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Investigating the Synergistic Effect of D2EHPA and Cyanex 302 on Zinc and Manganese Separation

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The synergistic effect of Cyanex 302 on the extraction of zinc and manganese with D2EHPA in sulfate media was investigated. Experiments were carried out in the pH range of 1.0–5.0, temperature of 23, 40, and 60°C with sole D2EHPA and Cyanex 302 as extractant and D2EHPA to Cyanex 302 ratios of 1:3, 1:1, and 3:1. The experimental results showed that the co-extraction of zinc and manganese increased with increasing equilibrium pH and temperature. Increasing the D2EHPA to Cyanex 302 ratio in the organic phase, caused a left shifting of the extraction isotherm of zinc and a right shifting of the extraction isotherm of manganese. Thus, a better separation of zinc over manganese was achieved. At low pHs, the separation factor is low when pure D2EHPA is used as an extractant; however, using Cyanex 302 as a synergist, the separation factor increases and results in a better separation of zinc from manganese. Stoichiometric coefficient of zinc for single D2EHPA and Cyanex 302 and their mixture was calculated to be close to 6.

INTRODUCTION

Solvent extraction of metallic ions is an important unit operation used in chemical and hydrometallurgical industries. Selective extraction of heavy metals from low grade ores, industrial wastes, and effluents attracted the attention of researchers due to the environmental aspects and economical concerns (1–4). Di-(2-ethylhexyl) phosphoric acid (D2EHPA) and bis-(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) have been successfully used as extractants for various metal ions, including zinc and manganese, from sulphate solutions.

D2EHPA has been used for the separation of cobalt from nickel and can also be used for the separation of zinc, beryllium, copper, vanadium, indium, gallium, and rare earth elements (5). There exist numerous studies on the extraction of zinc with D2EHPA (6–10). However, studies on zinc and manganese separation at low pH showed a low separation factor when D2EHPA is used as the extractant (11). To overcome this problem, employing, a secondary extractant as synergist is very needful. The term "synergism" is used to describe cases where the extractive capability of a mixture of extractants is greater than the sum of their individual extractive capabilities. Devi et al. (12) studied the separation of Mn and Zn from sulfate solutions using Cyanex 272 at a high ionic strength, i.e., high concentration of H^+, NaCl, NaSCN, and Na_2SO_4 solutions. Cheng et al. (13) studied the separation of divalent metal ions from a synthetic laterite leach solution containing Zn, Ca, Mn, Cu, Ni, Co, and Mg with D2EHPA and found low separation of zinc and manganese. Nathsarma and Devi (11), carried out the extraction and separation of zinc and manganese from a sulfate solution using sodium salts of D2EHPA, PC88A, and Cyanex 272 in kerosene. The sodium form of the extractant was prepared (60% neutral) by adding the requisite volume of concentrated NaOH solution to the extractant in kerosene and mixing the phases intimately to form a single phase. They showed that the extraction of metal ions increases with increasing pH and the extraction of zinc can be carried out at a lower pH than manganese. They also showed that the separation factor of zinc over manganese increased with decreasing equilibrium pH but decreased with increasing NaCl, NaSCN, and Na_2SO_4 concentration in solution.

Recovery of zinc and manganese from spent alkaline batteries using Cyanex 272 was studied by Salgado et al. (14). They focused mainly on the effect of equilibrium pH on the separation of zinc and manganese and found that the equilibrium pH for zinc extraction is less than that for manganese. Cyanex 272 can extract zinc at $2.0 < pH < 2.6$ where manganese extraction is not significant. On the other hand, the extraction of manganese is

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high at pH > 4.5. Nathsarma and Devi (11) performed solvent extraction using D2EHPA, PC88A, and Cyanex 272, separately. They reported that the separation factor was the highest with PC88A. Synergism was applied to this system by Devi et al. (4). They found that in the separation of Mn from sulfate solutions containing Zn ions, a mixture of Cyanex 272 (as extractant) and PC88A (as synergist) performs much better than the solvent extraction system involving PC88A as extractant and D2EHPA as synergist. Therefore, the use of synergists to improve the selectivity of existing reagents such as D2EHPA is an attractive alternative to the development of new reagents (15,16).

Cyanex 302, the mono-thio analogue of Cyanex 272, presented lower metal extraction levels and slower phase disengagement characteristics. However, using Cyanex 302 as the co-extractant with D2EHPA results in better separation of zinc from manganese (17). The synergistic effect of Cyanex 302 when mixed with D2EHPA has been used for separation of nickel and cobalt (18) and for the separation of zinc from iron(II) and iron(III) (19).

In the present work, the separation of Mn from Zn in sulfate media at different temperatures was studied using solvent extraction. Cyanex 302 was used as the synergist and mixtures of D2EHPA and Cyanex 302 in kerosene were employed as the organic phase. These two extractants had shown good extraction capacity for both Zn and Mn. Moreover, similar solvents had shown a synergistic effect in the separation of Zn from Mn. Thus, these two extractants were employed in the present work. Isotherms of manganese and zinc at low pHs are very close, i.e., at some pHs, simultaneous extraction of both manganese and zinc occurs. Thus, synergism could be helpful in this case.

EXPERIMENTS

Materials

Zinc sulphate (97% pure) and manganese sulphate (98% pure) salts were obtained from Merck, Germany. The organic solvents used in this work were industrial grade Di-(2-ethylhexyl) phosphoric acid (D2EHPA), 97% pure, from Bayer, Germany, and bis-(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302), 98% pure, from Fluka, Canada. The extractants were used without further purification. Kerosene, from Tehran Oil Refining Co., was used as the diluent. Sulfuric acid (98% pure) and sodium hydroxide 0.1 M, from Merck, Germany, were used as pH modifiers.

Experimental Procedure

Synthetic stock solutions of zinc and manganese (4 g/L each) were prepared by dissolving a sufficient amount of their sulfate salts in distilled water. A small amount of sulfuric acid was added to the solutions to prevent hydrolysis of the metal ions. Each extraction test was performed by mixing 200 mL of the aqueous phase solution with 200 mL of the organic phase containing 20% vol. of the extractant (either D2EHPA or Cyanex 302 or their mixture) and 80% kerosene. This aqueous to organic phase ratio (A/O) of 1:1 was applied in all tests. During mixing, the temperature of the system was controlled by a thermostatic bath. Experiments were carried out at 40°C and for the studying effect of temperature experiments were repeated at a lower and higher temperature (23, 60°C).

A PY-11 pH meter Sartorius (made in Germany) was used to monitor pH during the experiments. Initial pH of the mixture was adjusted to 1 and the mixture was agitated very well by a mechanical agitator for 7 minutes after which the pH was stable. Samples were taken at pH intervals of one over the pH range of 1.0 to 5.0 and pH fixed by adding either sulfuric acid or sodium hydroxide solution. At high pH (about 4 to 5), the phase separation was a little difficult but by spending time about 7–10 min., the phase separation became completed. The mixture was then transferred to a separatory funnel, equilibrated, and allowed to disengage. It is worth noting that the equilibrium pH was the pH measured after aqueous and organic phases were thoroughly mixed in the container. Of course, after separation each phase has a different pH.

After phase separation, the aqueous phase was analyzed for zinc and manganese concentration by titrating with EDTA in the presence of xylenol orange and eriochromblack T as indicators, respectively. The concentration of metal ions in the organic phase was calculated from the difference between concentrations in the aqueous phase before and after extraction by mass balance. Extraction tests at pH 2 and 4 were repeated three times to calculate standard deviation.

RESULTS AND DISCUSSION

The distribution coefficient (D) is the ratio of concentration of metal present in the organic phase to that in the aqueous phase at equilibrium. The percentage extracted (%E) can be then calculated from:

$$\%E = \frac{100D}{D + (V_{aq}/V_{org})} \tag{1}$$

where V_{aq} and V_{arg} are the volumes of aqueous and organic phases, respectively. Separation factor (ß) is defined as follows (20):

$$\beta = \frac{D_{Zn}}{D_{Mn}} \tag{2}$$

The highest value of the separation factor (ß) corresponds to the highest selectivity in separation of the desired metal ion.

The synergy coefficient is another parameter that can be used for judgment that synergism effect is useful or not. This ratio is defined as (21)

$$S_k = \log \frac{D_{1,2}}{D_1 + D_2} \tag{3}$$

where $D_{1,2}$ is the distribution ratio in the system with two extractants. D_1 is the distribution ratio in the system with extractant 1 alone, and D_2 is the distribution ratio in the system with extractant 2 alone. The effect of synergistic extraction is positive if the value of S_k is positive.

The pH-extraction curves of zinc and manganese were determined by experimental tests at different temperatures and ratios of extractants with an A/O ratio of 1:1. The distribution coefficients, separation factors, and synergy coefficient at different conditions were determined. The separation factor and synergy coefficient for all cases are listed in Tables 1 and 2, respectively.

Influence of Equilibrium pH

Figure 1 illustrates the percentage of zinc and manganese ions extracted as a function of equilibrium pH using 20% D2EHPA in kerosene at 40°C and A/O phase ratio of 1:1. The error bars on this figure correspond to the standard deviations of the measured values. As can be seen from this extraction isotherm, increasing the pH from 1 to 5 increases the extraction of both ions significantly. This is consistent with observations of Owsu et al. (7) and Nathsarma and Devi (11). From the figure, $pH_{0.5}$ values (the pH at 50% metal extraction) for zinc and manganese are 1.9 and 4.2, respectively, this indicates that zinc is being extracted at a lower pH than manganese when 20% D2EHPA in kerosene is used. Table 1 showed that the maximum separation factor is 162.02 at pH 5, while at low pH ($1 < pH < 2$) the separation factor is very low (less than 6). Therefore, reasonable zinc and manganese separation can be achieved at high pH.

Figure 2 shows the percentage of zinc and manganese ions extracted as a function of equilibrium pH using 20% Cyanex 302 in kerosene at 40°C and the A/O phase ratio of 1:l. The error bars on tins figure correspond to the standard deviations of the measured values. As it can be seen in this figure, by increasing pH from 1 to 5, zinc extraction increases from 19.5% to 99.8%. At $1 < pH < 2$ a steep slope can be seen in the curve. At equilibrium pH of ca. 5, extraction was completed to higher than 99% for zinc. In the case of manganese, ca. 43% of the ions were extracted at pH 1 which is considerably higher than the amount of zinc (4%) extracted at this pH. Nevertheless by increasing pH from 1 to 5, the increase in the amount of extracted manganese is insignificant i.e., pH has a negligible effect on Mn extraction. From Table 1 the maximum separation factor is 381.46 that could be achieved at pH 5.0.

Influence of Cyanex 302 as Synergist

Figure 3 shows the percentage of zinc and manganese ions extracted against pH at different D2EHPA to Cyanex 302 ratios and temperature 40°C. This figure illustrates significant synergistic shifts of zinc and manganese isotherms due to the addition of Cyanex 302 to D2EHPA. As can be seen in this figure, by increasing the ratio of Cyanex 302 to D2EHPA, the zinc extraction curve shifted more to the left and that of manganese to the right. In other words, the addition of Cyanex 302 to D2EHPA improves separation of zinc over manganese. That can be seen from Table 1 values of the separation factor increases in comparison to sole D2EHPA and Cyanex 302. It can be seen that the most selective extraction system for the conditions studied at

TABLE 1
Values of separation factors ($ß_{Zn/Mn}$) for different pHs, ratios of D2EHPA to Cyanex 302 and temperatures

		pH				
Temperature (°C)	D2EHPA : Cyanex 302	1	2	3	4	5
23	20% : 0%	1.24	5.82	16.32	72.63	144.04
	15% : 5%	2.65	11.90	53.16	193.12	841.38
	10% : 10%	4.36	21.84	131.53	594.68	2418.68
	5% : 15%	3.76	26.50	167.15	942.18	3624.07
	0% : 20%	0.29	2.30	16.87	120.09	912.96
40	20% : 0%	1.40	5.70	29.72	99.19	162.02
	15% : 5%	2.48	11.96	87.33	445.18	778.88
	10% : 10%	3.88	21.81	148.30	793.75	2156.93
	5% : 15%	4.80	24.77	250.80	1155.53	2873.64
	0% : 20%	0.31	2.22	21.79	64.33	381.46
60	20% : 0%	1.65	6.92	33.53	92.36	158.46
	15% : 5%	3.26	14.00	112.42	442.85	1371.03
	10% : 10%	5.15	24.76	394.14	2617.63	3983.93
	5% : 15%	5.18	30.02	258.46	1661.45	12687.33
	0% : 20%	0.33	2.79	42.86	725.05	1483.47

TABLE 2
Values of synergy coefficient (S_k) for different pHs, ratios of D2EHPA to Cyanex 302 and temperatures

Temperature (°C)	D2EHPA : Cyanex 302		pH 1	2	3	4	5
23	15% : 5%	$S_{k(Zn)}$	−0.03	−0.04	−0.05	−0.07	−0.08
	10% : 10%	$S_{k(Zn)}$	0.15	0.13	0.17	0.15	0.13
	5% : 15%	$S_{k(Zn)}$	0.20	0.20	0.24	0.23	0.13
	15% : 5%	$S_{k(Mn)}$	−0.78	−0.60	−0.55	−0.39	−0.49
	10% : 10%	$S_{k(Mn)}$	−0.81	−0.69	−0.72	−0.66	−0.74
	5% : 15%	$S_{k(Mn)}$	−0.70	−0.71	−0.76	−0.78	−0.92
40	15% : 5%	$S_{k(Zn)}$	−0.07	−0.02	0.01	0.30	0.09
	10% : 10%	$S_{k(Zn)}$	0.11	0.15	0.06	0.30	0.23
	5% : 15%	$S_{k(Zn)}$	0.19	0.20	0.26	0.36	0.23
	15% : 5%	$S_{k(Mn)}$	−0.74	−0.60	−0.53	−0.41	−0.47
	10% : 10%	$S_{k(Mn)}$	−0.75	−0.68	−0.70	−0.66	−0.77
	5% : 15%	$S_{k(Mn)}$	−0.77	−0.69	−0.74	−0.77	−0.89
60	15% : 5%	$S_{k(Zn)}$	−0.02	−0.07	−0.04	−0.33	0.01
	10% : 10%	$S_{k(Zn)}$	0.16	1.14	2.44	3.50	3.92
	5% : 15%	$S_{k(Zn)}$	0.16	0.17	0.15	−0.08	0.49
	15% : 5%	$S_{k(Mn)}$	−0.76	−0.61	−0.50	−0.45	−0.43
	10% : 10%	$S_{k(Mn)}$	−0.77	−0.67	−0.60	−0.67	−0.72
	5% : 15%	$S_{k(Mn)}$	−0.77	−0.7	−0.67	−0.76	−0.91

40°C can be achieved at equilibrium pH 5 and D2EHPA to Cyanex 302 volume ratio of 1:3. The separation factor increases from 162.02 (at 20% D2EHPA) to 2873.64 (at D2EHPA 5% : Cyanex 302 15%). The values of the synergy coefficient given in Table 2 show that adding Cyanex 302 increases the synergy coefficient for zinc extraction. The synergism effect decreases the manganese extraction which is confirmed by negative values of S_k. The highest value of S_k (0.36) is achieved at D2EHPA to Cyanex 302 ratio of 1:3 and at equilibrium pH of ca 4.

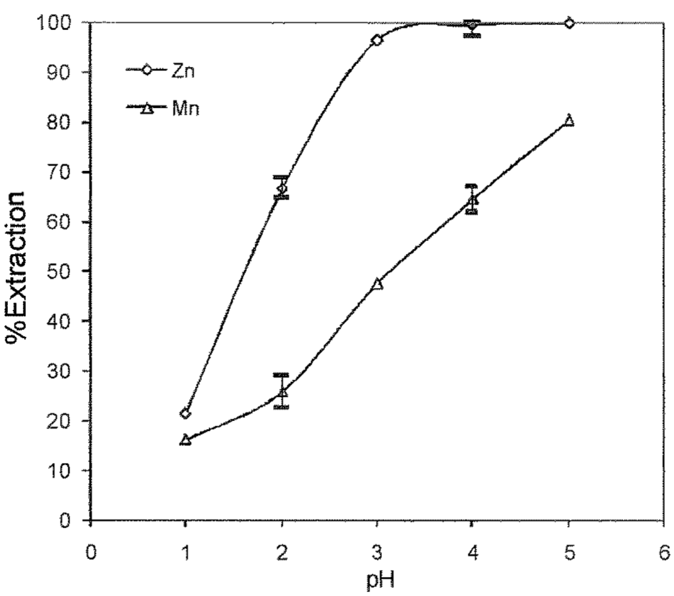

FIG. 1. Effect of equilibrium pH on extraction of zinc and manganese using 20% D2EHPA (80% kerosene) at 40°C and A/O ratio of 1:1.

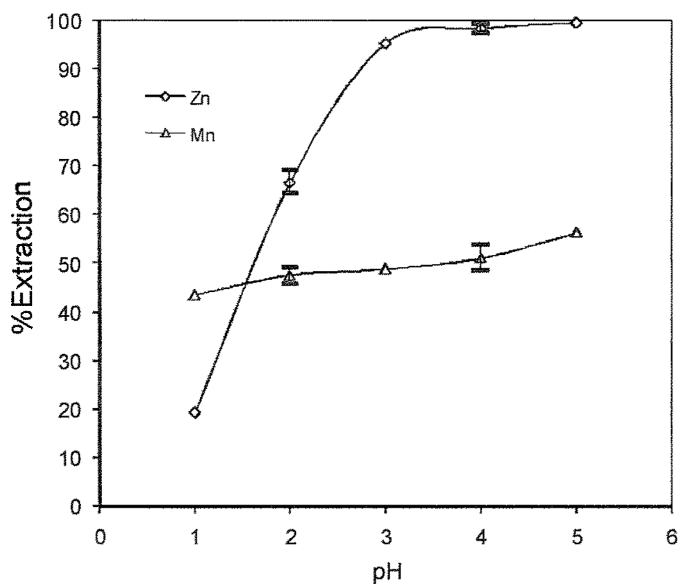

FIG. 2. Effect of equilibrium pH on extraction of zinc and manganese using 20% Cyanex 302 (80% kerosene) at 40°C and A/O ratio of 1:1.

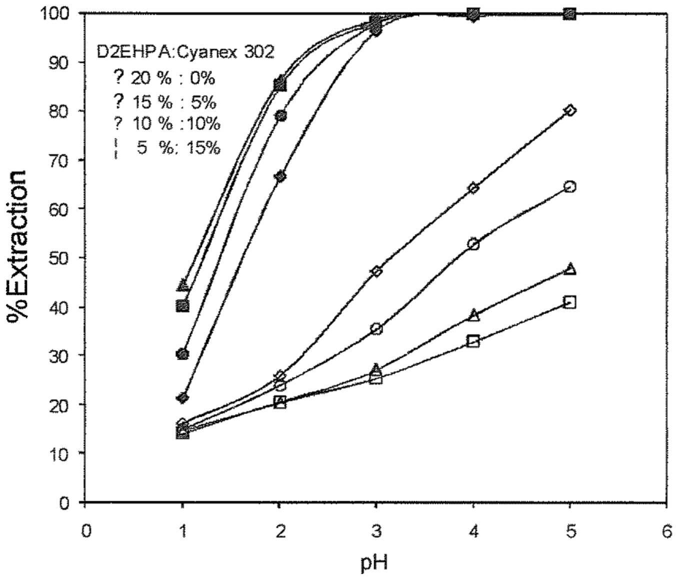

FIG. 3. Effects of adding Cyanex 302 with different ratios to D2EHPA, solid symbols are related to Zn extraction, hollow symbols correspond to Mn extraction.

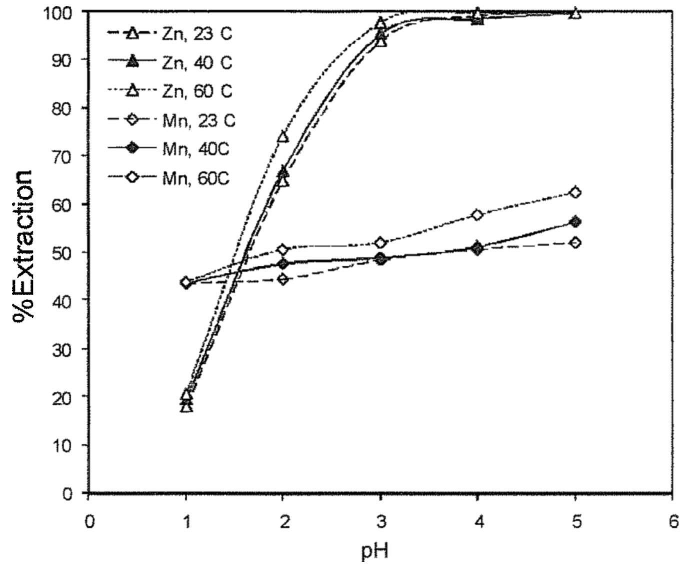

FIG. 5. Effect of temperature on extraction of zinc and manganese using 20% Cyanex 302 (80% kerosene) and A/O ratio of 1:1.

Influence of Temperature

The pH-extraction curves of zinc and manganese at 23, 40, and 60°C were determined to assess the effect of temperature. Figure 4 shows the extraction curves of zinc and manganese plotted at different temperatures for sole D2EHPA. At higher temperature, the zinc extraction isotherm was shifted towards lower pH while the isotherm shape remained unchanged. Generally, the extraction of zinc increased as the temperature increased; however, at $pH > 3.0$ the temperature had a negligible effect on the zinc extraction. Manganese extraction isotherms did not vary regularly. Extraction increased by increasing the pH and the temperature but at equilibrium pH of 1.0 and 3.0 extraction did not vary significantly. Observations of Cheng et al. (13) confirms this result. Extraction curves of zinc and manganese using sole Cyanex 302 at 23, 40, and 60°C are shown in Fig. 5. Based on the observations, changes in the zinc extraction curve is the same as sole D2EHPA in Fig. 4. Manganese extraction increased with increasing temperature, but at equilibrium pH 1.0, the temperature had a negligible effect on manganese extraction. From Tables 1 and 2 the maximum values of 12687.33 and 3.92 for the separation factor and synergy coefficient, respectively, confirm that D2EHPA to Cyanex 302 ratio of 1:3 at equilibrium pH of ca. 5.0 and 60°C is the most suitable condition for zinc and manganese separation.

Consequently, an increase in the temperature changes the $pH_{0.5}$ values for zinc and manganese. Figure 6 illustrates effect of temperature and adding Cyanex 302 as synergist on $pH_{0.5}$. Sole D2EHPA (0% Cyanex 302) and sole Cyanex 302 (20% Cyanex 302) are determined at the start and the end of the horizontal axis respectively. Figure 6, shows that adding Cyanex 302 to D2EHPA increased $pH_{0.5}$ values of manganese and decreased values of zinc. These results reveal that with adding Cyanex 302, $\Delta pH_{0.5}$ (difference between zinc and manganese $pH_{0.5}$) increased. Increasing the amount of Cyanex 302 beyond 15% has a negligible effect on the extraction efficiency. Since Cyanex 302 is more expensive than D2EHPA, increasing the percentage of Cyanex 302 is not advantageous. Sole D2EHPA or Cyanex 302 (at the start and end of the horizontal axis) showed less $\Delta pH_{0.5}$ values.

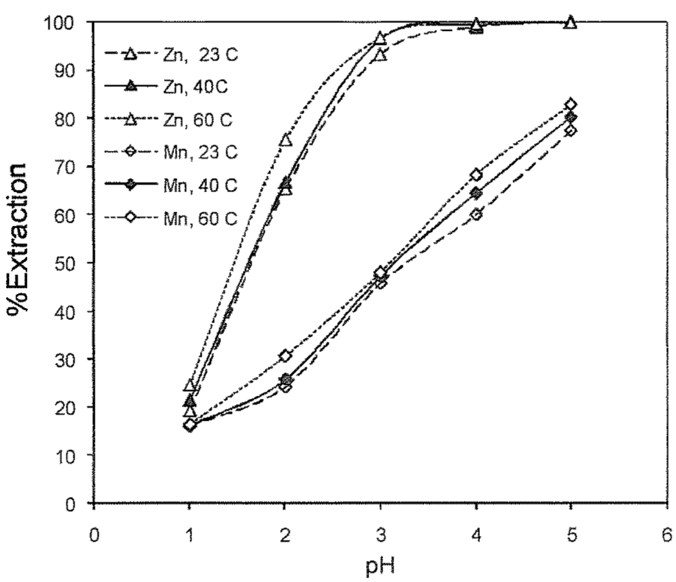

FIG. 4. Effect of temperature on extraction of zinc and manganese using 20% D2EHPA (80% kerosene) and A/O ratio of 1:1.

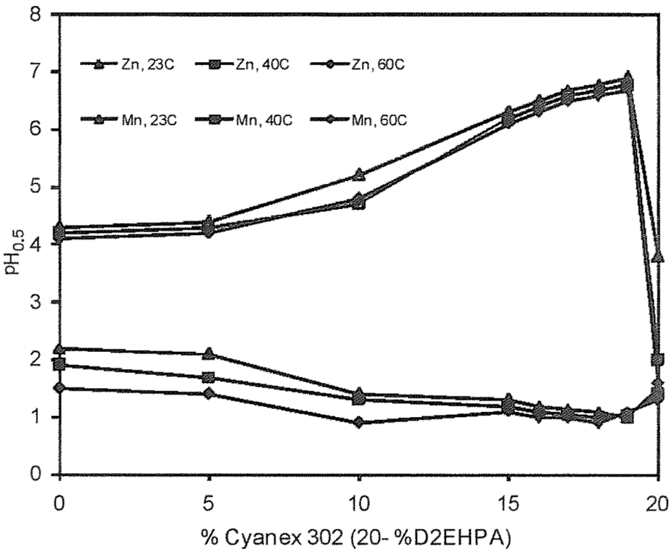

FIG. 6. Effect of temperature and adding Cyanex 302 on $pH_{0.5}$, 80% kerosene in organic phase and A/O ratio of 1:1.

Increasing the temperature increased the $pH_{0.5}$ values for both zinc and manganese. However, by increasing the amount of Cyanex 302, the temperature has a negligible effect on $pH_{0.5}$. The maximum Δ $pH_{0.5}$ value of 5.0 was obtained for D2EHPA to Cyanex 302 ratio of 1:3 (D2EHPA 5% and Cyanex 302 15%) and 60°C; confirms that D2EHPA to Cyanex 302 ratio of 1:3 at 60°C is more effective mixture for zinc and manganese separation.

Estimation of Stoichiometric Coefficient (n) and Equilibrium Constant (K) for Zinc Extraction

Zinc is a divalent metal ion and participates in the extraction reaction in the presence of mixed organophosphorus acid by equation and can be shown as follows (18)

$$Zn^{2+} + n(R/R')H \longrightarrow Zn(R/R')_2((R/R')H)_{n-2} + 2H^+ \quad (4)$$

where R and R′ stand for phosphoric and phosphinic acid extractant groups, respectively. In the above equation n is the stoichiometric coefficient of zinc in the extraction reaction. Equilibrium constant (K) and distribution ratio (D_M) are related by these equations and can be written as:

$$K = D_M \frac{[H^+]^2_{equ}}{[(R/R')H]^n_{equ}} \quad (5)$$

The logarithm of this equation gives a linear equation:

$$\log K = \log D_M - 2pH - n \log[(R/R')H]_{equ} \quad (6)$$

Equation (6) has two unknown parameters, n and K, which can be estimated for the zinc system using the experimental data of this work.

Based on Eq. (6), plotting ($\log D_M - n \ \log [RH]_{equ}$) against pH for sole D2EHPA and Cyanex 302 should give a straight line with a slope of 2. This will happen only for a special value of n. Therefore, to determine n and K from the experimental data, such a plot should be drawn for different values of n (not shown here). The value of n for which the slope of the line is closest to 2 should be considered as the correct value. The value of K then can be calculated from the intercept of the line. The above-mentioned procedure and Eq. (5) was employed in the present study for determining n at different mixtures of D2EHPA and Cyanex 302, temperature 40°C, and an A/O ratio of 1:1. The results showed that the stoichiometric coefficient for zinc is equal to 6 when using D2EHPA or Cyanex 302 as monomer extractant. Equality of n for D2EHPA and Cyanex 302 in the pH range of the experimentation suggests that D2EHPA and Cyanex 302 have a similar behavior in the zinc extraction (18). This present investigation reveals a coefficient of 6 for zinc when extracted with different D2EHPA–Cyanex 302 mixture. This result confirms that the extraction potential of the mixture is the same as that of sole D2EHPA and Cyanex 302. Values of $\log K$ for sole D2EHPA and Cyanex 302 and mixtures of D2EHPA–Cyanex 302 are plotted in Fig. 7. From the figure, sole D2EHPA and Cyanex 302 that have been shown at the start and end of the horizontal axis have lower values than the mixtures. Adding Cyanex 302 to D2EHPA increases $\log K$, however, this increment as mentioned for Fig. 6 has a maximum. The maximum value of $\log K$ was achieved at D2EHPA to Cyanex 302 volume ratio of 1:3.

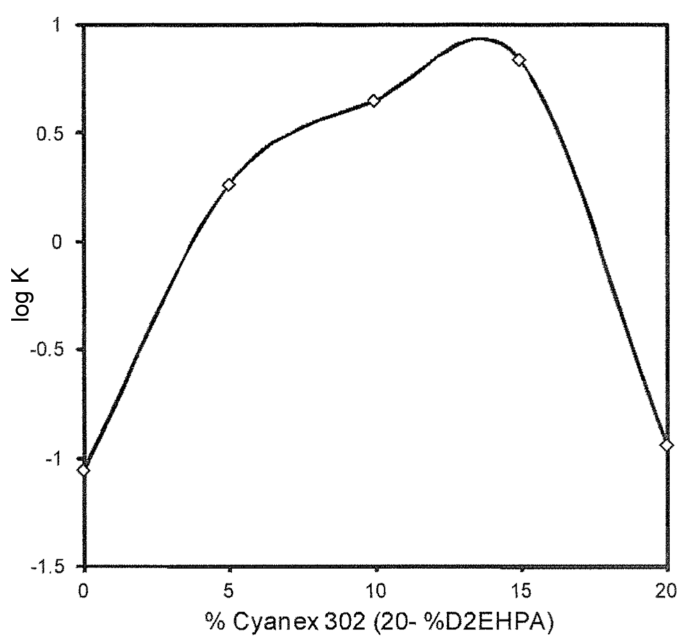

FIG. 7. Effect of adding Cyanex 302 on $\log K$, at 40°C, 80% kerosene in organic phase and A/O ratio of 1:1.

As mentioned before, this mixture has a greater tendency to form a complex and extracts zinc.

CONCLUSIONS

1. In the presence of sole D2EHPA the percentage of extraction for both zinc and manganese increased with increasing equilibrium pH but the separation factor was very low at low pHs.
2. In the presence of sole Cyanex 302 the percentage of zinc extraction increased with increasing equilibrium pH, and the pH had a negligible effect on manganese extraction.
3. Adding Cyanex 302 to D2EHPA caused a synergistic effect and shifted the extraction curve of zinc and manganese to left and right, respectively. The separation factor, synergy coefficient, and Δ $pH_{0.5}$ value increased. Increasing Cyanex 302 to D2EHPA ratio, the zinc separation from the zinc-manganese solution improved. D2EHPA 5%, Cyanex 302 15% mixture resulted in the highest separation factor, synergy coefficient, and Δ $pH_{0.5}$.
4. The stoichiometric coefficient of zinc in extraction (n) was estimated to be close to 6 for single D2EHPA and Cyanex 302 and their mixture. The extraction potential of the mixture is the same as that of sole D2EHPA and Cyanex 302.

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