Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Diluent effect on the solvent extraction rate of copper

Pardon K. Kuipa[a]; Michael A. Hughes[b]
[a] Department of Chemical Engineering, National University of Science and Technology, Bulawayo, Zimbabwe [b] Department of Chemical Engineering, University of Bradford, Bradford, West Yorkshire, UK

To cite this Article Kuipa, Pardon K. and Hughes, Michael A.(2002) 'Diluent effect on the solvent extraction rate of copper', Separation Science and Technology, 37: 5, 1135 — 1152
To link to this Article: DOI: 10.1081/SS-120002246
URL: http://dx.doi.org/10.1081/SS-120002246

SEPARATION SCIENCE AND TECHNOLOGY, 37(5), 1135–1152 (2002)

DILUENT EFFECT ON THE SOLVENT EXTRACTION RATE OF COPPER

Pardon K. Kuipa[1,*] **and Michael A. Hughes**[2]

[1]Department of Chemical Engineering, National University
of Science and Technology, P.O. Box AC 939, Ascot,
Bulawayo, Zimbabwe
[2]Department of Chemical Engineering, University of
Bradford, Bradford BD7 1DP, West Yorkshire, UK

ABSTRACT

The effect of diluents on the rate of extraction of copper using di-2-ethylhexylphosphoric acid and 5-nonylsalixylaldoxime as extractants has been explored. The metal extraction rates using a number of extractant/diluent combinations have been related to some physical property of the diluents, i.e., the dipole moment, solubility parameter, dielectric constant, and interfacial surface pressure. Diluent properties that favor interaction between the extractant and the diluent result in lower metal extraction rates. The nature of interaction between the extractant and both aromatic and aliphatic diluents may be described in terms of physical parameters. The choice of the diluent is shown to affect the rate of metal extraction. Our results confirm that in order to achieve good kinetics, aliphatic diluents should be employed, but it is also known that these diluents should contain a certain percentage of aromatics in order to limit the extractant soluble losses to the

---

*Corresponding author. Fax: (263) 964-363; E-mail: nustelec@esanet.zw

www.dekker.com

aqueous effluent. Satisfactory linear correlations were observed between the extraction flux and a few diluent parameters, namely: dipole moment, solubility parameter, interfacial surface pressure, and the extractant distribution constant.

Key Words: Diluent effect; Interfacial surface pressure; Solubility parameter; Extractant distribution coefficient; Dipole moment; Dielectric constant

INTRODUCTION

In the solvent extraction of metals, the solvent is made up of an extractant dissolved in a diluent since many extractants are viscous materials in their undiluted form. In some cases a third component, a modifier, may be added to the organic phase to prevent third phase formation. Chemical energy is spent in transferring the metal from the aqueous phase and it would seem advantageous to use the extractant in a highly concentrated form, but practical problems suggest that 10–40% extractant is often optimum. At higher extractant loadings, the concentration effect of the solvent on the extraction is enhanced but other features such as slow rates of mass transfer might then develop. To overcome viscosity and mass transfer problems, some plants may be operated purposely at temperatures greater than ambient. In this case, diluents with sufficiently high flash points may be required. In choosing a solvent for a particular liquid extraction process, there are several principles that can be used as a guide (1,2). These include low solubility in the aqueous phase, low toxicity, good extraction and stripping characteristics, consistence in quality, high selectivity, high distribution coefficient for the solute to be removed, low volatility and low flammability, high resistance to degradation by temperature or chemicals, easy separation of the extract phase from the aqueous phase, easy commercial availability, and the ability to interface with the remainder of the hydrometallurgical flowsheet. It is known that the diluent does not act merely as a carrier but also participates in the extraction process since rates of metal extraction can often be related to the diluent and the modifier selection (3–6). Ritcey and Lucas (3), for example, demonstrated a relationship between the extractant performance and the solubility parameter of the diluent. Smelov et al. (4) also observed that the value of the extraction constant for zinc using di-2-ethylhexyl phosphoric acid (D2EHPA) as an extractant decreased with increasing ability of the solvent to solvate the polar extractant. In this work, the effect of the diluents on the rate of extraction of copper using D2EHPA and 5-nonylsalixylaldoxime (P50) as extractants has been explored further. The rates of metal extraction were measured with a rotating diffusion cell (RDC). It is expected that the diluent will affect the rate by modifying the extent to which the reagent is present in the preferred form in the organic phase. The solvation of the extractant in the organic phase to form extractant–diluent species is expected to result in a lower concentration of "free extractant" within this phase and thus affect the partition equilibrium. The end result will be a lower concentration of the extractant in the region close to the liquid–liquid interface; i.e., less extractant will be available for the reaction resulting in a lower extraction rate.

In this work, the metal extraction rates of a particular extractant in different diluents have been compared more closely to some physical property of the diluents, e.g., the dipole moment, solubility parameter, dielectric constant interfacial surface pressure, and the Schmidt–Marcus diluent parameter (DP). The Schmidt–Marcus DP is an empirical DP that was introduced by Schmidt (7) and later expanded by Marcus (8).

The dipole moment may be used to characterize the tendency of the molecules of a substance to deviate from the simple intermolecular attraction that is characteristic of the spherically symmetrical nonpolar molecules. Thus, the dipole moment may be used as a qualitative measure of the strength of the intermolecular attraction between the extractant and the diluent. Extractants that were employed in this study are essentially polar because of the presence of O–H and N–OH groups in P50 and P = O, C–O–P and P–OH groups in D2EHPA. Diluents with a high dipole moment are expected to interact more strongly with the extractant. As a general rule, nonpolar molecules interact more strongly with nonpolar molecules and vice versa. The strong interaction between the diluent and the extractant is expected to impose an additional energy barrier for the extractant to leave the diluent environment and take part in metal complex formation.

The dielectric constant (relative permitivity) of a substance is large if its molecules are polar and highly polarizable. Generally, aliphatic diluents have a lower dielectric constant than the aromatic diluents (heptane has a dielectric constant of 1.92 while that for toluene is 2.38 (9). Diluents with a higher dielectric constant will interact more with water, e.g., it is known that the π electrons of aromatic rings interact with water (10). Interaction with water will lead to the possible co-extraction of water together with the metal complex from the interfacial aqueous region. This reduces the capacity of the solvent and should result in less extractant being available for reaction at the aqueous boundary layer that is adjacent to the monomolecular liquid–liquid interface.

The solubility parameter is a measure of the extent to which the molecules of a diluent will form a stable homogeneous mixture with the molecules of the extractant. Thus, diluents and extractants with similar solubility parameters will form good mixtures. Strong interactions between the extractant molecules themselves or with the diluent molecules result in a lower concentration of the free extractant being available for reaction at the liquid–liquid interface. Most commercial diluents are a mixture of straight-chain paraffins, branched-chain paraffins, cycloparaffins, dicycloparaffins, and some aromatic components. The aromatic content of the commercial diluent may vary from virtually nil to aromatic being the major constituent. In this study, *n*-heptane represents the straight-chain paraffins, methylcyclohexane represents the cycloparaffins, decalin represents the dicycloparaffins (naphthenes) and toluene represents the aromatic components. *n*-Octanol and isopropyl ether were included to provide a wider range of the studied DPs, rather than for their potential suitability as solvent extraction diluents.

EXPERIMENTAL PROCEDURE

Reagents

All inorganic compounds and reagents were of pure analytical reagent grade. The diluents used were *n*-heptane, methylcyclohexane, toluene, decalin, *n*-octanol, and isopropyl ether. Di-2-ethylhexylphosphoric acid was 99.1% pure and P50 was 98% pure. Water for interfacial tension measurements was double distilled.

Measurement of Interfacial Tension

The interfacial tensions for the extractants in different diluents were measured by the drop volume method (11). In these experiments, great care was taken to clean all apparatus, e.g., with chromic acid followed by distilled water washes. Interfacial tensions of solutions were measured at a constant pH and compared to the rate of extraction when the same conditions of pH are imposed.

Extractant 'Solubility' in the Aqueous Phase

The solubility of D2EHPA in water was determined by contacting 0.05 *M* solutions of the extractant in the appropriate diluent, with water at pH 4.5, followed by the total oxidation of the aqueous phase samples by potassium persulphate. The liberated phosphate ion was then determined spectrophotometrically as the molybdivanado-phosphoric acid complex at 460 nm with a 4 cm pathlength cell (12). The calibration graph was plotted on results that were obtained by converting known amounts of potassium dihydrogen orthophosphate into the molybdivanado-phosphoric acid complex. Blank solutions were prepared by contacting the appropriate diluent (without extractant) with water at pH 4.5 and subsequent treatment of the resultant aqueous sample as outlined above.

In the case of P50, aqueous washing of the 0.05 *M* solvent phase (diluent + P50) was first carried out in order to minimize the presence of any low molecular weight oximes. The Pye–Unicam ultraviolet spectrophotometer (SP8-100) was used to scan the wavelengths of the aqueous solutions from the shakeouts of 0.05 *M* solutions of the P50 in the appropriate diluent and water at pH 4.5. A calibration was carried out on the areas under the peaks between 400 and 258 nm. Blank solution was prepared by subjecting aqueous shakeouts of pure diluents and water to the same routine as outlined for P50.

Kinetic Experiments

The rates of metal extraction were studied with the use of an RDC. The technique together with auxiliary equipment used to measure the rate of proton release into the aqueous phase has been described elsewhere (1,13).

RESULTS AND DISCUSSION

In this work, an attempt was made to relate the extraction flux to the above-mentioned DPs. These parameters have been regarded as a qualitative measure of the strength of the intermolecular attraction between the diluent molecules and those of the extractant.

Effect of Diluent Dipole Moment

The rate of copper extraction is shown to decrease with the increasing dipole moment (Figs. 1 and 2). When decalin is excluded, linear relations between the extraction flux and the dipole moment are obtained. In the case of extraction with P50 as extractant the linear relation is $y = -6.2597x + 12.509$ with a least-squares correlation coefficient, $R^2 = 0.9983$. For extraction with D2EHPA the relation is a bit poorer and $y = -1.3247x + 5.8975$ and $R^2 = 0.7428$. In these expressions, y is the extraction flux and x is the DP under consideration, i.e., the dipole moment.

Diluents with a high dipole moment tend to "interact" with the extractant more than those with a low dipole moment [the dipole moment for *n*-heptane is zero whilst that for toluene is 0.36 Debye (9)].

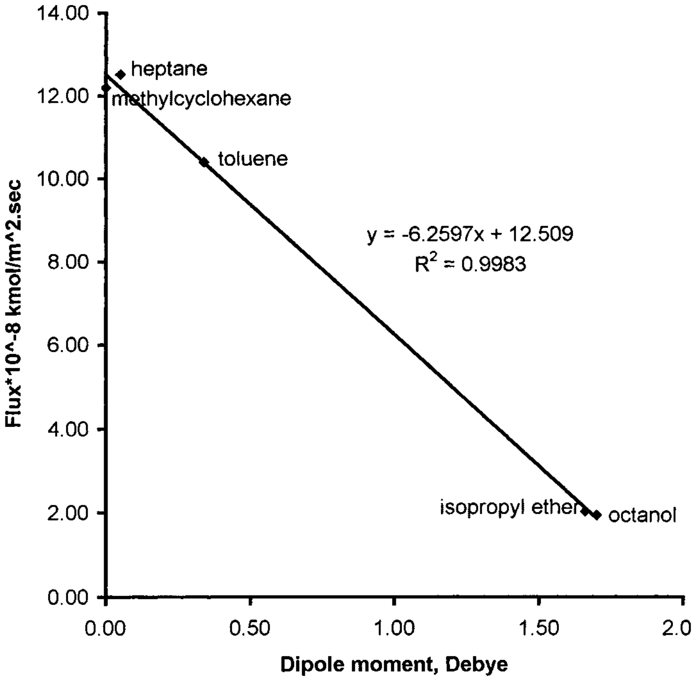

Figure 1. The effect of diluent dipole moment on the extraction flux for the Cu^{2+}-SO_4^{2-}/P50/diluent system ($C_{P50} = 0.05\,M$, $C_{Cu^{2+}} = 0.01\,M$, pH = 4.5, $T = 25°C$).

Effect of Diluent Dielectric Constant and the Schmidt–Marcus Diluent Parameter

The rate decreases exponentially up to a limit as the dielectric constant of a diluent becomes lower. The decrease is nonlinear and no useful correlation between the extraction flux and the diluent dielectric constant was obtained. No useful trend was observed when the Schmidt–Marcus DP is used to characterize our diluents probably because of the seven diluents used in our study, only four of these have their parameters listed in the literature.

Effect of Diluent Solubility Parameter

The effect of the diluent solubility parameter on extraction rates is shown in Figs. 3 and 4. A near linear relation is observed between the extraction flux and the diluent solubility parameter. Thus, $y = -4.0056x + 43.121$ ($R^2 = 0.8625$)

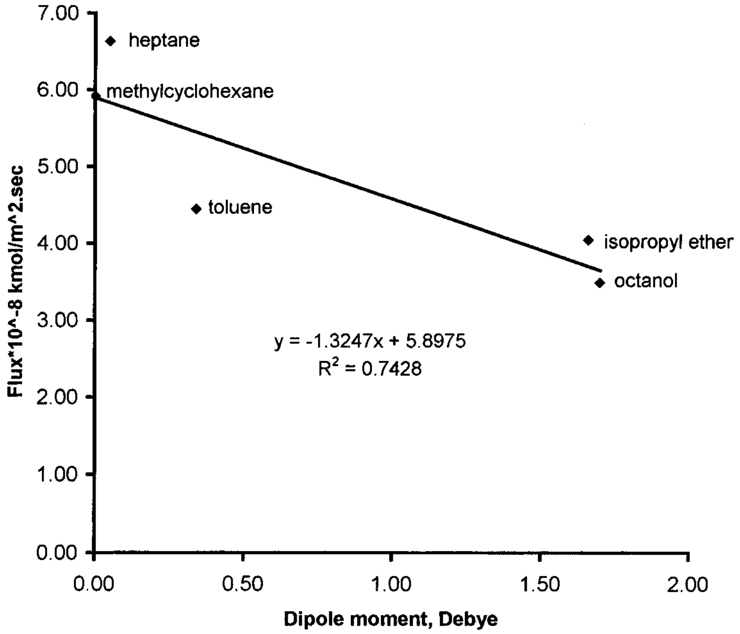

Figure 2. The effect of diluent dipole moment on the extraction flux for the Cu^{2+}-SO_4^{2-}/D2EHPA/diluent system ($C_{\mathrm{D2EHPA}} = 0.05\,M$, $C_{\mathrm{Cu^{2+}}} = 0.01\,M$, pH = 4.5, $T = 25°\mathrm{C}$).

for extraction with P50 and $y = -1.1597x + 14.909$ ($R^2 = 0.8667$) for extraction with D2EHPA. Isopropyl ether was excluded from the correlations due to its low solubility parameter (7.0) and low observed extraction rate. With the exception of isopropyl ether, extraction rates are lower for diluents with higher solubility parameters. Thus, the flux vs. solubility parameter trend in our work suggest that the extractant molecule does not readily "leave" an aromatic diluent environment for the aqueous phase due to the strong interaction between the aromatic diluent and extractant molecules. Interpretation of the relation between extraction rates and solubility parameters may also be made by use of the equation that was originally derived by Hildebrand (14), using the regular solution theory and later used by Kolarik et al. (15–17)

$$\frac{\log D}{\delta_{\mathrm{aq}} - \delta_{\mathrm{org}}} = \frac{V_{\mathrm{HR}}}{2.30RT}\delta'_{\mathrm{org}} + \frac{V_{\mathrm{HR}}}{2.30RT}(V_{\mathrm{org}}^{-1} - V_{\mathrm{aq}}^{-1}) \qquad (1)$$

where $\delta'_{\mathrm{org}} = \delta_{\mathrm{org}} + RT(\delta_{\mathrm{aq}} - \delta_{\mathrm{org}})^{-1}(V_{\mathrm{org}}^{-1} - V_{\mathrm{aq}}^{-1})$ is a modified solubility parameter ($R = 1.98\,\mathrm{cal/mol\,K}$); δ_{aq}, δ_{org}, and δ_{HR} are the solubility parameters of the aqueous phase, diluent, and extractant, respectively [Hildebrands =

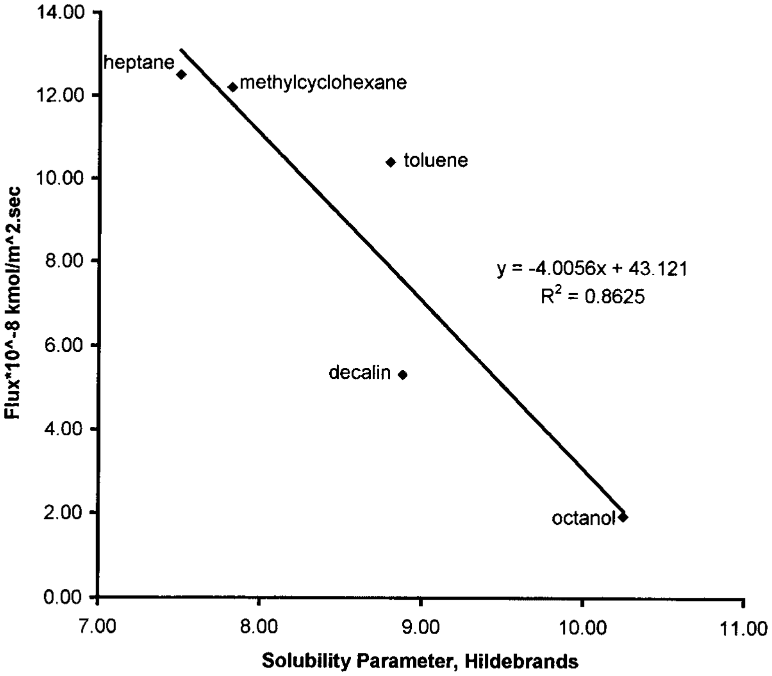

Figure 3. The effect of diluent solubility parameter on the extraction flux for the Cu^{2+}-SO_4^{2-}/P50/diluent system ($C_{P50} = 0.05\,M$, $C_{Cu^{2+}} = 0.01\,M$, pH = 4.5, $T = 25°C$).

$(cal/cm^3)^{0.5}$]; V_{aq}, V_{org}, and V_{HR} are molar volumes (cm^3/mol); and D is the distribution coefficient of the extractant (in terms of mole fractions) between the aqueous and organic phase. D varies with the type of diluent employed. The plot $\log D(\delta_{aq} - \delta_{org})^{-1}$ vs. δ'_{org} is a straight line with slope $V_{HR}/2.30RT$ where V_{HR} is the molar volume of the extractant molecule. Positive deviation from this line will indicate the formation of molecular complexes of the extractant with the diluent. Negative deviation from the line does not indicate formation of the diluent–extractant complexes and is of no consequence in this analysis. The solubility parameter of the aqueous phase was taken as $\delta_{aq} = 15.5\,cal/cm^3$ (16). This value is lower than the reported value for pure water, $\delta_{H_2O} = 23.8\,cal/cm^3$ (18). The solubility parameter of the organic phase, δ_{org}, was taken as that of the pure diluent since the concentration of the extractant in the diluent was low ($0.05\,M$) for this study. The molar volume of an extractant molecule was calculated by the method of LeBas (19) using incremental atomic volume.

Thus, the molar volumes (V_{HR}) of P50 and D2EHPA were calculated to be 345.6 cm^3/mol and 426.5 cm^3/mol, respectively.

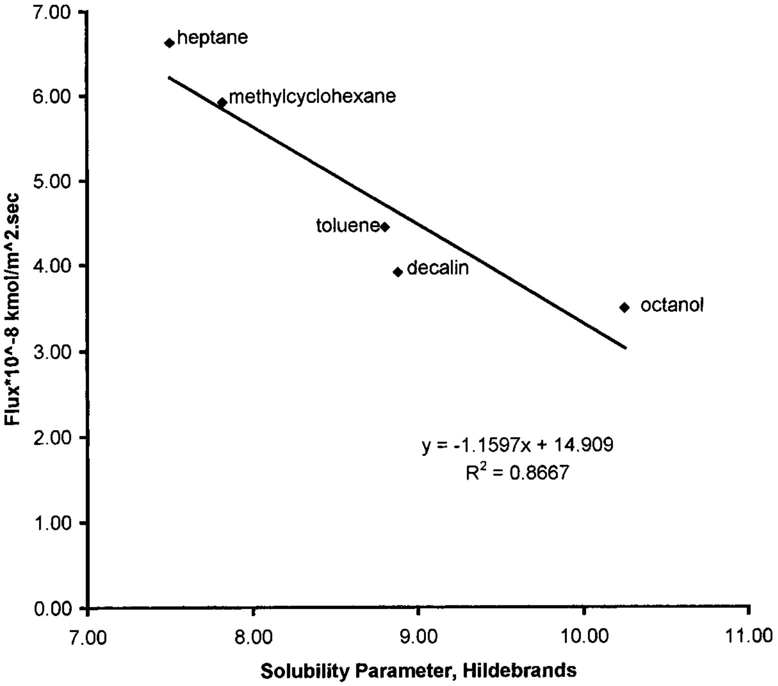

Figure 4. The effect of diluent solubility parameter on the extraction flux for the Cu^{2+}-SO_4^{2-}/D2EHPA/diluent system ($C_{D2EHPA} = 0.05\,M$, $C_{Cu^{2+}} = 0.01\,M$, pH $= 4.5$, $T = 25°C$).

The plot $\log D(\delta_{aq} - \delta_{org})^{-1}$ vs. δ'_{org} has lines of best fit with fixed gradients ($= V_{HR}/2.3RT$) of 0.25 and 0.31 for P50 (Fig. 5) and D2EHPA (Fig. 6) as extractant, respectively. From Figs. 5 and 6, it can be seen that only isopropyl ether exhibits appreciable positive deviation from the line of expected slope [Eq. (1)]. Only in the case of this diluent can it be assumed that interaction with both extractants plays a significant role and determines the value of the partition coefficient. In the case of the other diluents, it may be assumed that chemical interaction with P50 and D2EHPA is of no significance and the partition coefficient will be determined by the value of the activity coefficients of the extractant monomeric species in these diluents. These conclusions are semi-quantitative since the influence of the dipole moment on the activity of HR species in various diluents has not been included and the presence of water in the organic phase would have to be included if more precise conclusions were to be drawn.

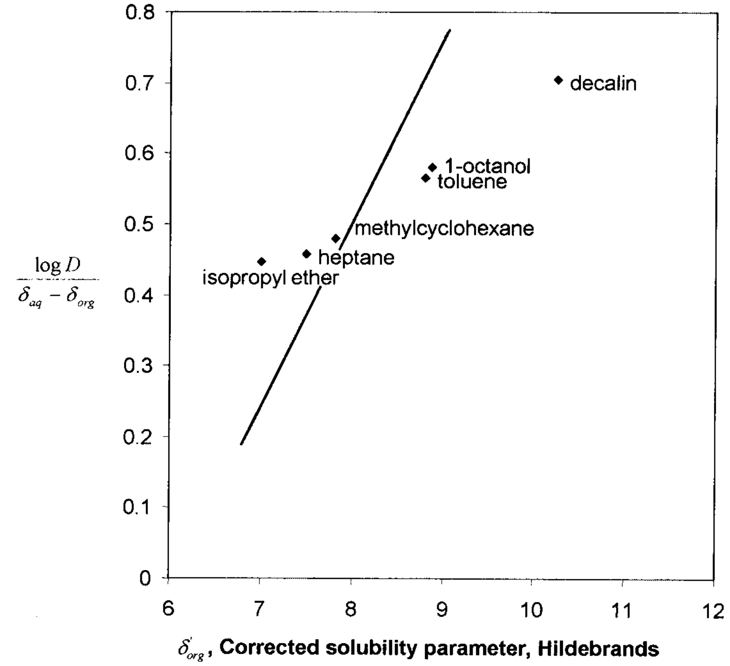

Figure 5. The fit of the Hildebrand Correlation [Eq. (1)] to the extraction flux for the Cu^{2+}-SO_4^{2-}/P50/diluent system ($C_{P50} = 0.05\,M$, $C_{Cu^{2+}} = 0.01\,M$, pH = 4.5, $T = 25°C$).

Effect of Interfacial Surface Pressure

The choice of the diluent was also shown to affect the interfacial surface pressure at the water-extractant/solvent interface (see Figs. 7 and 8). The interfacial surface pressure is defined by the following equation (20):

$$\pi = \gamma_W - \gamma_{HR} \tag{2}$$

where γ_w is the interfacial tension between the aqueous phase and the pure diluent phase (dynes/cm), γ_{HR} the interfacial tension between the aqueous phase and the solvent phase (dynes/cm), and π the interfacial pressure (dynes/cm).

From Figs. 7 and 8 it is seen that the extraction flux increases linearly with an increase in the interfacial pressure. Thus, $y = 0.3793x + 0.5583$ ($R^2 = 0.9147$) for extraction with P50 and $y = 0.0773x + 3.3446$ ($R^2 = 0.5896$) for extraction with D2EHPA. The linear relation is poorer for the extraction with D2EHPA. It seems toluene and decalin are responsible for the poor fit in this case. The interfacial pressure is generally higher for aliphatic diluents and lowest for

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

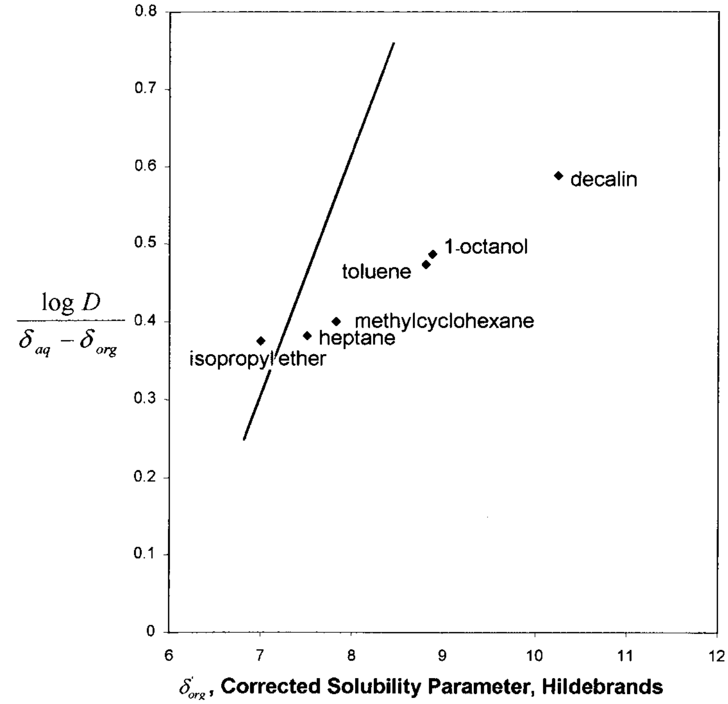

Figure 6. The fit of the Hildebrand Correlation [Eq. (1)] to the extraction flux for the Cu^{2+}-SO_4^{2-}/D2EHPA/diluent system ($C_{D2EHPA} = 0.05\,M$, $C_{Cu^{2+}} = 0.01\,M$, pH = 4.5, $T = 25°C$).

highly polar diluents. Adsorption at the interface is the resultant effect of the various molecular interactions in the system and will depend on the extent of the solvation of the extractant by the diluent. The greater the extent of the solvation the lower the tendency of the reagent to adsorb at the interface.

A similar increase in the flux with an increase in the surface pressure was observed by Whewell et al. (21) in their studies on the role of diluents in the liquid–liquid extraction of copper by LIX64N.

Several workers have used interfacial pressures or Gibbs excess concentrations as ways to correlate kinetics with the behavior of extractant molecules at the molecular liquid–liquid interface (22–24). Indeed, reviews of the surface activity of extractants have been published by Cox and Flett (25) and Osseo-Assare (26).

However, it has to be said that the liquid–liquid interface has always been recognized as being more diffuse than the air–liquid interface (20). Nevertheless,

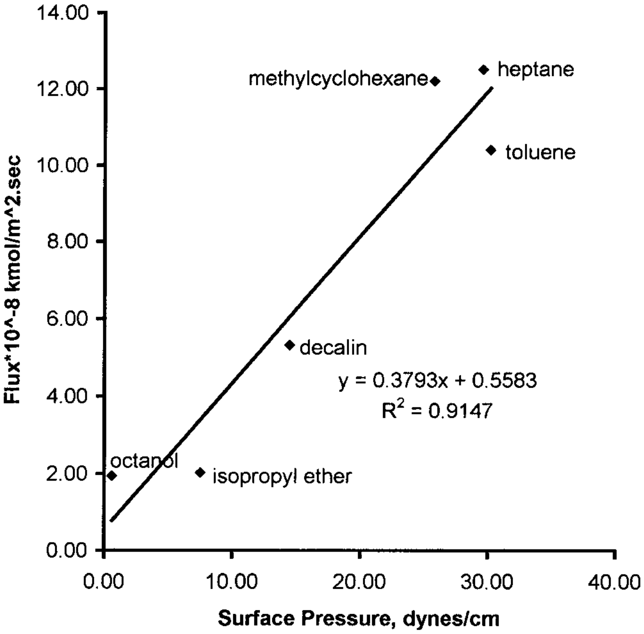

Figure 7. The effect of interfacial surface pressure on the extraction flux for the Cu^{2+}-SO_4^{2-}/P50/diluent system ($C_{P50} = 0.05\,M$, $C_{Cu^{2+}} = 0.01\,M$, pH = 4.5, $T = 25°C$).

some workers use the concepts of monomolecular layers for the interpretation of liquid–liquid kinetics. In our earlier work (1) we have accommodated reaction layers of different thicknesses in our kinetic model. In the case of very water "insoluble" extractants the thickness must approach that of molecular dimensions. If this is the case, then a parameter such as interfacial pressure or interfacial tension should become important. However, it should be remembered that in realistic concentrations of extractants for commercial purposes the interface layer will be saturated with the extractant molecules, i.e., the reaction rate should be independent of the extractant concentration in the organic phase, which is not normally the case.

Effect of Diluent Type on the Extractant Aqueous Phase Solubility

Of particular interest here is the relationship between the extraction flux for copper and the extractant aqueous phase solubility when employing different

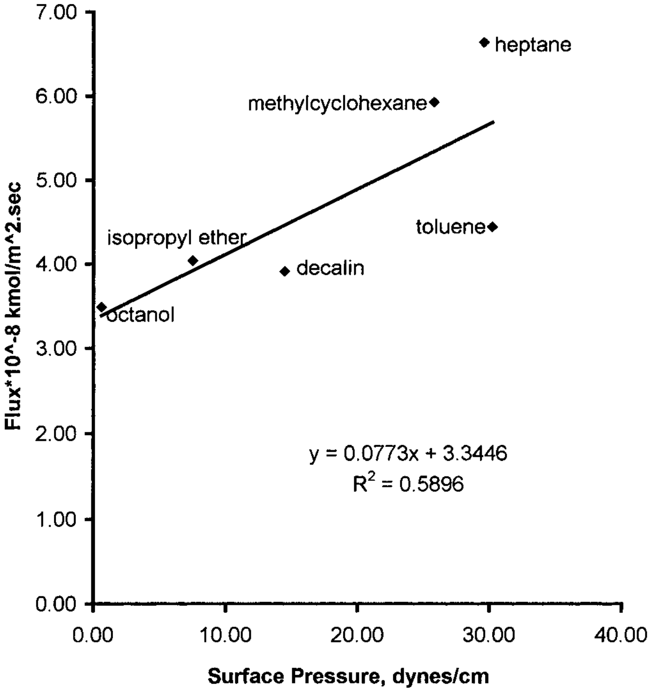

Figure 8. The effect of interfacial surface pressure on the extraction flux for the Cu^{2+}-SO_4^{2-}/D2EHPA/diluent system ($C_{D2EHPA} = 0.05\,M$, $C_{Cu^{2+}} = 0.01\,M$, pH = 4.5, $T = 25°C$).

solvents in which the diluent is varied (Figs. 9 and 10). Extraction rate increases almost linearly with decrease in the extractant distribution constant between the aqueous phase and the solvent phase. Thus, $y = -0.0043x + 30.635$ ($R^2 = 0.7547$) for extraction with P50 and $y = -0.0056x + 12.676$ ($R^2 = 0.9815$) for extraction with D2EHPA. Toluene and decalin are responsible for the poorer fit in both instances. The reason why toluene and especially decalin do not follow the above-observed trends is not clear. The distribution constant is lower in aliphatic diluents, where extraction rates are higher and lower in polar diluents, where extraction rates are lower. In the Hughes and Rod (27) model for extraction kinetics, at one extreme when the solubility of the extractant in the aqueous phase is low, the film thickness approaches zero and a true molecular surface involving a monolayer may be involved. On the other hand, when the reaction rate is slow and the extractant is very soluble in the aqueous phase, the film thickness will approach "infinity" and the reaction occurs in the bulk of the aqueous phase. The

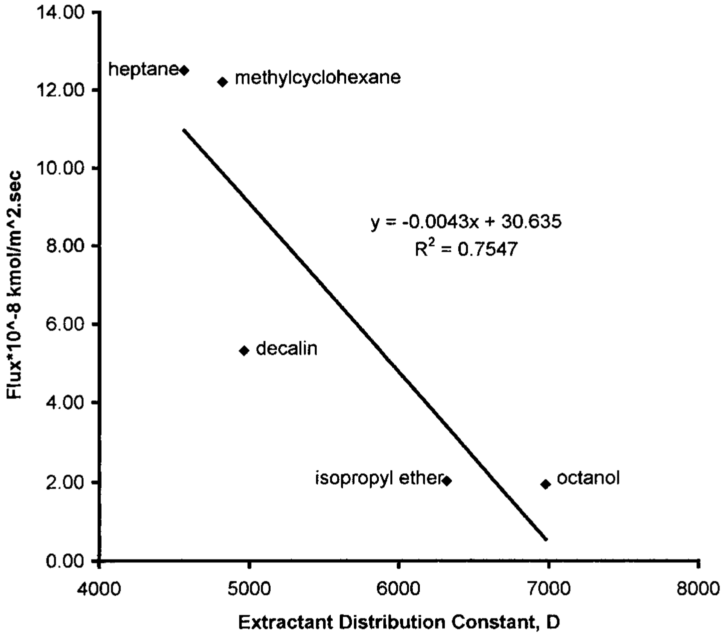

Figure 9. The effect of diluents on the extractant distribution coefficient for the water/P50/diluent system ($C_{\mathrm{P50}} = 0.05\,M$, pH $= 4.5$, $T = 25°\mathrm{C}$).

situation is not true of the systems studied in this work, as the extractant solubility in water is limited and the reaction rates are fast, i.e., a reaction zone of finite thickness and within the diffusion layers is involved. That the extraction reaction occurs in a thin zone adjacent to the monomolecular interface is supported by known facts that for reagents having appreciable aqueous-phase solubility, precipitation of the copper complex in the aqueous phase may occur in competition with extraction of the metal into the organic phase. In addition, since ionic species are involved in the reaction, it is very unlikely for the reaction site to be in the organic phase due to its low dielectric constant when compared with water.

With lower extractant distribution coefficient more extractant is "available" for reaction within the reaction zone on the aqueous side of the interface. However, the increased solubility in the aqueous phase should result in higher losses of extractant to the effluent streams. For this reason, the aliphatic diluents should contain a small percentage of aromatic content in order to limit extractant soluble losses to the aqueous effluent.

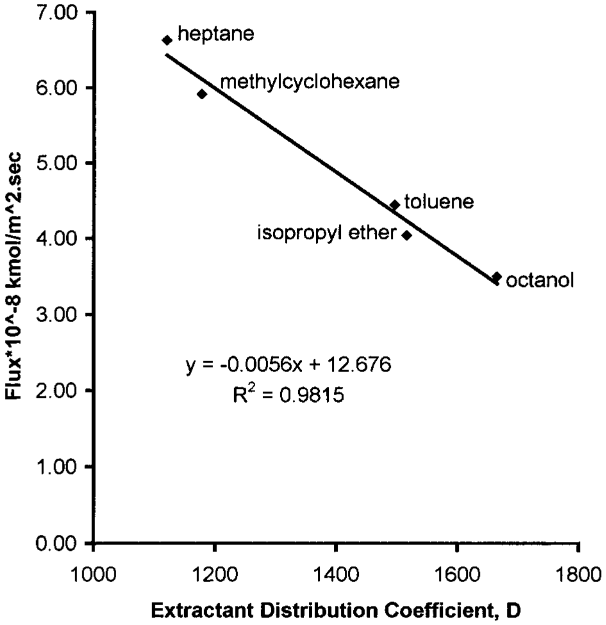

Figure 10. The effect of diluents on the extractant distribution coefficient for the water/D2EHPA/diluent system ($C_{\mathrm{D2EHPA}} = 0.05\,M$, pH = 4.5, $T = 25°\mathrm{C}$).

CONCLUSIONS

The rates of copper extraction using P50 and D2EHPA have been shown to decrease with increasing tendency for the diluent to interact with the extractant. The effect of the diluent on the extraction rate is best observed when the diluent is described through the dipole moment, solubility parameter, interfacial surface pressure, and the extractant distribution constant. In liquid–liquid extraction any interaction between the extractant and the diluent imposes an additional energy barrier that has to be overcome when the extractant molecule leaves the diluent environment to take part in the metal complex formation in the aqueous region of the interface. Analysis of our extraction rate data using the regular solution theory has shown that the interaction is not chemical in nature, i.e., interaction is physical in nature, except for the case where isopropyl ether is used as diluent. It thus seems that both the aromatic and aliphatic diluents in our study affect the extractant by lowering its activity coefficient in the solvent and thus the observed lower extraction rates. Our results suggest that the application of simple physicochemical tests to a diluent might provide a preliminary assessment of the possible diluent performance when in combination with a desired extractant. The observed increases in the extraction rates with decreasing extractant distribution coefficient are in support of the general model of Hughes and Rod (27) in which the extractant complex formation is envisaged to occur in a thin aqueous region that is adjacent to the monomolecular interface.

ACKNOWLEDGMENTS

Pardon K. Kuipa acknowledges the Staff Development Fellowship awarded by the National University of Science and Technology, Bulawayo, Zimbabwe.

REFERENCES

1. Kuipa, P.K. The Kinetics of Metal Extraction Relating to Extractant Interfacial Activity and Aqueous Phase Solubility. Ph.D. Thesis, Department of Chemical Engineering, University of Bradford, Bradford, 1995.
2. Cox, M. Liquid–Liquid Extraction in Hydrometallurgy. In *Science and Practice of Liquid–Liquid Extraction*; Thornton, J.D., Ed.; Oxford Engineering Science Series 27, Clarendon Press: Oxford, 1992; Vol. 2, 27–32.
3. Ritcey, G.M.; Lucas, B.H. Diluents and Modifiers—Their Effect on Mass Transfer and Separation. Int. Solvent Extr. Conf. ISEC'74 **1974**, *3*, 2437–2481.
4. Smelov, V.S.; Lanin, V.P.; Smyk, Z.A.; Chubukov, V.V. The Extraction of Zinc by Di-2-ethylhexylphosphoric Acid from Nitric and Perchloric Acid Solutions. Radiokhimiya **1972**, *14* (3), 352–356.
5. Akiba, K.; Freiser, H. The Role of the Solvent in Equilibrium and Kinetic Aspects of Metal Chelate Extractions. Anal. Chim. Acta **1982**, *136*, 329–337.
6. Hogfeldt, E. The Diluent Not Only a Solvent for the Extractant But Also a Participant in the Extraction Process. Chem. Ind. (Soc. Chem. Ind., Lond.) **1976**, 184–189.
7. Schmidt, V.S. Linear Free Energy Relations as a Means of Generalising and Analysing Extraction Data. Russ. Chem. Rev. **1978**, *47* (10), 929–943.
8. Marcus, Y. Diluent Effects in Solvent Extraction. Solvent Extr. Ion Exch. **1989**, *7* (4), 567–575.
9. Lange, N.A.; Dean, J.A. *Lange's Handbook of Chemistry*; 13th Ed.; Dean, J.A., Ed.; McGraw-Hill: New York, 1985; Table 10-35.

10. Good, R.J.; Elbing, E. *Chemistry and Physics of Interfaces*; American Chemical Society Publications: Washington D.C., 1971; 72.
11. Levitt, B.P. (Ed.) *Findlay's Practical Physical Chemistry*; 9th Ed.; Longmans: London, 1973; 104–105.
12. Menzel, D.W.; Corwin, N. The Measurement of Total Phosphorus in Seawater Based on the Liberation of Organically Bound Fractions by Persulphate Oxidation. Limnol. Oceanogr. **1965**, *10*, 280–282.
13. Hughes, M.A.; Kuipa, P.K. Kinetics and Mechanism of Copper Extraction with Di-alkylphosphoric Acids and Hydroxyoximes Studied by a Rotating Diffusion Cell. Ind. Eng. Chem. Res. **1996**, *35* (6), 1976–1984.
14. Hildebrand, J.H.; Scott, R.L. *Solubility of Nonelectrolytes*; Reinhold: New York, 1950; 131–268.
15. Kolarik, Z.; Hejna, J.; Pankova, H. Acidic Organophosphorus Extractants—VII: The Dissociation, Self-association and Distribution of Di-*n*-butyl Phosphoric Acid. J. Inorg. Nucl. Chem. **1968**, *30*, 2795–2906.
16. Kolarik, Z. Interactions of Acidic Organophosphoruc Extractants in the Organic Phase. In *Solvent Extraction Reviews*; Marcus, Y., Ed.; Marcel Dekker, Inc.: New York, 1973; Vol. 1, 1–50.
17. Kolarik, Z.; Hejna, J.; Pankova, H. Acidic Organophosphorus Extractants—V: The Dissociation, Self-association and Distribution of Di-*n*-butyl Phosphoric Acid. J. Inorg. Nucl. Chem. **1968**, *30*, 253–262.
18. Barton, A.F.M. *Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press: Boca Raton, 1983.
19. LeBas, C. *The Molecular Volumes of Liquid Chemical Compounds*; Longmans: Edinburgh, 1915.
20. Davies, J.T.; Rideal, E.K. *Interfacial Phenomena*, 2nd Ed.; Academic Press: New York, 1963; Chap. 7.
21. Whewell, R.J.; Hughes, M.A.; Hanson, C. The Role of the Diluent in the Solvent Extraction of Copper with LIX 64N. In *Advances in Extractive Metallurgy*; Jones, M.J., Ed.; Institution of Mining and Metallurgy: London, 1977; 21–25.
22. Juang, R.S.; Chang, Y.T. Kinetics and Mechanism of Copper II Extraction from Sulfate Solutions with Bis(2-ethylhexyl)phosphoric Acid. Ind. Eng. Chem. Res. **1993**, *32*, 207–213.
23. Szymanowski, J. Adsorption of Hydroxyoximes at the Organic/Aqueous Interface and the Interfacial Mechanism of Copper Extraction. In *Surfactants in Solutions*; Mittal, B.K.L., Lindman, B., Eds.; Plenum Press: New York, 1989; 485.
24. Szymanowski, J.; Cierpiszewski, R. Kinetics Model for Interfacial Process of Copper Extraction with 2-Hydroxy-5-alkylbenzaldehyde Oximes. Solvent Extr. Ion Exch. **1992**, *10*, 663.

25. Cox, M.; Flett, D.S. The Significance of Surface Activity in Solvent Extraction Reagents. Int. Solvent Extr. Conf. ISEC'77, CIM Special Vol. 21 **1977**, *21* (2), 63–71.
26. Osseo-Asare, K. Interfacial Phenomena in Hydrometallurgical Liquid–Liquid Extraction Systems. In *Hydrometallurgical Process Fundamentals*; Bautista, R.G., Ed.; 1984; 357–405.
27. Hughes, M.A.; Rod, V. A General Model to Account for the Liquid/Liquid Kinetics of Extraction of Metals by Organic Acids. Faraday Discuss. Chem. Soc. **1984**, *77*, 75–84.

Received October 2000
Revised July 2001

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Downloaded At: 10:35 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081SS120002246