

## Solvent extraction of manganese from sulphate-acetato medium with Cyanex 272

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The solvent extraction of Mn(II) from sulphate-acetato medium by bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272, BTMPPA,  $H_2A_2$ ) dissolved in distilled aliphatic kerosene has been investigated, the equilibration time being < 5 min. It is found that the extraction ratio ( $D$ ) is independent of initial or equilibrium Mn(II) concentration in the aqueous phase provided equilibrium  $pH$  and extractant concentration are kept constant. Extraction of Mn(II) is found to increase with the increase in equilibrium aqueous  $pH$ , extractant concentration in the organic phase and temperature. The  $pH$  and extractant dependences are 2 and 1 respectively, from which the extraction equilibrium reaction of Mn(II) by Cyanex 272 can be presented as  $Mn^{2+} + H_2A_{2(o)} \rightleftharpoons MnA_{2(o)} + 2 H^+$ . Acetate is used to buffer the aqueous phase which has no effect on the extraction ratio but the coexisting sulfate ion has an adverse effect; and  $D$  is found to be inversely proportional to the term  $(1 + 1.9 [SO_4^{2-}])$ . The extraction equilibrium constant ( $K_{ex}$ ) has been determined to be  $10^{-6.17}$  at 303 K. The temperature dependence data show that the process is endothermic with  $\Delta H$  value of  $-42$  kJ/mol. At a particular set of experimental parameter,  $D$  is very much dependent on the nature of diluent used to constitute the organic phase. The loading capacity is found to be 9.52 g Mn(II)/100 g Cyanex 272. The loading study also indicates that the organic phase speciation is not changed with the extent of loading. Stripping behaviors of Mn(II) from loaded organic phase with dilute  $H_2SO_4$ , HCl and  $HNO_3$  solutions have also been examined and it is found that quantitative stripping is possible by 0.10 mol/L solutions of these acids. Using Cyanex 272, separations of Mn(II) from its binary mixtures with Sc(III), Ti(IV), V(V), V(IV), Cr(III), Fe(III), Ni(II), Co(II), Zn(II) or Gd(III) can be achieved by single-stage or multiple-stage extractions at specified aqueous eq.  $pH$  values; but Mn(II)-Cu(II) separation is not at all possible.

**Keywords:** Cyanex 272, Kerosene, Manganese(II), Solvent extraction, Sulfate-acetato medium

In the hydrometallurgical processing of manganeseiferous shales, copper converter slag, deep sea manganese nodules, waste catalysts and batteries (Zn-C, Ni-Cd, etc), sulphide ores the acidic leach liquors often contain Fe(II), Fe(III), Mn(II) Cu(II), Co(II), Ni(II), Cd(II) and Zn(II), while the ammoniacal leach liquor contains almost negligible amounts of Fe(II)/Fe(III) and Mn(II)<sup>1</sup>. On carefully going through the related literature<sup>1-7</sup>, it is revealed that the purification/separation of these metal ions is feasible by the use of solvent extraction technique with the advent of extractants like di-(2-ethyl hexyl) phosphoric acid (D2EHPA or DAPA), mono-(2-ethylhexyl) phosphoric acid mono-(2-ethylhexyl) ester (PC 88A), LIX reagents (hydroximes) and phosphonic/thiophosphinic acid derivatives (Cyanex 272, Cyanex 302 and Cyanex 301). In the liquid-liquid extractions of Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) from sulfate solutions

using Cyanex 272, Cyanex 302 and Cyanex 301, and their binary mixtures with Aliquot 336, it has been reported<sup>8</sup> that Cyanex 301 is more effective than Cyanex 302, while extracting power is decreased in presence of Aliquot 336. A comparative extraction behavior of Cyanex 272, Cyanex 301 and Cyanex 302 towards first row transition metal ion from acidic sulfate medium has also been reported<sup>9</sup> and it is found that the extraction ratio shifts to lower  $pH$  value with increasing sulphur substitution (decreasing  $pK_a$  value of the extractant) in the extractant. The Co(II) - Mn(II) separation from sulfate solutions using sodium salts of D2EHPA, PC 88A and Cyanex 272 has been reported<sup>10</sup>. The separation of Mn(II) from Zn(II) in sulfate medium by D2EHPA, PC 88A and Cyanex 272 has also been investigated<sup>11</sup>. Although the Mn(II)-D2EHPA system has been extensively investigated by a number of workers from both equilibrium<sup>12-17</sup> and kinetic<sup>18-23</sup> points of view, the Mn(II)-Cyanex 272 system has been investigated to a lesser extent. Virtually, there is no work especially devoted to either the equilibrium or kinetics studies

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on the latter system. This study provides a thorough investigation on the extraction equilibria of Mn(II) from sulfate-acetato media by Cyanex 272 dissolved in kerosene.

## Experimental Procedure

### Materials

Cyanex 272 (84% BTMPPA, 5% RPO(OH)<sub>2</sub> and 11% R<sub>3</sub>PO), supplied by Cytec Canada Inc, was used without further purification. Kerosene procured from the local market was distilled to collect the colorless aliphatic fraction obtained within 200°-260°C. Other diluents and reagents were of AR grade (E. Merck – BDH) products and used as such.

### Methods

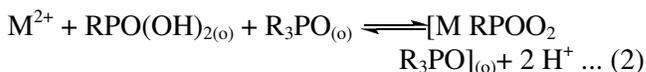
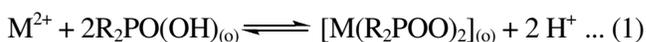
The Mn(II) content of the aqueous phase was estimated by the KIO<sub>4</sub>-oxidative spectrophotometric method<sup>24</sup> at 545 nm. For estimation of other metallic ions in solution, either colorimetric or AAS method was used. The pH values of the aqueous solutions were measured by a Mettler Toledo 320 pH-meter. For pH adjustments of aqueous solutions, either anhydrous Na<sub>2</sub>CO<sub>3</sub> or dilute H<sub>2</sub>SO<sub>4</sub> was used.

### Procedure for extraction of Mn(II)

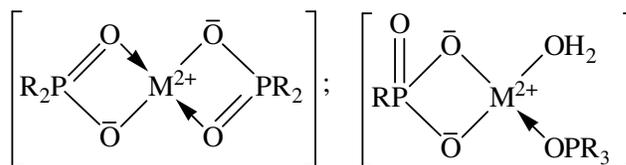
Equal volumes (25 mL) of the aqueous and organic phases were taken in a stoppered bottle (125 mL) and shaken for a definite time period of 5 min (otherwise stated) in a thermostatic water bath at 303 ± 0.50 K (otherwise stated). After attainment of equilibrium, the phases were allowed to settle and disengaged. The aqueous phase was subjected for equilibrium pH measurement and the metal ion content. In all cases, phase separations occurred quickly. The equilibrium organic phase metal ion concentrations were estimated by mass balance. The extraction ratio (*D*) of Mn(II) was calculated as a ratio of total [Mn(II)] in the organic phase to that in the aqueous phase at equilibrium. In the case of loading, the organic phase was repeatedly contacted with fresh equal volume of aqueous solutions until the saturation of the organic phase with the metal ion was attained. In stripping, 25 mL portion of an organic solution containing Mn(II) and practically no free Cyanex 272 (organic phase at maximum loading on dilution with kerosene) was equilibrated for 5 min at 30°C with an equal volume of H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl solutions of definite strengths (0.001, 0.01 or 0.10 mol/L).

### Treatment of Mn(II)-extraction equilibrium data

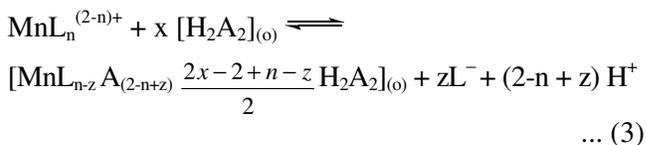
Cyanex 272 is a commercial extractant. It contains 84% bis-(2,4,4-trimethylpentyl = R) phosphinic acid (BTMPPA, R<sub>2</sub>POOH), 5% RPO(OH)<sub>2</sub> and 11% R<sub>3</sub>PO. It can be purified to contain about 99% BTMPPA by microemulsion formation method<sup>25</sup>. But as-received Cyanex 272 has been used in this investigation. BTMPPA and RPO(OH)<sub>2</sub> are both acidic chelating extractants but R<sub>3</sub>PO is an ion pair solvating agent. Therefore, all the components of Cyanex 272 have the extracting power. Moreover, equimolar mixture of RPO(OH)<sub>2</sub> and R<sub>3</sub>PO may behave as BTMPPA (R<sub>2</sub>POOH), as illustrated below:



The respective structures of the extracted species being:



In aqueous solution, Mn<sup>2+</sup> may be complexed with coexisting OH<sup>-</sup>, HSO<sub>4</sub><sup>-</sup> or CH<sub>3</sub>COO<sup>-</sup> (L<sup>-</sup>). Consequently, if Mn<sup>2+</sup> exists in the aqueous phase as MnL<sub>n</sub><sup>(2-n)+</sup> (L being the coexisting anion of unit charge) and BTMPPA is considered as dimeric (H<sub>2</sub>A<sub>2</sub>) in nonpolar solvents like kerosene<sup>26</sup>, then the extraction equilibrium reaction may be modeled as



where subscript (o) represents organic species. The equilibrium constant (*K<sub>ex</sub>*) of Eq. (3) can be expressed as

$$\log D = \log K_{ex} + (2-n+z)pH + x \log [H_2A_2]_{(o)} - z \log [L^-] \dots (4)$$

where *D* represents extraction ratio. Equation (4) represents the basic equation for a chelate forming solvent extraction system involving a metal ion by an acidic extractant. It is worth noting here that all concentrations and pH terms in Eq. (4) refer to the

equilibrium values. Consequently, Eq. (4) represents that the value of  $\log D$  should be independent of initial or equilibrium metal ion concentration at a constant set of equilibrium  $pH$  and extractant concentration, while it would be dependent on equilibrium  $pH$ , equilibrium extractant concentration and coexisting ligand concentration in the aqueous phase. Moreover, as equilibrium constant of a reaction is related to temperature by Vant Hoff equation,  $\log D$  will also depend on temperature.

## Results and Discussion

### Extraction equilibrium

The study on the extraction equilibrium has been carried out by determining the effects of time of phase mixing,  $[Mn(II)]_{(ini)}$ ,  $pH_{(eq)}$ ,  $[H_2A_2]_{(o, eq)}$ ,  $[SO_4^{2-}]$ ,  $[Ac^-]$  and temperature on the extent of extraction in the  $Mn(II)-SO_4^{2-}-Ac^- - H_2A_2$ -kerosene system. It has been experimentally observed that  $[Mn(II)]$  in the aqueous solution is decreased gradually during the progress of extraction (Aqueous phase:  $[Mn(II)]_{(ini)} = 0.40 \text{ kg/m}^3$ ,  $[Ac^-] = 0.25 \text{ kmol/m}^3$ ,  $[SO_4^{2-}] = 0.008 \text{ kmol/m}^3$ ,  $pH_{(ini)} = 4.60$ ; and Organic phase:  $[H_2A_2]_{(o, ini)} = 0.025 \text{ kmol/m}^3$  in kerosene; temp. = 303 K, O/A = 1, shaking speed = 300 strokes/min) and this behavior continues up to 4 min. It is therefore concluded that the equilibration time for the system is about 4 min. In subsequent experiments, a phase contact time of 5 min has been used in order to ensure equilibrations at different experimental parameters. It is mentionable here that the equilibration time of 3 min and 10 min has been reported for the extractions of  $Mn(II)$  from sulphate<sup>15</sup> and sulphate-acetate<sup>17</sup> media, respectively by D2EHPA.

The aqueous phases containing  $0.018 \text{ kmol/m}^3$  sulfate,  $0.025 \text{ kmol/m}^3$  acetate and different amounts of  $Mn(II)$  ranging from  $0.003 \text{ kmol/m}^3$  to  $0.0356 \text{ kmol/m}^3$  at initial  $pH$  of 4.6 have been equilibrated for 5 min with  $0.025 \text{ kmol/m}^3$  Cyanex 272 solution in kerosene at O/A of 1 (A = 25 mL) and at 303 K. It is found that  $\log D$  values decrease (though the equilibrium  $[Mn(II)]_{(o)}$  being increased) with the increase in  $[Mn(II)]_{(ini)}$  in the aqueous phase. It is also noticeable that the equilibrium  $pH$  values differ from the initial  $pH$  values significantly as expected. The  $\log D$  vs.  $\log ([Mn(II)]_{(ini)}, \text{ kmol/m}^3)$  plot is a curve. The reason for this nature may be the variability of equilibrium  $pH$  and free extractant concentration. After determining the  $pH$  and extractant dependences, the corrected  $D$  values ( ${}^cD$ ) and subsequently  $\log {}^cD$  values at a

chosen constant equilibrium  $pH$  and free extractant concentration can be calculated. If the  $pH$  and extractant dependences are 2 and 1 respectively (referred to the following two sections), the equation for calculating  $\log {}^cD$  at  $pH_{(eq)} = 4.6$  (constant) and  $[H_2A_2]_{(o, eq)} = 0.025 \text{ kmol/m}^3$  (constant) will be as follows:

$$\log {}^cD = \log D + 2 (\text{constant } pH_{(eq)} \text{ chosen} - pH_{(eq)} \text{ experimental}) + \{ \log (\text{constant } [H_2A_2]_{(o, eq)} \text{ chosen}) - \log ([H_2A_2]_{(o, ini)} - [Mn(II)]_{(o, eq)}) \} \dots (5)$$

where all concentration terms are in  $\text{kmol/m}^3$ . The  $\log {}^cD$  vs  $\log \{ [Mn(II)], \text{ kmol/m}^3 \}$  plot is found to be horizontal which is in consistent with Eq. (4) or with the fundamental aspect of solvent extraction chemistry. This independency indicates that the  $Mn(II)$  speciation change does not occur with its concentration change.

Equation (4) indicates that the plot of  $\log D$  vs. equilibrium  $pH$  ( $pH_{(eq)}$ ) should be a straight line with slope equaling to  $(2 - n + z)$ . The aqueous solutions containing  $0.40 \text{ kg/m}^3$   $Mn(II)$ ,  $0.008 \text{ kmol/m}^3$   $SO_4^{2-}$  and  $0.25 \text{ kmol/m}^3$   $Ac^-$  at different  $pH$  values have been prepared and each solution is equilibrated with both  $0.025$  and  $0.10 \text{ kmol/m}^3$  Cyanex 272 solutions in kerosene at O/A = 1 and 303 K. The logarithm of corrected  $D$  values ( $\log {}^cD$ ) at equilibrium extractant concentration has been calculated by the following relationship:

$$\log {}^cD = \log D + \{ \log (\text{constant } [H_2A_2]_{(o, eq)} \text{ chosen}) - \log ([H_2A_2]_{(o, ini)} - [Mn(II)]_{(o, eq)}) \} \dots (6)$$

Figure 1 represents the  $\log {}^cD$  vs.  $pH_{(eq)}$  plots at constant equilibrium extractant concentrations of  $0.025$  and  $0.10 \text{ kmol/m}^3$ . Straight lines are obtained with slopes of 2.00 and 2.01 for  $0.025$  and  $0.10 \text{ kmol/m}^3$  equilibrium extractant concentration systems respectively. The respective intercepts are  $-7.77$  and  $-7.22$ . Therefore, the value of  $(2 - n + z)$  is found to be 2.

According to Eq. (4), the plot of  $\log D$  vs.  $\log [H_2A_2]_{(o, eq)}$  at a particular constant equilibrium  $pH$  should be a straight line with slope (x) giving the number of moles of Cyanex 272 associated with 1 g ion of  $Mn(II)$  to form the extractable species. But it is very difficult to gather  $\log D$  values at constant equilibrium  $pH$  values. Consequently,  $\log {}^cD$  values should be evaluated as earlier. Three aqueous solutions each containing  $0.40 \text{ kg/m}^3$   $Mn(II)$ ,  $0.008 \text{ kmol/m}^3$   $SO_4^{2-}$  and  $0.25 \text{ kmol/m}^3$   $Ac^-$  at initial  $pH$

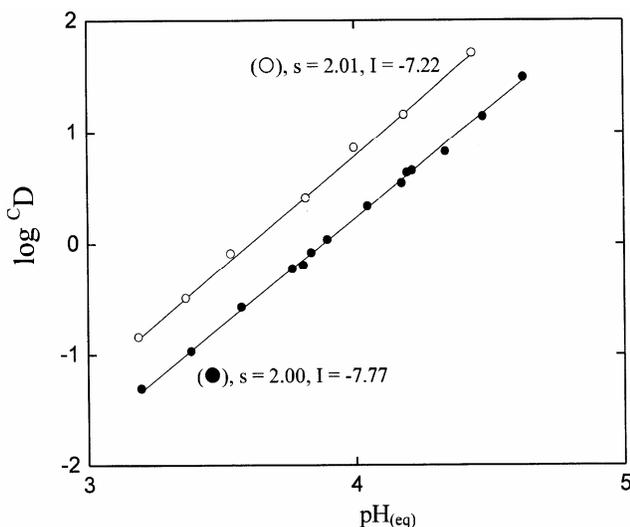


Fig. 1—Effect of equilibrium  $pH$  on extraction  $[Mn(II)]_{(ini)} = 0.40$   $kg/m^3$ ,  $[Ac^-] = 0.25$   $kmol/m^3$ ,  $[SO_4^{2-}] = 0.008$   $kmol/m^3$ , equilibration time = 5 min, temperature =  $(303 \pm 0.50)$  K,  $O/A = 1$ . [(●)— $[H_2A_2]_{(o,ini)} = 0.025$   $kmol/m^3$ ,  $C D = D$  at constant  $[H_2A_2]_{(o,eq)} = 0.025$   $kmol/m^3$ ; (O)— $[H_2A_2]_{(o,ini)} = 0.10$   $kmol/m^3$ ,  $C D = D$  at constant  $[H_2A_2]_{(o,eq)} = 0.10$   $kmol/m^3$ ]

values of 3.75, 4.15 and 4.45 have been prepared, and each solution is equilibrated with Cyanex 272 solutions of different concentration in kerosene. The  $\log D$  vs.  $\log ([H_2A_2]_{(o,ini)}$ ,  $kmol/m^3$ ) plots at initial  $pH$  values of 3.75, 4.15 and 4.45 are shown in Fig. 2. Straight lines are obtained indeed with slopes of 1.03, 1.02 and 1.07 for constant initial  $pH$  values of 4.45, 4.15 and 3.75 respectively, with respective intercepts of 2.48, 1.90 and 1.45. Considering extractant dependency of unity,  $\log [H_2A_2]_{(o,eq)}$  values have been calculated ( $= \log [H_2A_2]_{(o,ini)} - [Mn(II)]_{(o,eq)}$ ), while on considering  $pH$  dependency of 2, the values of  $\log C D$  have been calculated using the following relationship:

$$\log C D = \log D + 2 (\text{constant } pH_{(eq)} \text{ chosen} - pH_{(eq)} \text{ experimental}) \quad \dots (7)$$

Figure 2 also shows the  $\log C D$  vs.  $\log [H_2A_2]_{(o,eq)}$  plots at constant equilibrium  $pH$  values of 3.74, 4.13 and 4.35. In all the cases, straight lines are obtained with respective slopes of 1.07, 1.01 and 1.00, and intercepts of 1.47, 2.06 and 2.51. It is therefore concluded that the value of 'x' in Eq. (4) i.e. the extractant dependency is 1.

Two sets of aqueous solutions, one at  $pH$  3.7 and other at  $pH$  4.25 containing  $0.407 \pm 0.08$   $kg/m^3$   $Mn(II)$  and  $0.008$   $kmol/m^3$   $SO_4^{2-}$  and variable amounts

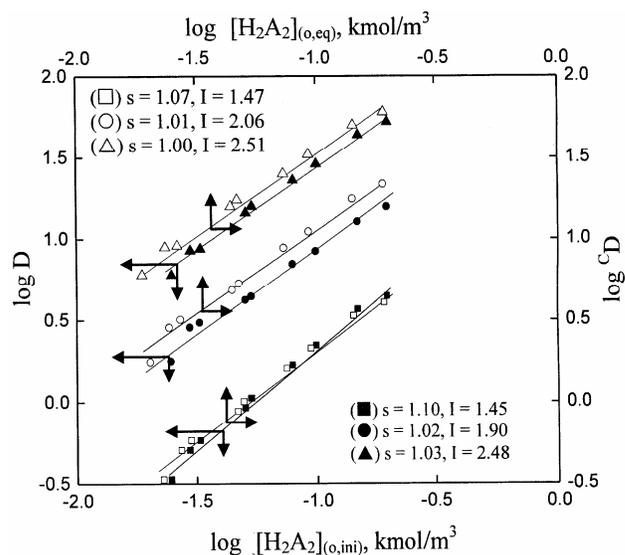


Fig. 2—Effect of extractant concentration on extraction  $[Mn(II)]_{(ini)} = 0.40$   $kg/m^3$ ,  $[Ac^-] = 0.25$   $kmol/m^3$ ,  $[SO_4^{2-}] = 0.008$   $kmol/m^3$ , equilibration time = 5 min, temperature =  $(303 \pm 0.50)$  K,  $O/A = 1$ . [(■, □)— $pH_{(ini)} = 3.75$ ,  $C D = D$  at constant ( $pH_{(eq)} = 3.74$ ), (▲, △)— $pH_{(ini)} = 4.45$ ,  $C D = D$  at constant ( $pH_{(eq)} = 4.35$ ), (●, ○)— $pH_{(ini)} = 4.15$ ,  $C D = D$  at constant ( $pH_{(eq)} = 4.13$ )]

of acetate ions ( $0.10 - 2.00$   $kmol/m^3$ ) have been prepared. The set of solutions at  $pH$  3.7 is equilibrated with either  $0.025$   $kmol/m^3$  or  $0.10$   $kmol/m^3$  Cyanex 272 solution at  $O/A = 1$ , while the other set with  $0.025$   $kmol/m^3$  Cyanex 272 solution. The  $\log C D$  values have been calculated by Eq. (5). The  $\log C D$  vs.  $\log ([Ac^-]$ ,  $kmol/m^3$ ) plots at three different sets of experimental parameters are found to be horizontal, i.e. the extraction ratio of  $Mn(II)$  is not at all varied with increasing acetate ion concentration in the aqueous phase, provided equilibrium  $pH$  is maintained constant. The result also indicates that  $0.10$   $kmol/m^3$  acetate buffer is as effective as  $2$   $kmol/m^3$  acetate buffer.

Two sets of aqueous solutions, one at  $pH$  3.82 and other at  $pH$  4.3 containing  $0.402 \pm 0.01$   $kg/m^3$   $Mn(II)$ ,  $0.25$   $kmol/m^3$   $Ac^-$  and variable amounts ( $0.008 - 2.00$   $kmol/m^3$ ) of  $SO_4^{2-}$  have been prepared and each solution is equilibrated with  $0.025$   $kmol/m^3$  Cyanex 272 solution at  $303$  K and  $O/A$  of 1 in order to calculate the values of extraction ratios. The  $\log C D$  values have been calculated as usual. The  $\log C D$  vs.  $\log ([SO_4^{2-}]$ ,  $kmol/m^3$ ) plots are shown in Fig. 3. In either of the cases, experimental points fall on a curve rather than on a straight line. In lower concentration region of  $SO_4^{2-}$ , the extraction ratio is seldom changed, while in the higher concentration region, the extraction ratio is considerably decreased

with increasing sulfate ion concentration. The experimental points in each case fall on a curve, as represented by

$$\log {}^C D = \log K_{\text{ex}} + 2 \text{pH}_{(\text{eq})} \text{ (chosen as constant)} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} \text{ (chosen as constant)} - \log (1 + 1.9 [\text{SO}_4^{=}] ) \quad \dots (8)$$

The above equation indicates that the extraction ratio is inversely proportional to the term  $(1 + 1.9 [\text{SO}_4^{=}] )$ .

An aqueous phase containing  $0.40 \text{ kg/m}^3 \text{ Mn(II)}$ ,  $0.008 \text{ kmol/m}^3 \text{ SO}_4^{=}$  and  $0.25 \text{ kmol/m}^3 \text{ Ac}^-$  at  $\text{pH } 3.8$  has been prepared and equal aliquots of this solution ( $25 \text{ cm}^3$ ) and either  $0.025$  or  $0.10 \text{ kmol/m}^3$  extractant in kerosene are equilibrated at various temperatures ( $288 - 318 \text{ K}$ ) to find out the values of  $D$  as usual. A similar aqueous phase at  $\text{pH } 4.25$  has also been prepared and equal portions of this solution are equilibrated with  $0.025 \text{ kmol/m}^3$  Cyanex 272 solutions at different temperatures for the same purpose. As the equilibrium  $\text{pH}$  values differ, the  $\log {}^C D$  values are calculated by using Eq. (5). The Vant Hoff plots [ $\log {}^C D$  vs.  $(1/T)$ ,  $\text{K}^{-1}$ ] are drawn and it is found in all three cases that the extraction ratio is increased with increasing temperature and the straight line relationship holds. From the slopes of the plots, the values of the heat of extraction reaction ( $\Delta H$ ) have been calculated (slope =  $-\Delta H/2.303 \text{ R}$ ) to be  $43.2$ ,  $43.8$  and  $41.0 \text{ kJ/mol}$  for (constant  $\text{pH}_{(\text{eq})}$  chosen / constant  $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$  in  $\text{kmol/m}^3$  chosen) values of  $3.8/0.025$ ,  $3.78/0.10$  and  $4.2/0.025$  respectively. It is therefore concluded that extraction of  $\text{Mn(II)}$  by Cyanex 272 is remarkably increased with an increase in temperature with  $\Delta H$  value of  $\sim 42 \text{ kJ/mol}$ . In other words, the extraction system is endothermic and the constancy of  $\Delta H$  value indicates that the extraction mechanism is not changed with the change in experimental parameters, including the temperature range used in extraction.

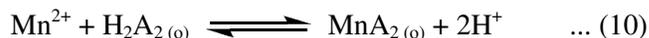
#### Mechanism of extraction

The stability constant<sup>27a</sup> of  $\text{Mn(OH)}^+$  at  $25^\circ\text{C}$  and  $1.0 \text{ mol/L}$  ionic strength is  $10^3$ , which indicates the presence of ppb level concentration of the monohydroxylated species at around  $4.0 \text{ pH}$ . So, the extraction of  $\text{Mn(II)}$  by reaction of  $\text{Mn(OH)}^+$  with extractant can be ruled out. In aqueous solutions of  $\text{MnSO}_4$ , the species like  $\text{MnHSO}_4^+$  may exist due to the following equilibrium:



The stability constants of the monobisulphato<sup>27b</sup> and monosulphato<sup>28</sup> complexes of  $\text{Mn}^{2+}$  are  $10^{2.26}$  and  $10^{2.28}$  respectively at  $25^\circ\text{C}$  and zero ionic strength. Considering the stability constants of  $\text{H}_2\text{O}$ ,  $\text{HSO}_4^-$ ,  $\text{MnHSO}_4^+$ ,  $\text{MnSO}_4$ ,  $\text{MnOH}^+$ ,  $\text{Mn(OH)}_2$  together with probable mass balance and charge balance equations, Sausa (Jr) *et al.*<sup>29</sup> have found the distributions of  $\text{Mn}^{2+}$  species together with  $\text{SO}_4^{=}/\text{HSO}_4^-$  distribution using a certain sort of computer programming. They have shown that  $\text{HSO}_4^-$  exists up to 100% at  $\text{pH} \sim 0$ , but the maximum amount of  $\text{MnSO}_4$  species exists around  $\text{pH } 2$ . Free  $\text{SO}_4^{=}$  and  $\text{MnSO}_4$  concentrations in the system increase with increasing  $\text{pH}$  with a maximum of  $\sim 73\%$  and  $\sim 27\%$  respectively over  $\text{pH } 3.2$ . Consequently, at  $\text{pH } 4$ , the existing species may be regarded as  $\text{Mn}^{2+}$  ( $\sim 73\%$ ) and  $\text{MnSO}_4$  ( $\sim 27\%$ ). However, the percentages of existence of the above species will undoubtedly depend on  $\text{Mn}^{2+}$  and  $\text{SO}_4^{=}$  concentrations in the system.

At lower sulfate concentration region, the value of 'z' in Eq. (4) is zero, so that the value of n will be zero and consequently '2-n+z' will be equal to 2. Thus, on putting  $n = 0$ ,  $x = 1$  and  $z = 0$  in Eq (3), one gets



Equation (10) represents the extraction equilibrium reaction at lower sulfate concentration region in the aqueous phase. At higher sulfate concentration region, the value of 'z' in Eq. (4) approaches to -1. Hence, the extraction equilibrium reaction at higher concentration region can be depicted as



At intermediate concentration regions of sulfate, parallel reactions as represented by Eqs (10) and (11), proceed to produce the same extractable species ( $\text{MnA}_2$ ).

The stability constant of  $\text{MnAc}^+$  complex ( $[\text{MnAc}^+]/[\text{Mn}^{2+}][\text{Ac}^-]$ ) is  $10^{0.69}$  at  $25^\circ\text{C}$  and unity ionic strength<sup>30</sup>. Simple calculations show that  $0.85\%$  and  $0.4\%$  acetato complex of  $\text{Mn}^{2+}$  exists in medium containing  $0$  and  $0.1 \text{ kmol/m}^3$  acetate ion respectively, and  $0.01 \text{ kmol/m}^3 \text{ Mn(II)}$ . Since negligible amount of acetato complex of  $\text{Mn(II)}$  exists in the extraction medium, the extraction ratio is found to be independent of acetate ion concentration.

#### Loading of Cyanex 272 solutions with Mn(II)

An aliquot (100 cm<sup>3</sup>) of 0.05 kmol/m<sup>3</sup> Cyanex 272 solution in kerosene has been repeatedly equilibrated with 100 cm<sup>3</sup> portions of fresh aqueous solutions containing 1.05 kg/m<sup>3</sup> Mn(II), 0.019 kmol/m<sup>3</sup> SO<sub>4</sub><sup>2-</sup> and 0.25 kmol/m<sup>3</sup> Ac<sup>-</sup> at pH 6.0. A similar study has been made with 0.025 kmol/m<sup>3</sup> Cyanex 272 solution. It is observed that loading of the organic phase with Mn(II) is ended up at the 6th and 5th contacts for 0.025 and 0.05 kmol/m<sup>3</sup> Cyanex 272 systems respectively. The maximum loadings of 1.378 and 2.76 kg/m<sup>3</sup> Mn(II) are obtained for 0.025 and 0.05 kmol/m<sup>3</sup> Cyanex 272 systems, respectively. Calculation shows that 1 L portion of 0.025 kmol/m<sup>3</sup> Cyanex 272 solution can extract 0.02508  $\approx$  0.025 mol Mn(II), while 1 L portion of 0.050 kmol/m<sup>3</sup> Cyanex 272 solution can extract 0.0502  $\approx$  0.05 mol Mn(II). Therefore, in saturated condition of Mn(II) in the organic phase, the mole ratio of Mn(II) to Cyanex 272 is found to be 1, supporting the reaction represented by Eq. (10) as the extraction equilibrium reaction. In other words, the mechanism of extraction of Mn(II) is not changed with the extent of loading. The loading capacity (defined as the maximum amount of a metal ion in g, being extracted by 100 g extractant) is a very useful parameter in selecting an extractant for a metal ion extraction system, at least when to be used in an industry. A calculation shows that the loading capacity of Cyanex 272 (dissolved in kerosene) towards Mn(II) is  $\sim$  9.52 g Mn(II) per 100 g Cyanex 272.

#### Effect of diluent on extraction ratio of Mn(II)

Although by definition the term diluent as used in solvent extraction chemistry is inert, in actual practices it is observed that the nature of diluent may tremendously affect the metal-ion distribution in a solvent extraction process. Some scientists tried to correlate this behavior with the dipole moment of the diluent while others tried to correlate this with the effective extractant concentration difference at the interface due to different degree of adsorption of extractant molecules at the interface.

In this work, the extraction ratios have been measured when the same aqueous phase is extracted by 0.10 kmol/m<sup>3</sup> Cyanex 272 dissolved in different diluents, keeping all other parametric conditions identical. It is observed that the extraction ratio increases in the following order with the variation of diluent: *n*-heptanol ( $D = 0.154$ ) < chloroform ( $D = 0.35$ ) < *n*-hexanol ( $D = 0.364$ ) < 1,2-dichloroethane ( $D = 0.50$ ) < *n*-hexane ( $D = 0.67$ ) <

benzene ( $D = 0.73$ ) < carbon tetrachloride ( $D = 0.784$ ) < cyclohexane ( $D = 0.875$ ) < kerosene ( $D = 1.31$ ) < *n*-heptane ( $D = 1.885$ ). The study reveals that the kerosene is a very good diluent just next to *n*-heptane for the extraction of Mn(II) by Cyanex 272.

The effective cross-sectional areas of BTMPPA (Cyanex 272) at the 0.5 kmol/m<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>/BTMPPA in various diluent interfaces have been measured by Biswas and Singha<sup>31</sup>. When the log  $D$  values are plotted against the logarithm of the reported values of the cross-sectional area of BTMPPA ( $A, \text{\AA}^2$ ), a very good fit correlation is found to exist among *n*-heptane, kerosene, benzene, chloroform and *n*-heptanol. In these cases, the extraction ratio decreases with the increase in cross-sectional area of BTMPPA. A comparatively weak fit correlation also exists among cyclohexane, carbon tetrachloride, toluene, benzene and *n*-hexanol. For the first set of five diluents, the variation in log  $D$  with log ( $A, \text{\AA}^2$ ) is very sharp compared to the second set of five diluents. All point fit correlation is not obtained, probably due to the change in interface composition in the present case from that reported by Biswas and Singha<sup>31</sup>.

#### Evaluation of extraction equilibrium constant ( $K_{ex}$ ) at 303 K

From the intercepts of the lines in Figs 1-3, the values of  $K_{ex}$  have been evaluated based on Eq. (8). The average log  $K_{ex}$  value at 303 K is calculated to be -6.1696 with standard deviation of 0.0633. The log  $K_{ex}$  value has also been estimated by the graphical method. Equation (8) indicates that the plot of log  $^cD$  vs.  $[2 \text{pH}_{(eq)} + \log [H_2A_2]_{(o,eq)} - \log (1 + 1.9 [SO_4^{2-}])] = \log f(R)$  should be a straight line with slope equaling to unity and intercept equaling to log  $K_{ex}$ . All equilibrium data at 303 K, presented so far have been considered for this treatment and the calculated X-axis parameters are shown against the Y-axis parameter (log  $^cD$ ), as shown in Fig. 4. A straight line is indeed obtained with the Least Squares slope of 0.9902 (should be 1.0) and correlation coefficient of 0.9862. The line has the intercept of -6.1783, which refers to the log  $K_{ex}$  value. So, the value of log  $K_{ex}$  obtained by two methods matches well with each other.

#### Stripping of Mn(II) loaded organic phase by mineral acids

The maximum Mn(II) loaded organic phase having theoretically no free extractant has been subjected for stripping study with 0.001, 0.01 and 0.10 kmol/m<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl solutions at 303 K and O/A of 1. The stripping results are given in Table 1.

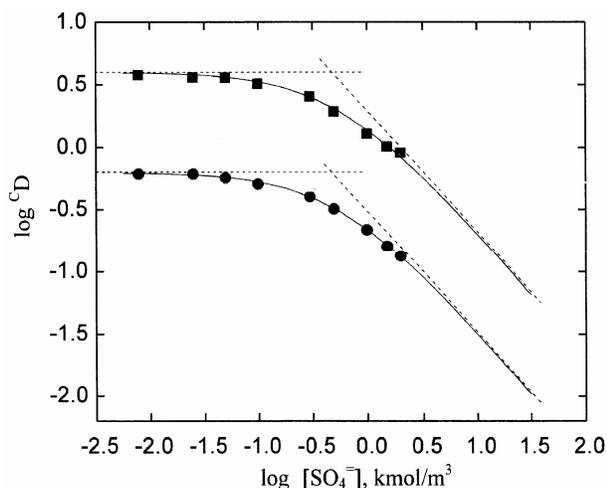


Fig. 3—Effect of co-existing sulphate ion in the aqueous phase on extraction  $[\text{Mn(II)}]_{(\text{ini})} = (0.402 \pm 0.01) \text{ kg/m}^3$ ,  $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$ , temperature =  $(303 \pm 0.50) \text{ K}$ , equilibration time = 5 min. (■)—  $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3 = [\text{H}_2\text{A}_2]_{(\text{o,eq})}$  chosen,  $\text{pH}_{(\text{ini})} = 4.30$ , constant  $\text{pH}_{(\text{eq})}$  chosen = 4.22. The points are experimental and the solid curve is theoretical representing:  $\log C_D = \log K_{\text{ex}} + 2 \text{pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log \{1 + K_{\text{SO}_4^2}^{\text{Eq}} [\text{SO}_4^2-]\}$ , where  $K_{\text{SO}_4^2}^{\text{Eq}}$  is a proportionality constant and its value has been evaluated to be 1.90 by the Curve-Fitting method as follows the horizontal dashed line is the asymptote at lower sulfate concentration region:  $\log C_D = \log K_{\text{ex}} + 2 \text{pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} = 0.60$  and the inclined dashed line is the asymptote at higher sulfate concentration region:  $\log C_D = 0.60 - K_{\text{SO}_4^2}^{\text{Eq}} - \log [\text{SO}_4^2-]$ . At the point of intersection of the two asymptotes,  $-\log K_{\text{SO}_4^2}^{\text{Eq}} - \log [\text{SO}_4^2-]$  is equal to zero, giving,  $\log K_{\text{SO}_4^2}^{\text{Eq}} = -\log [\text{SO}_4^2-] = 0.28$ ; so that  $\log K_{\text{SO}_4^2}^{\text{Eq}} = 1.90$ . (●)—  $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3 = [\text{H}_2\text{A}_2]_{(\text{o,eq})}$  chosen,  $\text{pH}_{(\text{ini})} = 3.82$ , constant  $\text{pH}_{(\text{eq})}$  chosen = 3.80. The points are experimental and the solid curve is theoretical representing,  $\log C_D = -0.2 - \log \{1 + 1.9 [\text{SO}_4^2-]\}$ . The treatment is as above

It is found that  $0.1 \text{ kmol/m}^3 \text{ H}_2\text{SO}_4$ ,  $\text{HCl}$  or  $\text{HNO}_3$  can strip  $\text{Mn(II)}$  quantitatively. With decrease in the concentration of stripping acid, percentage of  $\text{Mn(II)}$ -stripped is decreased appreciably. The results are given for the organic phase  $\text{Mn(II)}$  concentration of  $0.20 \text{ kg/m}^3$ . If the organic phase  $\text{Mn(II)}$  concentration is very high, then either more concentrated acid solution or stage-wise stripping or change of O/A may be needed.

#### Separation of Mn(II) from some of its binary mixtures

Table 2 shows the extraction percentages of  $\text{Sc(III)}$ ,  $\text{Ti(IV)}$ ,  $\text{V(IV)}$ ,  $\text{V(V)}$ ,  $\text{Cr(III)}$ ,  $\text{Fe(III)}$ ,  $\text{Co(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Cu(II)}$ ,  $\text{Zn(II)}$  or  $\text{Gd(III)}$  –  $\text{Mn(II)}$  binary systems at various equilibrium  $\text{pH}$  values. It is obvious from the table that the complete separation of  $\text{Sc(III)}$ ,  $\text{Ti(IV)}$ ,  $\text{V(V)}$  and  $\text{Cr(III)}$  from  $\text{Mn(II)}$  are obtainable at equilibrium  $\text{pH}$  values of 2, 2, 5 and 5 respectively in

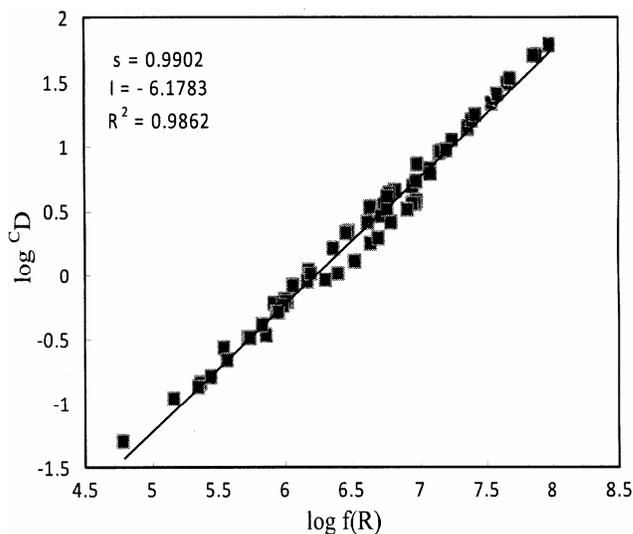


Fig. 4—Plot of  $\log C_D$  vs.  $\log f(R)$  for the estimation of extraction equilibrium constant ( $K_{\text{ex}}$ ) of  $\text{Mn(II)}$  by Cyanex 272 at  $(303 \pm 0.5) \text{ K}$ , where  $\log f(R) = [2 \text{pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log (1 + 1.9 [\text{SO}_4^2-])]$

Table 1—Stripping of  $\text{Mn(II)}$  loaded organic phase using different acid solutions

$\{[\text{Mn(II)}]_{(\text{o,ini})} = 0.20 \text{ kg/m}^3, [\text{SO}_4^2-] = 0.00364 \text{ kmol/m}^3,$ $\text{equilibration time} = 5 \text{ min, temperature} = (303 \pm 0.50) \text{ K, O/A} = 1\}$			
Stripping agent	Acid concentration $\text{kmol/m}^3$	$[\text{Mn(II)}]_{(\text{aq})} \text{ kg/m}^3$	% of $\text{Mn(II)}$ stripped
$\text{H}_2\text{SO}_4$	0.100	0.2000	100.00
	0.010	0.1890	94.50
	0.001	0.1080	54.00
$\text{HNO}_3$	0.100	0.2000	100.00
	0.010	0.1740	87.00
	0.001	0.0800	40.00
$\text{HCl}$	0.100	0.2000	100.00
	0.010	0.1740	87.00
	0.001	0.0732	37.00

single stage extraction. Separations of  $\text{V(IV)}$ ,  $\text{Fe(III)}$ ,  $\text{Zn(II)}$  or  $\text{Gd(III)}$  from their binary mixtures with  $\text{Mn(II)}$  are also possible at eq.  $\text{pH}$  2.5; but in these cases, clear-cut separations might be achieved by two to three extraction stages. The complete separation of  $\text{Mn(II)}$  from  $\text{Ni(II)}$  can be achieved by a three-stage extraction process at eq.  $\text{pH}$  4.0 leaving all  $\text{Ni(II)}$  in the aqueous phase. Since the extraction characteristics of  $\text{Mn(II)}$  and  $\text{Cu(II)}$  are too much similar, their separation cannot be done by Cyanex 272. Separation of  $\text{Mn(II)}$  from  $\text{Co(II)}$  appears as complicated; however, multi-stage extractions at aqueous eq.  $\text{pH}$  of 4 - 4.5 may separate one from other.

Table 2—Separation of Mn(II) from its binary mixtures with Sc(III), Ti(IV), V(V), Cr(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) or Gd(III) {[Mn(II)]<sub>(ini)</sub> = 0.40 kg/m<sup>3</sup>, [SO<sub>4</sub><sup>2-</sup>] = 0.1 mol/L above pH<sub>eq</sub> of 1.5 (at pH<sub>eq</sub> < 1.5; [SO<sub>4</sub><sup>2-</sup>] ≈ [H<sub>2</sub>SO<sub>4</sub>], [Cyanex 272] = 0.10 mol/L, O/A = 1, equilibration time = 10 min, temp. = 30°C)

pH(eq) (±0.05)	Extraction, %											
	Mn(II)	Sc(III)*	Ti(IV)#	V(IV)#	V(V)#	Cr(III)#	Fe(III)#	Co(II)*	Ni(II)#	Cu(II)#	Zn(II)#	Gd(III)*
0.0	<sup>f</sup> NE	56.0	6.6	3.0	22.0	NE	NE	NE	NE	NE	NE	
0.5	NE	87.0	73.8	5.0	17.0	NE	NE	NE	NE	NE	NE	
1.0	NE	98.5	97.3	9.0	12.0	NE	0.8	NE	NE	NE	1.1	1.8
1.5	NE	99.8	99.8	35.0	8.0	NE	8.2	NE	NE	NE	9.1	22.0
2.0	NE	<b>CE</b>	<b>CE</b>	56.0	6.0	NE	41.4	NE	NE	0.2	50.0	66.6
2.5	0.3 ± 0.1	CE	CE	<b>74.0</b>	5.0	NE	<b>86.3</b>	NE	NE	1.0	<b>89.9</b>	<b>97.5</b>
3.0	5.5 ± 0.5	CE	CE	87.0	5.0	NE	98.1	0.5	NE	7.4	98.0	99.4
3.5	42.5 ± 1.5	CE	CE	95.0	3.0	NE	99.8	2.0	NE	44.3	99.8	99.8
4.0	87.3 ± 1.5	CE	CE	97.5	1.0	NE	CE	8.0	NE	91.8	CE	CE
4.5	98.0 ± 0.5	CE	CE	98.9	NE	NE	CE	<b>15.0</b>	<b>NE</b>	97.3	CE	CE
5.0	99.8 ± 0.1	CE	CE	CE	<b>NE</b>	<b>NE</b>	CE	35.0	1.5	99.2	CE	CE
5.5	<sup>f</sup> CE	CE	CE	CE	NE	NE	CE	84.0	4.0	CE	CE	CE
6.0	CE	CE	CE	CE	NE	NE	CE	96.0	12.0	CE	CE	CE
6.5	CE	CE	CE	CE	NE	NE	CE	98.8	70.0	CE	CE	CE
7.0	CE	CE	CE	CE	NE	NE	CE	CE	90.0	CE	CE	CE

Initial metal ion concentration in the aqueous phase = 0.10 kg/m<sup>3</sup> (\*) and 1.0 kg/m<sup>3</sup> (#). NE = Un-extractable and CE = Complete extraction.

## Conclusion

Manganese(II) can be extracted by Cyanex 272 having dissolved in kerosene. The pH and extractant dependences are found to be 2 and 1 respectively. The sulfate ion concentration has an adverse effect on extraction. Acetate ion concentration has no effect on extraction. The extraction equilibrium constant ( $K_{ex}$ ) is found to be  $10^{-6.17}$ . The extraction processes are endothermic with  $\Delta H$  values of 42 kJ/mol. The loading capacity is 9.52 g Mn(II) per 100 g of extractant. A single stage stripping by 0.1 kmol/m<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>/HCl/HNO<sub>3</sub> (O/A = 1) can bring 100% Mn(II) in the aqueous phase. Distribution ratio ( $D$ ) is found to be highly dependent on the diluents used in this investigations and its value in different diluents is not fitted well with the cross-sectional area of BTMPPA molecule at the interfaces. Clear-cut separations of Mn(II) from Sc(III), Ti(IV), V(V) and Cr(III) in single-stage extraction; from V(IV), Fe(III), Zn(II), Ni(II) and Gd(III) in three stage extraction and from Co(II) in multi-stage extraction can be obtained by selecting suitable aqueous eq. pH values. Separation of Mn(II) from Cu(II) is not at all possible by this extractant.

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