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ANION EXCHANGE IN TERNARY MIXTURES OF ALIPHATIC ACIDS, MINERAL ACIDS AND WATER

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SUMMARY

The anion-exchange behaviour of bivalent cobalt, copper, zinc and cadmium towards the strong base anion exchanger Dowex 1-X8 is studied as a function of the composition of ternary mixtures of aliphatic acids (acetic acid, propionic acid and butyric acid), mineral acids (hydrochloric and nitric) and water. The experimental data could be interpreted on a qualitative physico-chemical basis in terms of the gradual building-up of metal-ligand complexes (including those with a ligand number less than 2) and of the dielectric constant of the solvent.

INTRODUCTION

Aliphatic organic acids with low dielectric constants (ϵ) and a wide range of miscibility with water are interesting media, as they favour metal-complex formation and can thus enhance adsorbabilities in ion-exchange systems; this has been shown for both anion and cation exchangers in previous studies from this laboratory¹⁻⁵. The present work was aimed at comparing the effects of acetic acid, propionic acid and butyric acid (HAc, HPr and HBu, respectively) on the distribution coefficients of some metals in ternary mixtures of these organic acids with mineral acids (hydrochloric and nitric acids) and water. The adsorption isotherms at 25° have been examined as a function of the aliphatic and mineral acid concentration for the bivalent transition metals copper, cobalt, zinc and cadmium, and an attempt has been made to interpret the experimental results on a physico-chemical basis, taking into account additional information from the results of a spectrophotometric investigation of the metal complexes involved.

EXPERIMENTAL

Resin

Dowex 1-X8 (Cl⁻ or NO₃⁻; 100-200 mesh) was conditioned before use⁶ and dried *in vacuo* over phosphorus pentoxide; after conversion into nitrate form, the

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residual chloride content was determined by activation analysis⁷; it was found to be 0.5% of the original capacity.

Solvents

The solvents were prepared by mixing appropriate amounts of the aliphatic acids (purity 99%), mineral acids (analytical grade) and water. The metal under investigation was introduced into the system as a solution of its acetate, propionate or butyrate in a mineral or aliphatic acid. The composition of the solvent is expressed in terms of mole fractions for the organic acids (compared with the sum of organic acid and water) and of molarities for the mineral acids.

Radioactive tracers

Tracers of copper-64, cobalt-60, zinc-69m and cadmium-115 were obtained by neutron irradiation in the Thetis reactor (Gent, Belgium).

Radiometric analysis

The activity in the solvent phase was counted by means of a NaI(Tl) well-type detector coupled to a single-channel analyser. Purity checks were made with the use of a lithium-drifted germanium detector coupled to a 4000-channel analyser. For cadmium-115–indium-115m, an appropriate decay period was allowed to ensure transient mother–daughter equilibrium.

Determination of K_d values

The adsorbabilities were expressed as weight-distribution coefficients (K_d = amount of metal per g of dry resin/amount of metal per ml of solution). They were determined by the batch-equilibration technique, with use of 100 mg of resin and 21 ml of solvent. Agitation times of 15 h and metal loadings below 1% of the total exchange capacity were used.

Spectrophotometry

Absorption spectra of the solvent phase for Cu(II) were obtained by using 1.00-cm silica cells and the visible source and detection mode of a Beckman DK-1A recording spectrophotometer. The blank solutions were solvents treated identically but not containing the metal.

RESULTS AND DISCUSSION

The K_d values at constant chloride or nitrate molarity were plotted as a function of the aliphatic acid mole fraction. From these curves it was possible to plot K_d versus chloride or nitrate molarity; the results are shown in Figs. 1–3.

An attempt was made to give a qualitative physico-chemical interpretation of the phenomena observed, based on the theories of Marcus and Coryell⁸ for media with high ϵ values (dissociated species) and of Penciner *et al.*⁹ for media with low ϵ values (ion-paired species).

It follows from the former theory that, at high values of ϵ , *e.g.*, in aqueous media, the distribution curves can be described in terms of the gradual building-up of cationic, neutral and anionic metal–ligand complexes with increasing ligand con-

tent, respectively corresponding to positive, zero and negative slopes of the adsorption isotherms [\log (distribution coefficient) *versus* \log (ligand content)]. The highest value of the distribution coefficient (corrected for ligand invasion⁹), and thus zero slope, occurs at a ligand content such that the neutral metal–ligand complex predominates in the solution.

At low ϵ values⁹, *e.g.*, in acetone or ethanol medium, the metal is introduced into the system as, for instance, its chloride (if chloride is the ligand); thus, the adsorption isotherm begins horizontally with zero slope. When the ligand content is increased, formation of higher metal–ligand complexes commences, resulting in a negative slope.

In the present work, however, the metal is introduced into the system as its acetate, propionate or butyrate; this means that:

(1) The existence of lower metal–ligand complexes (with a ligand number less than 2) becomes possible, so that the adsorption isotherm will show a positive slope at low ligand concentration.

(2) The metal acetates, propionates or butyrates are gradually transformed into higher metal–ligand complexes with increasing ligand content. This means that an increase in the aliphatic acid mole fraction (lower value of ϵ) will influence the distribution not only because of the transition from dissociated to ion-paired species, but also because the aliphatic acids contribute to the equilibria.

(3) The maximum of the adsorption isotherms will no longer exactly correspond to the predominance of neutral metal–ligand complexes in the solvent phase, unless the distribution coefficient is corrected for ligand invasion as well as for solvent invasion.

If these considerations are taken into account together with the fact that the presence of an organic solvent with a low ϵ value favours the formation of metal complexes, the distribution curves can be interpreted as follows. Fig. 1 shows a typical example of dependence of K_d for Cu(II) on the aliphatic acid mole fraction for six discrete values of hydrochloric acid molarity. The plots for the other metals investigated showed the same qualitative picture. At low mole fractions of the organic acids, where the ϵ values of the mixed solvents are still relatively high ($\epsilon_{\text{H}_2\text{O}} = 78.5$, $\epsilon_{\text{HAc}} = 6.2$, $\epsilon_{\text{HPr}} = 3.4$ and $\epsilon_{\text{HBu}} = 3.0$ at 25°), and at low ligand concentration, the fraction of the neutral metal complex does not attain a maximum. This fraction increases, and thus the K_d values become higher with increasing hydrochloric acid molarity at a constant mole fraction, and with increasing mole fraction at a constant hydrochloric acid molarity. At very high mole fractions (low ϵ values), the neutral complex predominates in the solution even at low hydrochloric acid concentration. Addition of hydrochloric acid leads to the formation of higher complexes and thus results in a decrease in K_d values. Even so, the increase in the organic solvent mole fraction at constant (preferably high) chloride molarity should eventually result in decreasing K_d values. Although this effect was not observed for Cu(II) and Zn(II) up to the mole fractions investigated, it did occur with Cd(II). Obviously, the region of the above-mentioned sequence inversion should be positioned at a higher mole fraction when the ϵ value of the aliphatic acid is higher, *i.e.*, $\text{HBu} < \text{HPr} < \text{HAc}$.

Graphs of K_d *versus* chloride molarity for Cu(II) at aliphatic acid mole fractions of 0.55 and 0.80 are shown in Fig. 2. At the lower mole fraction (highest ϵ values) and low chloride concentrations, formation of the neutral complex is still incomplete and is further enhanced by increasing chloride concentration, thus giving higher K_d

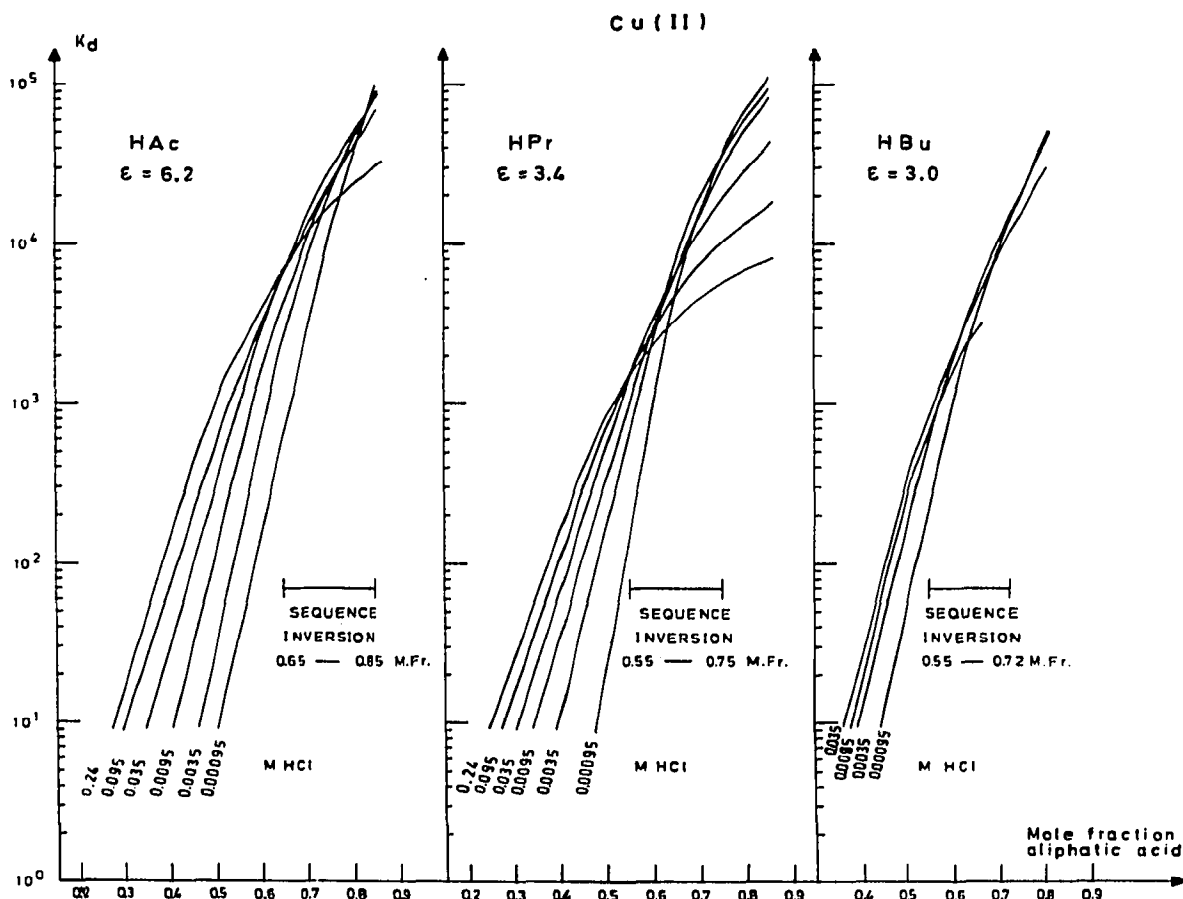


Fig. 1. K_d for Cu(II) versus aliphatic acid mole fraction at different hydrochloric acid molarities.

values. Moreover, the fraction of the neutral complex (and thus the value of K_d) is lower at higher ϵ values, so that in this region the K_d values follow the sequence $\text{HAc} < \text{HPr} < \text{HBu}$. An analogous reasoning leads to the K_d sequence $\text{HBu} < \text{HPr} < \text{HAc}$ at lower mole fractions and at very high chloride concentrations; this explains the observed inversion at intermediate chloride concentrations. On the hydrochloric acid molarity scale, the transition from increasing to max. and then decreasing K_d values will therefore follow the sequence $\text{HBu} < \text{HPr} < \text{HAc}$. At the higher mole fraction (lowest ϵ value), the adsorption is very high even in the absence of chloride ligand in the solvent. This is due to another adsorption mechanism, not involving metal-complex formation in the solution, but based on solvent extraction into the resin phase, followed by complex formation with the chloride counter-groups of the resin¹⁰. Because of this complication, the K_d sequence order at zero or extremely low ligand concentration can no longer be described in the same terms as mentioned above. However, with increasing hydrochloric acid content, the K_d sequence is again $\text{HAc} < \text{HPr} < \text{HBu}$ at low (and $\text{HBu} < \text{HPr} < \text{HAc}$ at high) ligand concentrations. As the ϵ values are low, the inversion occurs at a ligand concentration lower than a mole fraction of 0.55, thereby following the same sequence as on the hydrochloric acid molarity scale, viz., $\text{HBu} < \text{HPr} < \text{HAc}$.

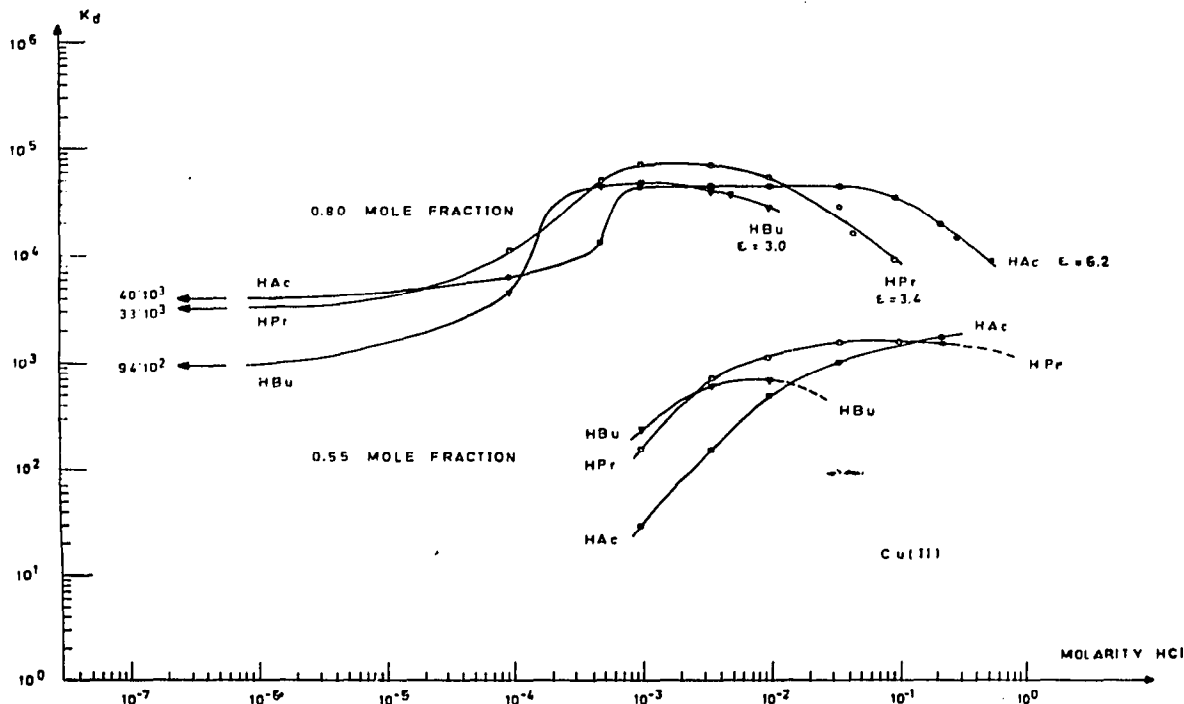


Fig. 2. K_d for Cu(II) versus chloride molarity at low and high aliphatic acid mole fraction.

Fig. 3 represents the dependence of K_d for Cu(II) on the nitrate molarity. As may be expected from the anion-exchange distribution behaviour of the elements in aqueous nitric acid¹¹, metal-complex formation with nitrate will occur with more difficulty, and thus only at a higher ligand concentration or at a higher aliphatic acid mole fraction (lower ϵ value) than with hydrochloric acid. At low mole fractions, no complexes are formed even at high nitrate concentrations; thus, no adsorption occurs. Even at high mole fractions (Fig. 3) and low nitrate concentrations, only the lower species are present, so that K_d first increases to a max. and then decreases with increasing nitrate molarity. This represents the gradual building-up of lower, neutral and higher metal nitrate complexes. As with low chloride concentration at low mole fraction of aliphatic acid, formation of the neutral complex is enhanced by lowering the ϵ value, thus resulting in the same K_d sequence, *viz.*, HAc < HPr < HBu. It should be noted that sequence inversion should occur at high nitrate molarity; this tendency is indeed observed in Fig. 3, but it was more marked in the case of Zn(II). Logically, as the nitrate concentration increases, predominance of the neutral metal species is reached earlier in a low- ϵ medium, so that the sequence of the max. is HBu < HPr < HAc.

Evidence of the above-outlined interpretation is obtained from spectrophotometric determination of the complex species in the solvent phase. Fig. 4 shows that, for Cu(II) in HAc-hydrochloric acid-water, the height of the absorption band at 383 nm, which can be ascribed to $[\text{CuCl}_4]$ (ref. 12), increases with increasing chloride concentration; this corresponds to a decreasing K_d value (see Fig. 2).

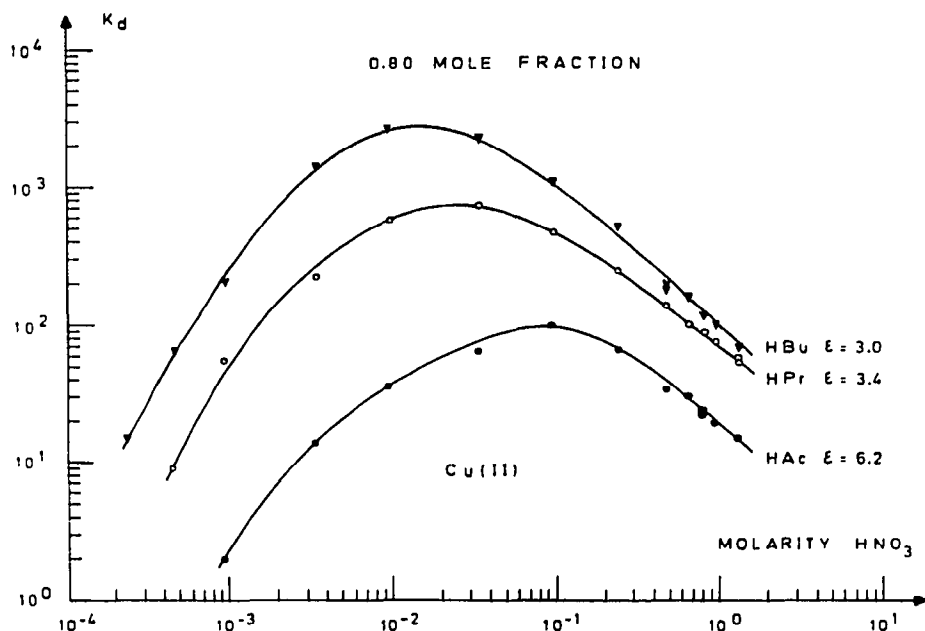


Fig. 3. K_d for Cu(II) versus nitrate molarity at high aliphatic acid mole fraction.

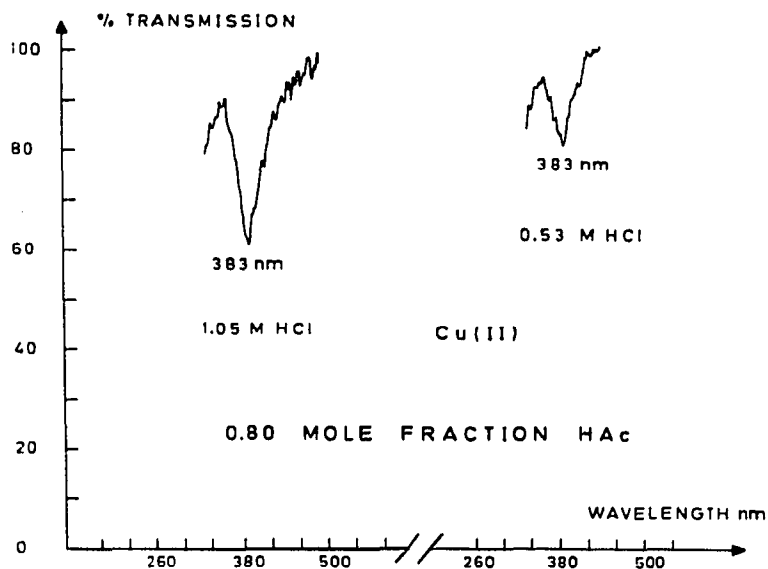


Fig. 4. Spectrophotometric absorption bands for Cu(II) in acetic acid (0.80 mole fraction) as a function of hydrochloric acid molarity.

CONCLUSION

It has been shown that anion exchange in ternary mixtures of aliphatic acids, mineral acids and water can be interpreted (at least qualitatively) in terms of the

gradual building-up of metal complexes and of the dielectric constant of the solvent. However, to obtain a quantitative treatment, it will be necessary to perform more refined experimental work, such as determination of solvent uptake, electrolyte invasion and spectrophotometric investigation of the metal complexes adsorbed on the resin. This work is in progress and will be reported in due course.

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REFERENCES

- 1 P. van den Winkel, F. de Corte, A. Speecke and J. Hoste, *Anal. Chim. Acta*, 42 (1968) 340.
- 2 P. van den Winkel, F. de Corte and J. Hoste, *Anal. Chim. Acta*, 56 (1971) 241.
- 3 P. van den Winkel, F. de Corte and J. Hoste, *J. Radioanal. Chem.*, 10 (1972) 139.
- 4 S. K. Jha, F. de Corte and J. Hoste, *Anal. Chim. Acta*, 62 (1972) 163.
- 5 P. van Acker, F. de Corte and J. Hoste, *Anal. Chim. Acta*, 64 (1973) 177.
- 6 W. Rieman, III and H. F. Walton, *Ion Exchange in Analytical Chemistry*, Pergamon Press, Oxford, 1970, p. 64.
- 7 F. de Corte and J. Hoste, *J. Inorg. Nucl. Chem.*, 35 (1973) 2049.
- 8 Y. Marcus and C. D. Coryell, *Bull. Res. Comm. Isr., Sect. A*, 8 (1959) 1.
- 9 J. Penciner, I. Eliezer and Y. Marcus, *J. Phys. Chem.*, 69 (1965) 2955.
- 10 P. van Acker, F. de Corte and J. Hoste, *J. Inorg. Nucl. Chem.*, in press.
- 11 J. P. Faris and R. F. I. Buchanan, *Anal. Chem.*, 36 (1964) 1158.
- 12 L. I. Katzin, *J. Chem. Phys.*, 36 (1962) 3034.