
2	0.16620	2.250
3	0.34961	2.900
4	0.44644	3.250
5	0.52362	3.500

TABLE 20(G) INTERFACIAL TENSION-40%D2EHPA

20% equilibration with NH_3

No.	metal loading in organic phase	interfacial tension (dynes/cm)
1	0.16245	0.75
2	0.26400	2.500
3	0.26184	3.000
4	0.31630	3.000
5	0.32649	3.500
6	0.34011	4.000

TABLE 20(H) INTERFACIAL TENSION-40%D2EHPA

40% equilibration with NH_3

No.	metal loading in organic phase	interfacial tension (dynes/cm)
1	0.17005	0.500
2	0.32723	2.000
3	0.42344	3.000
4	0.44373	3.500
5	0.44544	4.000
6	0.46585	4.000

TABLE 20(M) INTERFACIAL TENSION-40%D2EHPA

60% equilibration with NH_3

No.	metal loading in organic phase	interfacial tension (dynes/cm)
1	0.16985	1.000
2	0.45614	3.000
3	0.50833	3.000
4	0.51930	4.000
5	0.52020	4.500
6	0.53723	4.500

TABLE 20(N) INTERFACIAL TENSION-40%D2EHPA

80% equilibration with NH_3

No.	metal loading in organic phase	interfacial tension (dynes/cm)
1	0.17470	2.000
2	0.48210	3.500
3	0.54578	3.500
4	0.58490	4.000
5	0.60957	4.000
6	0.65884	4.500

TABLE 20(P) INTERFACIAL TENSION-40%D2EHPA

100% equilibration with NH_3

No.	metal loading in organic phase	interfacial tension (dynes/cm)
1	0.17138	3.000
2	0.49101	3.225
3	0.58660	4.250
4	0.63581	4.750
5	0.66650	5.500
6	0.73203	6.250

TABLE 20(Q) INTERFACIAL TENSION-40%D2EHPA

110% equilibration with NH_3

No.	metal loading in organic phase	interfacial tension (dynes/cm)
1	0.17342	4.000
2	0.48967	5.500
3	0.58320	6.000
4	0.66822	7.000
5	0.71838	7.000
6	0.72100	7.000

Interfacial ternsion between unloaded aqueous phase and organic phase

20% D2EHPA	0.050 dynes/cm
40% D2EHPA	0.025 dynes/cm

TABLE 21 COMPARISON OF STANDARD DEVIATIONS

Fig. no.	system	std. deviation Langmuir isotherm	std. deviation Freundlich isotherm
14	Co1020	0.0041	0.0153
15	Ni1040	0.0168	0.0192
16	Ni2020	0.0116	0.0130
17	CN2040	0.0130	0.0178
18	CN2080	0.0116	0.0153
19	CN20100	0.0192	0.0265
20	NC20100	0.0141	0.0227
21	Co4040	0.0271	0.0956
22	NC4040	0.0168	0.0297