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DISSOCIATION ASPECT IN SOLVENT EXTRACTION OF METALS

A.S. AHMED, M.Y. SHAHEEN, L. HUSSAIN AND A.B. CHAUDHRY
PCSIR Laboratories Complex, Lahore-54600

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The extraction of a single component (copper) from the aqueous solution with calcium salt of di-(2-ethylhexyl) phosphoric acid diluted in kerosene has been investigated. The equilibrium studies showed that the distribution of metals in conjugate phases is dependent not only on their distribution constants but it also dependent on their dissociation constants. A theoretical model has been proposed to predict the effect of various metal ions concentration on the solvent extraction process.

Key words: Dissociation constant, Electrical neutrality, Reflux action.

Introduction

A number of organic reagents are available for the extraction of metals from aqueous phases. In order to improve the extraction potential, various workers [1-3] used sodium ammonium or calcium salts of these reagents and placed emphasis on the following factors for a successful extraction process.

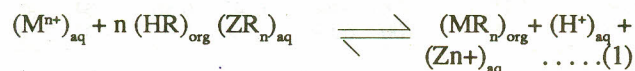
- (1) The concentration of extractant in the organic phase.
- (2) The concentration of metal in the aqueous phase.
- (3) The concentration of H⁺ ions (pH) in the aqueous phase.
- (4) The concentration of anions in the aqueous phase.

However, no exhaustive study which could completely characterize the behaviour of metal ions present in an equilibrated organic phase is available in literature.

The present study on a single component shows that final equilibrium depends not only on distribution constants of competing metal ions as reported by early workers [1,2,4] but is also influenced by dissociation constants of the species in the system.

The present paper highlights this fundamental fact and its influence on the recovery of copper from a single component feed.

Theory. Consider the extraction of metal cations Mⁿ⁺ from the aqueous solution by the organic extractant containing another metal cations Zⁿ⁺. The equilibrium between two conjugate phases may be represented as:



The equilibrium is influenced by distribution and dissociation constants of the two metal cations in accordance with the illustration in Fig. 1. Consider the dissociated ions in the aqueous phase:



The hydrogen ions concentration at working pH of 4.29 is low and may be neglected, therefore, the same holds true for

the concentration of OH⁻¹ ions. The extractant dissociates at a very low concentration and therefore, can be omitted from equation (2) which then reduces to:



The above equation (3) shows that the dissociated cations present in the aqueous phase compete for the anions and the cations with high dissociation constant remain in the aqueous phase and others transfer to the organic phase.

This effect has been studied by loading metal Zⁿ⁺ ions in the organic phase prior to the contact of two phases. On equilibrating organic and aqueous phases, the metal Zⁿ⁺ ions will be replaced by the metal Mⁿ⁺ due to their large difference in dissociation and distribution constants.

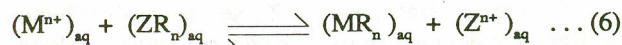
The following step may be considered to achieve equilibrium:

- (A) The partition constants of the metals:

$$K_Z = \frac{(ZR)_n_{org}}{(ZR)_n_{aq}} \dots (4)$$

$$K_M = \frac{(MR)_n_{org}}{(MR)_n_{aq}} \dots (5)$$

(B) The reaction takes place on the dissociation of extractant in the aqueous phase and the ionised equilibrium is given as:



The equilibrium constant K may be presented as:

$$K = \frac{(MR)_n_{aq} (Z^{n+})_{aq}}{(M^{n+})_{aq} (ZR)_n_{aq}} \dots (7)$$

By substituting equations (4), (5) and (6) into equation (7), the equilibrium constant K may be written as:

$$K = \frac{(MR)_n_{org}}{K_M (M^{n+})_{aq}} \frac{K_Z (Z^{n+})_{aq}}{(ZR)_n_{org}} \dots (8)$$

The separation factor may be expressed as:

$$\alpha = \frac{K K_M}{K_Z} \dots (9)$$

The maximum benefit from this new development is expected to be achieved by employing multistage countercurrent contact of two phases. The metal Z^{n+} in the organic phase will completely be exchanged with the metal M^{n+} from the aqueous phase during the process. This is analogous to a reflux action in an extractive distillation process.

Reagents. DEHPA was used as received from BDH and diluted in washed kerosene. The copper chloride and calcium chloride were of Analar grade and solution of various concentrations were made in distilled water. The pH of the aqueous phase was adjusted by the addition of hydrochloric acid.

Equilibrium distribution of metals. Partition of metals was determined by equilibrating 100 ml of 0.5 M solution of Ca-DEHPA salt in kerosene with 100 ml of 5g dm⁻³ aqueous solution of copper of known pH in a polythene stoppered glass bottles. The conjugate phases were shaken and kept in a thermostatically controlled water bath at 25°. One hour shaking time for equilibrium and further one hour for phase disengagement was allowed as recommended by other workers [4,5] in this field. The aqueous phase was separated carefully from the organic phase and its pH was recorded. Similar procedure was adopted for adjusted pH solutions of 1g dm⁻³ to 5g dm⁻³ copper solution and equilibrated with 0.1 M DEHPA.

The concentration of metal in the aqueous phase was analysed by Unicam SP90 atomic absorption spectrophotometer. The organic phase was also tripped with 5N hydrochloric acid and metal contents determined provided a check on the analysis of the aqueous phase. To ensure the experimental results reliability, three samples were processed concurrently and the equilibrium distribution data of the metals in each sample indicated the dependable accuracy.

Results and Discussion

The experimental results in Table 1 on the distribution of copper and calcium with varying concentration of chloride ions in the aqueous phase confirm that the overall distribution coefficient depends on the amount of copper and calcium ions and total chloride ions present in the system. The amount of chloride ions in the system varies from 0.56 g dm⁻³-2.80gdm⁻³ and distribution coefficient for copper vary from 27.6-1.13 whilst for calcium varies from 1.7-0.48. These results show that the increase in chloride ions whilst total metal concentration (copper + calcium) does not increase in proportion, causes reduction in the extraction of metal in the organic phase which consequently decreases the overall

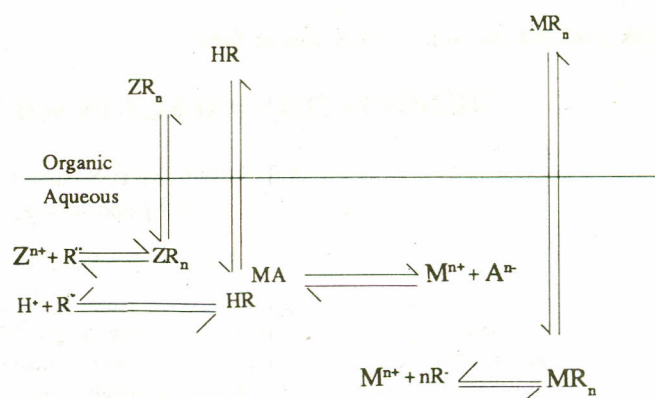


Fig. 1. Reaction mechanism of metal extraction.

distribution coefficient of the metals. From these results, it is also evident that copper having high distribution constant replaces calcium in the organic phase. It can also be observed that the dissociation constant of calcium is much higher than copper and therefore it transfers to the aqueous phase. This trend is also obvious in Table 2 and 3.

Further, Table 1 and 2 give the pH's values of the feed and equilibrated aqueous phase of various concentration of copper in contact with 0.1 and 0.5 M Ca-DEHPA solution. It

TABLE 1. DEHPA = 0.1M, FEED pH = 4.29.

Equilibrium pH	Aqueous Phase			Organic Phase			
	Chloride ions g dm ⁻³	Cu g dm ⁻³	Ca g dm ⁻³	Cu g dm ⁻³	Ca g dm ⁻³	D cu	D ca
5.84	0.56	0.035	0.600	0.965	1.040	27.60	1.70
5.43	1.12	0.200	0.780	1.800	0.860	9.00	1.10
4.50	1.68	0.800	0.930	2.200	0.710	2.75	0.76
4.25	2.24	1.680	1.035	2.320	0.605	1.38	0.58
4.10	2.80	2.350	1.108	2.650	0.532	1.13	0.48

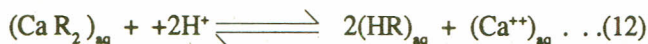
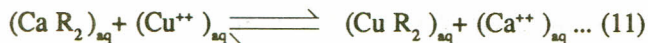
TABLE 2. DEHPA = 0.1 M, COPPER = 1.0 g dm⁻³

Feed pH	Equilib. pH	Organic Phase		Aqueous Phase		D Cu	D Ca
		Cu g dm ⁻³	Ca g dm ⁻³	Cu g dm ⁻³	Ca g dm ⁻³		
4.29	5.84	0.965	1.04	0.035	0.60	27.60	1.70
3.40	5.76	0.924	1.02	0.076	0.62	12.16	1.65
2.50	5.40	0.883	0.96	0.117	0.68	7.55	1.41
2.00	4.15	0.858	0.84	0.142	0.80	6.04	1.05
1.50	3.08	0.700	0.59	0.300	1.05	2.33	0.56

TABLE 3. DEHPA = 0.5 M, COPPER = 5 g dm⁻³

Feed pH	Equilib. pH	Organic Phase		Aqueous Phase		D Cu	D Ca
		g dm ⁻³	g dm ⁻³	g dm ⁻³	g dm ⁻³		
4.29	2.38	.995	1.160	4.005	1.200	0.25	0.967
3.40	2.36	.932	1.092	4.068	1.268	0.229	0.861
2.50	2.28	.750	1.080	4.250	1.280	0.176	0.844
2.00	2.16	.482	1.015	4.518	1.345	0.107	0.755
1.50	1.89	.165	0.900	4.835	1.460	0.034	0.616

is clear from the results that the increase in final pH is affected by the two metals present in the aqueous phase. This increase in pH may be explained by considering the following reaction mechanism:-



The results show that large quantities of calcium ions are transferred (equation 11, 12) to the aqueous phase which hydrolyses [5,6] and consequently increases the pH in favour of maximum extraction.

Table 2 and 3 give the values of the distribution constants of copper and calcium. In this case the total metal in the system remains the same but the anions concentration is increased by the addition of hydrochloric acid. As expected, the overall distribution coefficient for the metals decreases as the anions concentration increases and this supports the theoretical analysis presented earlier.

These results clearly indicate that the calcium has higher dissociation constant and replaces copper by ions exchange process from the aqueous phase. The higher concentration of calcium in the organic phase after one equilibration could be further reduced by exploiting the effect of difference in dissociation and distribution constants of competing metals by employing multistage mixer-settler. Moreover, the metal of high dissociation constant introduced in the organic phase will not be present as an impurity in the end product.

Conclusion

These studies conclude that in any solvent extraction process, an appropriate excess metal will increase the loading of the metal to be extracted in the organic phase and will not be a problem in the final product as an impurity. Moreover, excess metal will maintain the pH of the aqueous phase in favour of maximum extraction.

NOMENCLATURE

A ⁻	= Concentrations of inorganic anions.
Di	= Distribution coefficient of metal i.
H ⁺	= Concentration of hydrogen ions.
K	= Equilibrium constant.
Ki	= Distribution constant of metal i.
MZ	= Concentration of metals.
OH ⁻	= Concentration of hydroxyl ions.
R ⁻	= Concentration of organic anions.
	= Separation factor.

SUBSCRIPT

MZ = Represent metal.

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