

## KINETICS OF $Mn^{2+}$ EXTRACTION IN THE ACIDIC CHLORIDE-D2EHPA-KEROSENE SYSTEM USING THE CONSTANT INTERFACIAL AREA STIRRED CELL TECHNIQUE

R K Biswas\*, M A Habib, M R Ali and M Z Haque

Department of Applied Chemistry and Chemical Technology, University of Rajshahi, Rajshahi-6205, Bangladesh

(Received. 18 June 1996 accepted 20 September 1997)

Kinetics of the system ( $\mu=0.1 \text{ kmol m}^{-3}$ ) have been studied over a wide range of  $Mn^{2+}$  concentration, pH, extractant concentration and temperature conditions using the constant interfacial area stirred cell technique. The reaction orders with respect to  $Mn^{2+}$ , D2EHPA (di-2-ethylhexylphosphoric acid,  $H_2R_2$ ) and  $H^+$  concentrations have been estimated to be +1, +1 and -1 respectively. The value of the rate constant,  $k_f$  has been evaluated to be  $10^{-6.534} \text{ m s}^{-1}$  at lower investigated pH region. Kinetic data at higher pH region appear to be erroneous due to the instantaneous variation of interfacial pH. Temperature dependence data give  $E_a$  values of 76.5 and 8.7  $\text{kJ mol}^{-1}$  at lower and higher temperature regions respectively. The values of  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  have been evaluated. An analysis of the kinetic data suggests that the reaction step at the interfaces:  $Mn^{2+} + HR_{2(i)} \rightarrow [Mn(HR_2)]^+(i)$ , is the slowest at lower temperature region, and at the higher temperature region, the diffusion of the species to the interface to occur the above reaction is the slowest step. The entropy of activation suggests that the above reaction occurs through an  $SN_2$  mechanism.

**Key words:** Extraction, Kinetics, Manganese(II), D2EHPA, Lewis cell, kerosene-HCl interface.

### Introduction

The extraction equilibrium of  $Mn^{2+}$  by D2EHPA has been reported earlier (Ritcey and Ashbrook 1970; Sato *et al* 1978; Islam and Biswas 1981) and is established within a minute. As the extraction is fast, its cannot be investigated by the shake-out method (Sekine *et al* 1971b, 1973a; Islam and Biswas 1976, 1978, 1979 and 1980). So the kinetics of this system have already been reported earlier using the Rotating Diffusion Cell (RDC) (Hughes and Biswas 1993) and Single Drop techniques (Biswas *et al* 1996). This paper discusses the kinetics of the extraction of  $Mn^{2+}$  from an acidic chloride medium having constant ionic strength of  $0.1 \text{ kmol m}^{-3}$  by di-2-ethylhexylphosphoric acid dissolved in kerosene using a constant interfacial area stirred cell technique. This technique provides the interfacial area measurement which has a vital role in the kinetics of a liquid-liquid extraction (heterogeneous) system. Results obtained by this technique have been compared with those obtained from the Single Drop technique (Biswas *et al* 1996).

### Experimental

**Reagents.** Except kerosene, the chemicals used were of reagent grade. D2EHPA was procured from E. Merck (95% purity) and purified by the method of Sato (McDowell *et al*

1976). Kerosene was bought from the local market and distilled to collect a colourless fraction distilling over within 220-260°C.

**Analytical.** The concentration of  $Mn^{2+}$  in the aqueous phase was estimated by the  $HNO_3$ - $KIO_4$  colorimetric method (Bas-set *et al*) using a WPA-S104-Colorimeter. The pH values of the aqueous solutions were measured by a Corning-7A model pH meter equipped with a combination electrode. For adjusting the pH of the aqueous solutions, anhydrous  $Na_2CO_3$  was used. Organic phase  $Mn^{2+}$  concentration was estimated colorimetrically after stripping with  $1 \text{ kmol m}^{-3} HNO_3$ .

**Cell and Technique.** The cell consists of a jacketed glass container which facilitates temperature control ( $\pm 0.5^\circ C$ ). Identical aliquots ( $100 \text{ cm}^3$ ) of aqueous and organic solutions (pre-thermostated) can be taken in this glass container without much distributing the interface. The container has an air-tight lid which has three bores, one for inserting the rod of an electric stirrer and other two for introducing two glass-tubes to take out aqueous and organic solutions time to time from the middle of these phases with the aid of polythene tubes and plastic syringes. An electrical stirrer (1 cm long two blades) stirs the upper organic phase clockwise and a magnetic stirrer (2 cm long capsule) is used to rotate the lower aqueous solution in the same direction. The stirrer speeds are controlled at the maxima (2.5 Hz) which does not disturb

\*Author for correspondence

the interface (stable and flat). After certain interval (usually 2-6 min depending on reaction parameters), 2 cm<sup>3</sup> aqueous phase and 5 cm<sup>3</sup> organic phases are taken out for analyses. The amount of Mn<sup>2+</sup> transferred into the organic phase can be estimated from the analyses of either aqueous or organic phase and varies within  $\pm 1\%$ . All experiments have been carried out at  $(30 \pm 1)^\circ\text{C}$ , otherwise stated. The interfacial area in all experiments is kept at  $3.368 \times 10^{-3} \text{ m}^2$  which can be changed by setting the circular plastic rings within the cell where interface is formed.

#### Notations and Abbreviations:

D2EHPA = di-2-ethylhexylphosphoric acid;

$\text{H}_2\text{R}_2$  = dimeric D2EHPA;

$a^0\text{Mn}^{2+}$  = amount of Mn<sup>2+</sup> transferred in 100 cm<sup>3</sup> organic phase through interface A in time t, kmol;

$\mu$  = ionic strength, kmol m<sup>-3</sup>;

$k_f$  = forward extraction rate constant, m s<sup>-1</sup>;

$E_a$  = activation energy, kJ mol<sup>-1</sup>;

$\Delta H^\ddagger$  = enthalpy of activation, kJ mol<sup>-1</sup>;

$\Delta S^\ddagger$  = entropy of activation, J mol<sup>-1</sup>;

J = flux = rate of mass transfer per unit area per unit time, kmol m<sup>-2</sup> s<sup>-1</sup>;

A = interfacial area through which mass transfer takes place, m<sup>2</sup>;

t = time allowed for mass transfer through interface, s;

a = order with respect to manganese(II) concentration;

b = order with respect to hydrogen ion concentration;

c = order with respect to D2EHPA concentration;

(mn) = constant concentration of manganese(II), kmol m<sup>-3</sup>;

(h) = constant concentration of hydrogen ion, kmol m<sup>-3</sup>;

( $h_2r_2$ ) = constant concentration of dimeric D2EHPA, kmol m<sup>-3</sup>;

$f(r)$  = function of reactants =  $(mn)^a (h)^b (h_2r_2)^c$ ;

k = Boltzman constant;

h = Plank's constant;

T K = temperature in Kelvin;

$P_{\text{H}_2\text{R}_2}$  = partition coefficient of dimeric D2EHPA =  $[\text{H}_2\text{R}_2]_{(o)} / [\text{H}_2\text{R}_2]_{(i)}$ ;

$K_{\text{aH}_2\text{R}_2}$  = acid dissociation constant of dimeric D2EHPA at interface =  $[\text{H}_2\text{R}_2^-]_{(i)} [\text{H}^+]_{(i)} / [\text{H}_2\text{R}_2]_{(i)}$ , kmol m<sup>-3</sup>;

$K_2$  = dimerization constant of D2EHPA in organic phase =  $[\text{H}_2\text{R}_2]_{(o)}^{1/2} / [\text{HR}]_{(o)}$ , m<sup>3/2</sup> kmol<sup>-1/2</sup>

$P_{\text{HR}}$  = partition coefficient of monomeric D2EHPA =  $[\text{HR}]_{(o)} / [\text{HR}]_{(i)}$ ;

$K_{\text{aHR}}$  = acid dissociation constant of monomeric D2EHPA in aqueous phase =  $[\text{R}^-][\text{H}^+] / [\text{HR}]$ , m<sup>3</sup> kmol<sup>-1</sup>;

Subscript 'o' = organic phase;

Subscript 'i' = intercept;

Subscript 'b' = bulk phase.

*Treatment of data.* The rate of Mn<sup>2+</sup> transfer per unit area or flux, J can be calculated from the following relation (for notations vide section 'Notations and abbreviations'):

$$J \text{ (kmol m}^{-2}\text{s}^{-1}\text{)} = a^0\text{Mn}^{2+}/A.t \quad (1)$$

Again, the rate of extraction of Mn<sup>2+</sup> from an acidic chloride medium ( $\mu=0.1 \text{ mol dm}^{-3}$  by di-2-ethylhexylphosphoric acid (D2EHPA or  $\text{H}_2\text{R}_2$ ) at a constant temperature through an interfacial area, A (m<sup>2</sup>) can be expressed as follows:

$$J = k_f [\text{Mn}^{2+}]^a [\text{H}^+]^b [\text{H}_2\text{R}_2]_{(o)}^c \quad (2)$$

On taking logarithm of both the sides of eq. (2), one can get:

$$\log J = \log k_f + a \log [\text{Mn}^{2+}] + b \log [\text{H}^+] + c \log [\text{H}_2\text{R}_2]_{(o)} \quad (3)$$

Equation (3) states that when  $[\text{H}^+]$  and  $[\text{H}_2\text{R}_2]_{(o)}$  are kept constant at (h) and  $(h_2r_2)_{(o)}$  respectively, then the plot of  $\log J$  vs.  $\log [\text{Mn}^{2+}]$  should yield a straight line with slope equaling to 'a' and intercept equaling to  $\log k_f (h)^b (h_2r_2)_{(o)}^c$ ; from which the value of  $k_f$  can be evaluated after finding the values of 'b' and 'c' which can be obtained from the slopes of the  $\log J$  vs.  $\log [\text{H}^+]$  (or pH; in this case slope = '-b') and by  $\log J$  vs.  $\log [\text{H}_2\text{R}_2]_{(o)}$  plots respectively. Another set of the value of  $\log k_f$  can be evaluated from the intercepts of the above plots.

The effect of temperature on the rate of extraction of Mn<sup>2+</sup> by D2EHPA can be well treated by the well known Arrhenius equation:

$$\log J = -E_a / 2.303RT + C \quad (4)$$

The above equation states that the plot  $\log J$  vs  $1/T$  K will give straight line with slope equaling to  $-E_a/2.303R$ , from which the value of activation energy can be evaluated. The values of enthalpy of activation,  $\Delta H^\ddagger$  and entropy of activation,  $\Delta S^\ddagger$  can be estimated from the specific reaction rate theory:

$$\log (Jh/kT) = -\Delta H^\ddagger/2.303RT + \Delta S^\ddagger/2.303R + \log f(r) \quad (5)$$

## Results

The effects of interfacial area,  $[\text{Mn}^{2+}]$ ,  $[\text{H}^+]$ ,  $[\text{H}_2\text{R}_2]_{(o)}$  and temperature on rate of extraction of Mn from chloride medium by D2EHPA in kerosene have been investigated and the following results have been obtained:

(i) *Effect of interfacial area on rate of extraction:* The effects of interfacial area on the amount of manganese transferred into the organic phase and on flux of  $Mn^{2+}$  transfer are shown in Fig. 1; where  $a_{Mn^{2+}}$  and  $\log J$  have been plotted against interfacial area,  $A$  in  $m^2$ . It is found that the amount of manganese transferred into organic phase is directly proportional to the interfacial area, whereas flux of manganese transfer ( $kmol\ m^{-2}\ s^{-1}$ ) is independent of interfacial area. This result indicates that the rate of forward extraction of  $Mn^{2+}$  by D2EHPA is directly proportional to the interfacial area and the rate of extraction per unit area is independent of

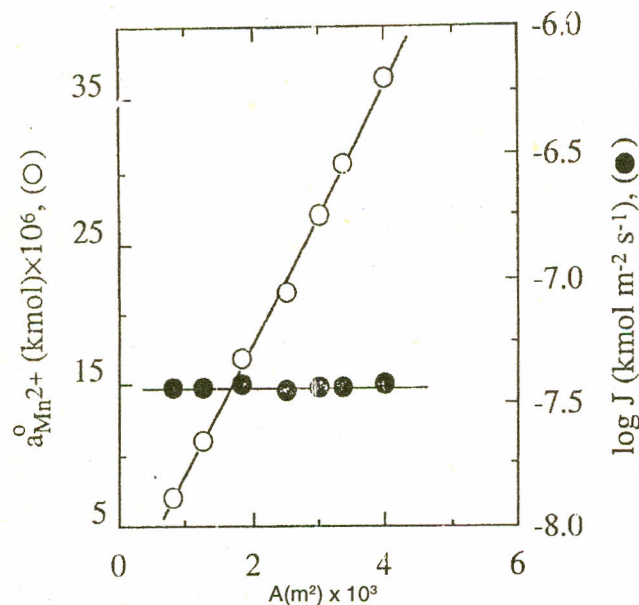


Fig. 1. Dependence of rate on interfacial area. Temp. =  $30^{\circ}C$ ,  $[Mn^{2+}] = 0.002\ kmol\ m^{-3}$ ,  $pH = 2.5$ ,  $[D2EHPA] = 0.3\ kmol\ m^{-3}$ .

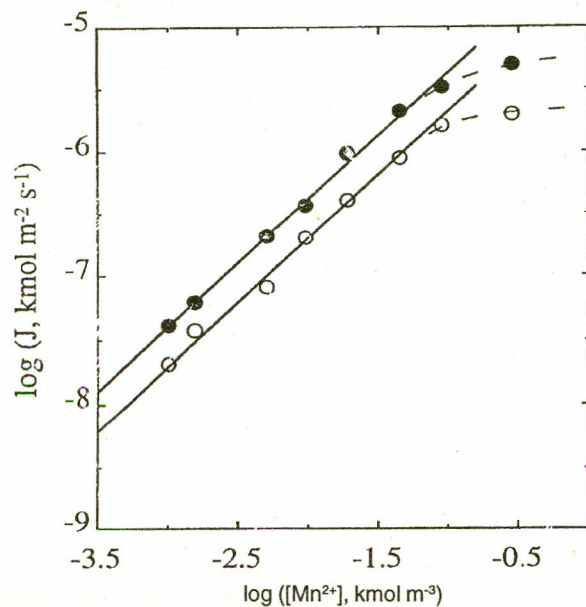


Fig. 2. Dependence of rate on metal ion concentration. Temp. =  $30^{\circ}C$ ,  $[D2EHPA] = 0.3\ kmol\ m^{-3}$ , (O),  $pH = 3.0$ , slope ( $s$ ) = 1, intercept ( $I$ ) = -4.40, (●),  $pH = 2.5$ ,  $s = 1$ ,  $I = -4.75$ .

interfacial area.

(ii) *Effect of  $Mn^{2+}$  concentration on rate of extraction:* Figure 2 represents the variation of rate of Mn extraction per unit area flux,  $J$  with initial  $Mn^{2+}$  concentration in aqueous phase. The plots of  $\log J$  vs  $\log ([Mn^{2+}],\ kmol\ m^{-3})$  have a slope of unity in lower concentration regions of  $Mn^{2+}$  ( $<0.10\ kmol\ m^{-3}$ ). This result indicates that the reaction order with respect to  $Mn^{2+}$  concentration is unity ( $a=1$ ) at its lower concentration region. At higher concentration region of  $Mn^{2+}$ , the slope decreases. It is therefore concluded that there are two possible mechanisms for the extraction of  $Mn^{2+}$ : one at

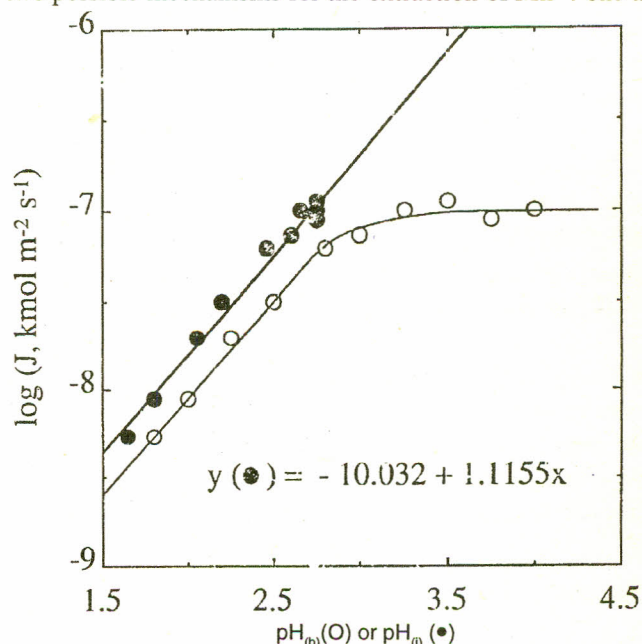


Fig. 3. Dependence of rate on acidity of aqueous phase. Temp. =  $30^{\circ}C$ ,  $[D2EHPA] = 0.30\ kmol\ m^{-3}$ ,  $[Mn^{2+}] = 0.002\ kmol\ m^{-3}$ .

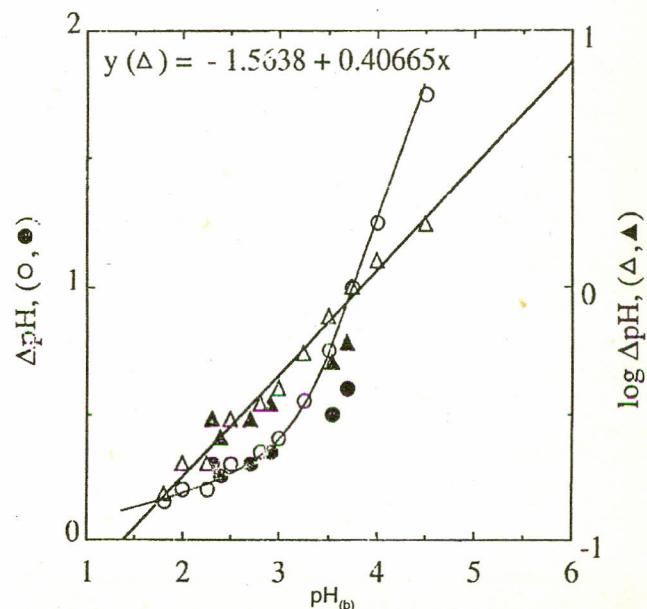


Fig. 4. Variation of pH correction term ( $\Delta pH$ ) with bulk pH. (●) and (▲) are from references 9 and 10 and (O) and (Δ) are from present work.

the lower concentration region involving chemical reaction as the rate determining and the other, at the higher concentration region involving diffusion of different species to and from the interface as the rate controlling. Similar results were obtained when RDC [Hughes and Biswas 1993] and single drop techniques (Biswas *et al* 1996) were used.

(iii) *Effect of  $H^+$  concentration on the rate of extraction:* The  $\log J$  vs  $pH_b$  plot for  $0.30 \text{ kmol m}^{-3}$  D2EHPA and  $0.002 \text{ kmol m}^{-3}$   $Mn^{2+}$  system is shown in Fig. 3. A straight line relationship is not obtained. The slope of the line varies from 1 at lower  $pH$  regions to zero at higher  $pH$  regions. If a  $\Delta pH$  term is introduced to calculate the interfacial  $pH$  by  $pH_i = pH_b - \Delta pH$ , then all the experimental points may fall on a straight line. The value of  $\Delta pH$  term varies with  $pH$  of the bulk phase as reported earlier (Hughes and Biswas 1993) (up to  $pH_b = 3.65$ ). If the experimental points of this case are supposed to be placed on a straight line of unity slope, then some values of  $\Delta pH$  terms are obtained corresponding to each  $pH$  of the bulk aqueous phase. The variation of  $\Delta pH$  term with  $pH_b$  is shown in Fig 4. This figure shows that the  $\Delta pH$  terms up to  $pH$  3 coincide well with those reported earlier and a little discrepancy is observed only around  $pH$  3.6. It is interesting to note that the variation of  $\log \Delta pH$  with  $pH$  appears to be linear with a slope of about 0.40. It is therefore concluded that rate of extraction of  $Mn^{2+}$  by D2EHPA is inversely proportional to  $H^+$  concentration at the interface rather than in

the bulk phase.

(iv) *Effect of  $H_2R_2$  concentration on extraction:* The  $\log J$  vs  $\log ([H_2R_2]_{(o)}, \text{ kmol m}^{-3})$  plots at two constant initial bulk  $pH$  values are shown in Fig. 5. In both cases, straight lines are obtained with slope equaling to unity. This result concludes that the rate of extraction of  $Mn^{2+}$  by D2EHPA is

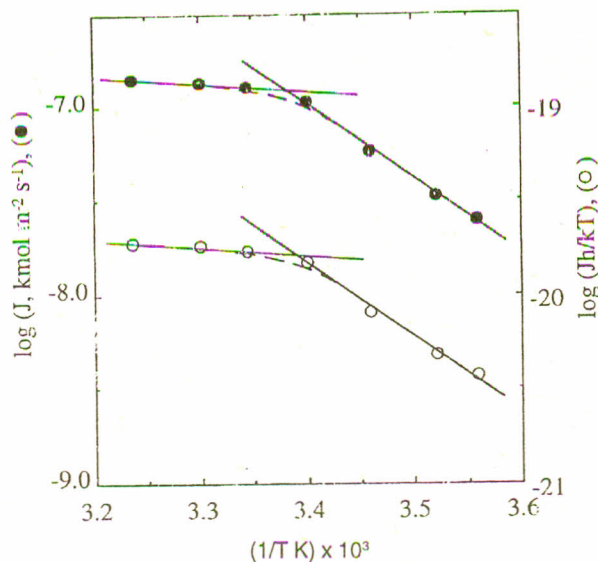


Fig. 6. Dependence of rate on temperature.  $[Mn^{2+}] = 0.0036 \text{ kmol m}^{-3}$ ,  $[H_2R_2] = 0.30 \text{ kmol m}^{-3}$ ,  $pH = 3$ ; (●),  $s_i = -4000$ ,  $s_h = -454$ ; (○),  $s_i = -3800$ ,  $s_h = -692$ ,  $s_h = -417$ ,  $I_h = -18.36$ ;  $f(r) = 1.065 \text{ kmol m}^{-3}$ .

**Table 1**  
Evaluation of Rate Constant,  $K_f$  ( $\mu = 0.1 \text{ kmol m}^{-3}$ ).

Fig.No.	$[Mn^{2+}]$ , $\text{kmol m}^{-3}$	$[H_2R_2]_{(o)}$ , $\text{kmol m}^{-3}$	$pH$	$\Delta pH$	Intercept	$\log k_f$	Average $\log k_f$	St. dev.
2	-	0.30	2.5	0.27	-4.75	-6.46		
2	-	0.30	3.0	0.40	-4.40	-6.48		
3	0.002	0.30	-	-	-10.03	-6.81	-6.534	0.157
5	0.002	-	2.5	0.27	-6.91	-6.44		
5	0.002	-	3.0	0.40	-6.58	-6.48		

**Table 2**  
Comparative results of the Rates of  $Mn^{2+}$  Extraction by D2EHPA Measured by using Different Techniques.

Tech nique	System	Order w.r.t $[Mn^{2+}]$	Order w.r.t [D2EHPA]	Order w.r.t $[H^+]$	$\log k_f$	$E_a$ $\text{kJ mol}^{-1}$ at $K < 293$	$E_a$ $\text{kJ mol}^{-1}$ at $K < 293$	Ref.
1.	Chloride/ Kerosene	1	1.0	-1	-6.55d	76.5	8.7	This work
2.	Chloride/ Kerosene	1	1.0	-1	-6.35d	77	7.7	10
3.	Sulfate/ n-hexane	1	0.5-0.2	-1	f	20	4.0	9

1, Constant interfacial area stirred cell; 2, single drop; 3, Rotating diffusion cell;  $d$ , Unit of  $k_f$  is  $\text{m s}^{-1}$ ,  $f$ , value of  $k_f = 3.57 \times 10^6 \text{ m}^3 \text{ s}^{-1} \text{ kmol}^{-1}$   
 $^1 = K_f P_{H_2R_2} \cdot K^{-1}$

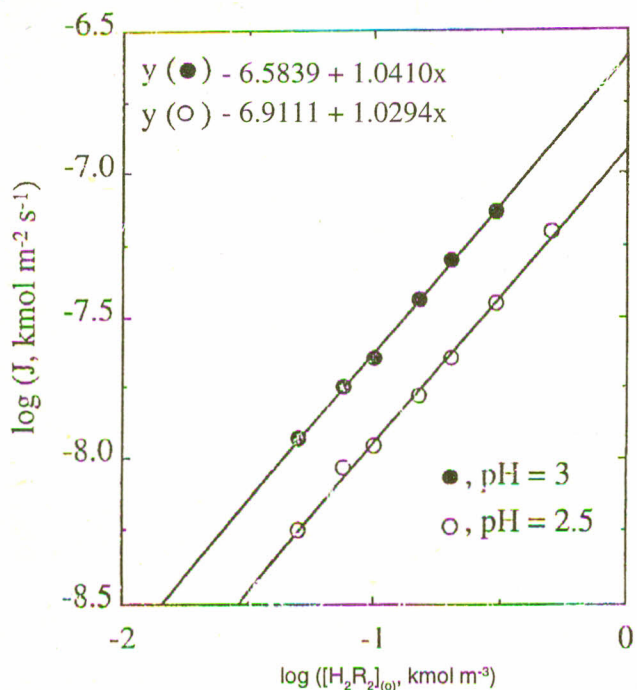


Fig. 5. Dependence of rate on organic phase extractant concentration. Temp. =  $30^\circ\text{C}$ ,  $[Mn^{2+}] = 0.002 \text{ kmol m}^{-3}$ .

directly proportional to the extractant concentration in the organic phase. Similar result was obtained from the Single Drop experiment (Biswas et al 1996), but a different result (rate proportional to square root of  $[H_2R_2]_{(o)}$ ) was reported for the rotating diffusion cell technique [Hughes and Biswas 1993] applied to extract Mn<sup>2+</sup> from a sulfate medium.

(v) *Evaluation of rate constant,  $K_f$ .* From the intercepts of the lines in Figs. 2, 3, and 5, the value of the forward extraction rate constant has been evaluated (Table 1). The value of  $k_f$  has been found to be  $10^{-6.534} \text{ m s}^{-1}$  with a standard deviation of  $\log k_f$  being 0.157.

(vi) *Effect of temperature on rate:* The Arrhenius plot for the extraction of Mn<sup>2+</sup> by D2EHPA is shown in Fig.6. The experimental points do not fall on a straight line but a curve is obtained. The slope of the tangential line at lower temperature region gives an activation energy of 76.5 kJ mol<sup>-1</sup>, whereas that at higher temperature region gives an activation energy of 8.7/mol<sup>-1</sup>. The  $\log (Jh/KT)$  vs  $1/T$  K plot is also shown in Fig. 6. From the slopes of the tangents at lower and higher temperature regions, the values of  $\Delta H^\ddagger$  are calculated to be 72.7 and 7.98 kJ mol<sup>-1</sup> respectively. The values of  $\Delta S^\ddagger$  are calculated to be -131.8 and -350.6 J mol<sup>-1</sup> K<sup>-1</sup> in the lower and higher temperature regions respectively from the respective intercepts of their tangents [the value of  $\log f(r)$  being 0.03].

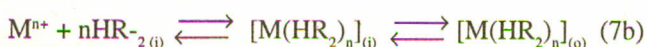
## Discussion

The reaction orders of +1, +1 and -1 with respect to  $[Mn^{2+}]$ ,  $[H_2R_2]_{(o)}$  and  $[H^+]$  at interface respectively together with the value of  $k_f$  ( $10^{-6.534} \text{ m s}^{-1}$ ) measured by using the constant interfacial area stirred cell technique suggest that the rate of extraction of Mn<sup>2+</sup> from 0.1 kmol m<sup>-3</sup> chloride medium by D2EHPA at (30±0.5)°C can be expressed as:

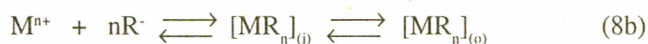
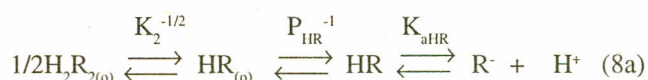
$$J (\text{kmol m}^{-2} \text{ s}^{-1}) = 10^{-6.534} [Mn^{2+}][H_2R_2]_{(o)}[H^+]_{(i)} \quad (6)$$

The extractant, D2EHPA is usually dimeric in organic non-polar solvents like benzene, hexane, heptane, etc. (Huang and Juang 1986). The dimerization constant  $K_2$  is  $3 \times 10^4 \text{ m}^3 \text{ kmol}^{-1}$  in n-hexane (Ulyanov and Sviridova 1970) and  $3.1 \times 10^4 \text{ m}^3 \text{ kmol}^{-1}$  in n-heptane (Komasawa *et al* 1980). So it is considered that D2EHPA can extract a metal ion in either of the following two ways:

(i) Dimeric model:



(ii) Monomeric model:



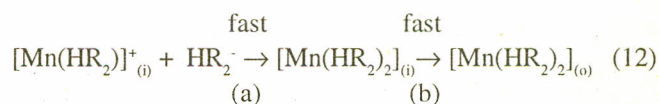
For dimeric model, the following relationship may be obtained:

$$[H_2R_2]_{(o)} = P_{H2R2} K_{aH2R2}^{-1} [HR_2^{-1}]_{(i)} [H^+] \quad (9)$$

so that the rate eq. (6) takes the form:

$$J = 10^{-6.534} P_{H2R2} K_{aH2R2}^{-1} [Mn^{2+}] [HR_2^{-1}]_{(i)} \quad (10)$$

Equation (10) suggests that among the following reaction steps:



the step represented by eq. (11) appears as the rate determining. Therefore it is concluded that the formation of 1:1 complex of Mn<sup>2+</sup> with HR<sub>2</sub><sup>-</sup> at the interface is the rate determining. The absolute rate constant of this reaction step should be equal to the products of  $K_f$ ,  $P_{H2R2}$  and  $K_{aH2R2}^{-1}$ . Unfortunately, these values are not available in literature due to the limitation in determining the concentrations of different species at the interface of molecular dimension.

Experimental results can be tested for fit by the monomeric model of D2EHPA represented by eqs. (8a and 8b). In this case, the flux equation becomes:

$$J = 10^{-6.534} K_2 P_{HR}^{-2} K_{aHR}^{-2} [Mn^{2+}][R^-]^2[H^+] \quad (13)$$

Equation (13) does not suggest any elementary reaction step since it involves four species. So rate data obtained in the extraction of Mn<sup>2+</sup> with D2EHPA dissolved in kerosene cannot yield any satisfactory extraction mechanism if the monomeric model of D2EHPA is considered.

The activation energy in the lower temperature region (76.5 kJ mol<sup>-1</sup>) suggests that the chemical reaction step given by eq. (11) is the rate determining. On the other hand, the activation energy in the higher temperature region (8.7 kJ mol<sup>-1</sup>) suggests that the diffusion of one or more species becomes rate determining. It is therefore concluded that the chemical reaction step represented by eq. (11) is not the rate determining, rather the diffusion of Mn<sup>2+</sup> or HR<sub>2</sub><sup>-</sup> to the interface is the rate determining at higher temperature. As temperature decreases, the chemical rate (governed by Arrhenius equation) decreases more than that of the diffusion rate (governed by

Stokes-Einstein equation), so that the chemical reaction step given by eq. (11) becomes the rate determining at lower temperature. Moreover, high negative entropy of activation ( $\Delta S^\ddagger = -131.8 \text{ J mol}^{-1} \text{ K}^{-1}$ ) at lower temperature region suggests that the reaction step represented by eq. (11) occurs via  $\text{SN}_2$  mechanism.

The results obtained for the extraction of  $\text{Mn}^{2+}$  by D2EHPA using the constant interfacial area stirred cell technique will be compared with those obtained by using the single drop (Biswas *et al* 1996) and rotating diffusion cell (Hughes and Biswas 1993) techniques. The comparative results are given in Table 2. Results obtained by using the present techniques are comparable with the results obtained by using the single drop technique. Same mechanism can be proposed based on the results obtained by these two techniques. The value of the rate constant obtained by using the single drop techniques is little higher than that obtained by using the present technique. It is probably due to the deformation of spherical drop during rising or falling, internal circulation of material within the drop and attachment and movement of a portion of stagnant aqueous phase in the direction of the drop. The first two reasons increase and the third decreases the rate of extraction.

However, the results obtained by the single drop and present technique are not comparable to the results obtained by the rotating diffusion cell technique because (1) the system is little different, (2) different hydrodynamics are involved, (3) in the latter case, experimental results have been fitted to the model of mass transfer with chemical reaction to elucidate the value of  $k_f$  etc.

## Conclusion

The following conclusions can be drawn:

1. The kinetic measurements on the extraction of manganese (II) from chloride medium with D2EHPA dissolved in kerosene using a constant interfacial area stirred cell give the reaction order with respect to  $[\text{Mn}^{2+}]$ ,  $[\text{H}_2\text{R}_2]_{(o)}$  and  $[\text{H}^+]$  as +1, +1 and -1 respectively and the value of  $k_f$  is  $10^{-6.534} \text{ m s}^{-1}$ .
2. Analysis of the results suggests the formation of 1:1  $\text{Mn}^{2+}$ -D2EHPA dimeric anion ( $\text{HR}_2^-$ ) complex ( $[\text{MnHR}_2]^-$ ) by the reaction of  $\text{Mn}^{2+}$  with  $\text{HR}_2^-$  at the interface is the rate controlling.
3. The temperature dependence data give an activation of 76.5 and 8.7  $\text{kJ mol}^{-1}$  at lower and higher temperature regions respectively. These values suggest that at lower temperature region, the reaction step to form the 1:1  $\text{Mn}^{2+}$ - $\text{HR}_2^-$  complex at the interface is the rate determining: whereas at higher temperature regions, the

diffusion of the species to the interface to form the 1:1 complex is the rate determining. The high negative entropy of activation ( $-131.8 \text{ J K}^{-1} \text{ mol}^{-1}$ ) at lower temperature region suggests that the formation of 1:1 complex occurs via  $\text{SN}_2$  mechanism.

4. Results obtained using this technique are comparable to those obtained by using the Single Drop technique. However, these results are different from those obtained by applying the Rotating Diffusion Cell technique.

## References

- Basset J, Denny R C, Jeffery G H, Menham 1978 *Vogel's text book of quantitative inorganic analysis*, Longman, New York, USA 4th ed pp 746-747.
- Biswas R K, Hanif M A, Bari M F 1996 Kinetics of forward extraction of manganese(II) from acidic chloride medium by D2EHPA in kerosene using the single drop technique. *Hydrometallurgy* **42** 399-409.
- Huang T Juang R 1986 Extraction equilibrium of zinc from sulphate media with bis(2-ethylhexyl) phosphoric acid. *Ind Eng Chem Fundam* **25** (4) 752-757.
- Hughes M A, Biswas R K 1993 The kinetics of manganese(II) extraction in the acidic sulphate-D2EHPA-n-hexane system using the rotating diffusion cell technique. *Hydrometallurgy* **32** 209-221.
- Islam F, Biswas R K 1978 Kinetics and mechanism of solvent extraction of Ti(IV) from acidic aqueous solutions with bis(2-ethylhexyl) phosphoric acid in benzene. *J Inorg Nucl Chem* **40** 559-566.
- Islam F, Biswas R K 1979 The kinetics and mechanism of solvent extraction of Cr(III) from acidic aqueous solution with bis(2-ethylhexyl)phosphoric acid in benzene. *Can J Chem* **57** (23) 3011-3016.
- Islam F, Biswas R K 1980 kinetics and mechanism of solvent extraction of V(IV) from acidic aqueous solutions with bis(2-ethylhexyl)phosphoric acid in benzene. *J Inorg Nucl Chem* **42** 421-429.
- Islam F, Biswas R K 1981 The solvent extraction of Ti(IV), Fe(III) and Mn(II) from acidic sulphate-acetate medium with bis(2-ethylhexyl)phosphoric acid in benzene. *J Inorg Nucl Chem* **43** 1929-1933.
- Komasawa T, Otake T, Hagaki Y 1981 Distribution of D2EHPA in nitrate-n-heptane system. *J Inorg Nucl Chem* **43** 3351-3355.
- McDowell W J, Perdue P T, Case G N 1976 Purification of D2EHPA. *J Inorg Nucl Chem* **38** 2129-2131.
- Ritcey M G, Ashbrook A W 1970 *Solvent extraction principles and application to process metallurgy*. Elsevier, Amsterdam, Netherland, Part-2 pp 263-267.

- Sekine T, Koike Y, Komatsu Y 1973a Kinetics studies of solvent extraction of metal complexes, II. The rate of the extraction of iron (III) with thenoyltrifluoroacetate into carbon tetrachloride. *Bull Chem Soc Jpn* **46** (8) 2356-2360. (1971b) Kinetics of extraction of beryllium (II) from perchlorate-chloride-nitrate media with MIBK into  $CCl_4$  or MIBK *Bull Chem Soc Jpn* **44** (10) 2903-2910.
- Sato T, Kawamura M, Nakamura T, Ueda M 1978 The solvent extraction of divalent manganese, iron, cobalt, nickel, copper and zinc from hydrochloric acid solution by di(2-ethylhexyl) phosphoric acid, *J Appl Chem Biotechnol* **28** (2) 85-94.
- Sekine T, Komatsu Y Honda H 1976 Kinetics of extraction of Fe(III) fromj pechlorate solution with acetylacetone, benzoylacetone, trifuloroacetone, benzoyl trifluoroacetone, 2-thenoyltrifluoroacetone and hexafluoro acetone in carbon tetrachloride, *J Inorg Nucl Chem* **38** 1861-1870.
- Ulyanov US, Sviridova RA 1970 Dissociation, dimerization and distribution of di-(2-ethylhexyl) phosphoric acid in the system n-hexane / iso-octane. n-octane-0.1M  $NaCl_4-HClO_4$ . *Radiokhimiya* **12** (1) 47-53.