Regular Article

Study of Activity Coefficient of Hydrochloric Acid in 2-Propanol-Water Mixture by Electromotive Force Measurement Method

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This paper is mainly focusing on the determination of mean molal activity coefficient of HCl in aqueous acidic medium. The present investigations have been carried out to determine the activity coefficients of hydrochloric acid in 2-propanol-water mixture solutions under various conditions to study the ion solvent interactions in different temperatures. The standard electrode potential E^0 of the cell Pt; $H_2(g)/HCl(m)$ x% 2-propanol; $Hg_2Cl_2(S)/Hg$ have been determined in 10%, 20% and 30% (w/w) of 2-propanol-water mixture solution at three different temperatures 308.15, 313.15 and 318.15 K and molality ranging from 0.005 to 0.1 mol kg^{-1}. E^o of the cell is computed by modified Davies equation as below,

$$E + k \log m_H.m_{Cl} - \frac{(2kA'\sqrt{\mu})}{1+\sqrt{\mu}} = E^0 - k\beta\mu$$

where k = 2.3026 (RT/F), and A´ = appropriate Debye-Hückel constant and mean molal activity coefficient, $\log \gamma_i = -\frac{\left(A'Z_i^2 \sqrt{\mu}\right)}{1+\sqrt{\mu}} + \beta_i\mu$

The mean molal activity coefficients of hydrochloric acid in aqua organic media and temperature are also computed. The primary and secondary ion-solvent effects are also reported.

Keywords: Activity coefficient, Hydrochloric acid, 2-Propnol, Davies equation

INTRODUCTION

The dissociation constant is an important parameter in determining the behavior of compounds in various applications. It is used to measure the strength of acids and bases which are widely used in pharmaceutical industries, spectroscopy, biological sciences, preparative chemistry and in structure elucidation of newly isolated species. The dissociation constant is a useful criteria for identifying the substances which do not melt [1-4]. The thermodynamic functions of transfer of solute from one solvent to another can be determined with the help of electromotive force

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measurement method. The signs of transfer functions have been considered as the sole criteria for knowing the structural status of the solvent [5]. The present investigations have been carried out to determine the activity coefficients of hydrochloric acid in aqueous 2-propanol solutions under various conditions to study the ion-solvent interactions in different temperatures. The quick method for this purpose is potentiometery while spectrophotometry is very accurate but it is time consuming [6-13]. The study of the ion-solvent interactions in dioxane-water mixture is reported the number of mono and dicarboxylic acids [14-17]. The hydrochloric acid-sodium chloride and hydrochloric acid-potassium chloride [18-25] are taken as electrolyte due to easy setting up of the cells

and their reliable verification.

The activity coefficient is the most important and fundamental property in the thermodynamic study of liquid mixtures. It is a measure of the deviation of the behavior of a component in a mixture from ideal behavior, which has been interpreted by various theories of liquid mixtures. In this work, the activity coefficient of hydrochloric acid in 2-propanol-water mixture is determined in three different temperatures by the use of electromotive force measurements. Parts of the results extend the temperature range of available literature data for the compounds under investigation.
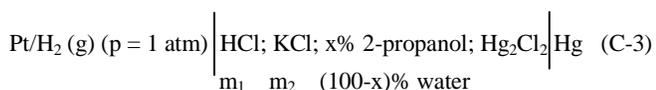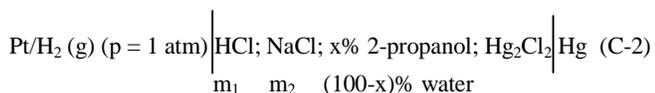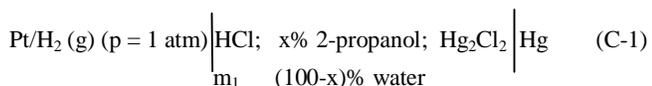
EXPERIMENTAL

Chemical Matters and Reagents

All the chemicals were purchased from E. Merck of A.R. grade used without further purification. Hydrochloric acid, sodium chloride and potassium chloride were prepared as 0.1 M standard solutions diluted to the desired molalities and checked by means of titration. The concentration of 2-propanol was in weight percent and that of electrolyte in mol kg^{-1} corrected to the micro mol kg^{-1}. The solutions were prepared in double distilled water after removal of dissolve gases.

Procedure

To determine the activity coefficient of ion in mixed electrolytes and thermodynamics of HCl in 2-propanol-water media, following cells, (C-1), (C-2) and (C-3) were set up as.

$$\text{Pt/H}_2 \text{ (g) (p = 1 atm)} \left| \begin{array}{c} \text{HCl; } \quad x\% \text{ 2-propanol; } \text{Hg}_2\text{Cl}_2 \\ m_1 \quad\quad (100\text{-}x)\% \text{ water} \end{array} \right| \text{Hg} \quad \text{(C-1)}$$

$$\text{Pt/H}_2 \text{ (g) (p = 1 atm)} \left| \begin{array}{c} \text{HCl; NaCl; } x\% \text{ 2-propanol; } \text{Hg}_2\text{Cl}_2 \\ m_1 \quad m_2 \quad (100\text{-}x)\% \text{ water} \end{array} \right| \text{Hg} \quad \text{(C-2)}$$

$$\text{Pt/H}_2 \text{ (g) (p = 1 atm)} \left| \begin{array}{c} \text{HCl; KCl; } x\% \text{ 2-propanol; } \text{Hg}_2\text{Cl}_2 \\ m_1 \quad m_2 \quad (100\text{-}x)\% \text{ water} \end{array} \right| \text{Hg} \quad \text{(C-3)}$$

Where x = 10%, 20% and 30%(w/w).
Setting up of all cells, thermostat, emf, assembly and *etc*. has been explained earlier [26]. They were tested for the

absence of bromide, iodide method followed by pinching and bates [27]. The cells were completely filled with the electrolyte solutions and placed in an air thermostate (±0.05). The experiments were performed under nitrogen atmosphere inside a glove box to prevent CO_2 from air absorbing into the electrolyte solutions. The cells were connected to potentiometer (±0.1 mV). A stop-cock was opened and kept for about 3 hours until the cell equilibrium is reached. The e.m.f constant was noted at different temperatures and concentrations. This e.m.f was used to calculate the mean activity coefficient [28-29], various thermodynamic parameters and ion-solvent interaction.

RESULTS AND DISCUSSION

The e.m.f. of the cells (C-1), (C-2) and (C-3) is given as:

$$E = E^0 - k \log m_H \cdot m_{Cl} - k \log \gamma_H \cdot \gamma_{Cl} \tag{1}$$

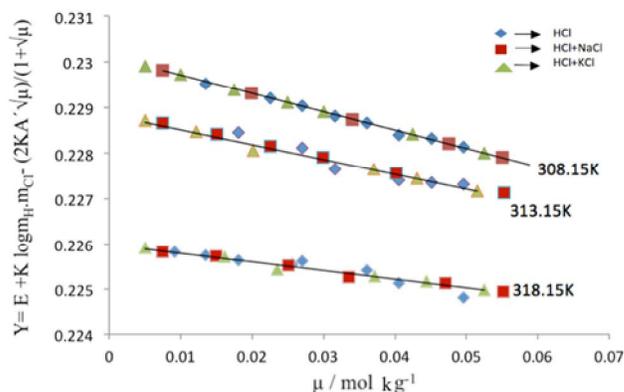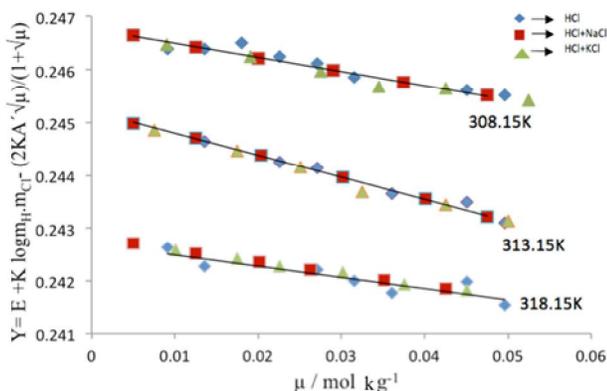Which becomes to Eq. (2), since it has been established that modified Davies equation is valid in this case [30].

$$E + k \log m_H m_{Cl} - \frac{\left(2kA' \sqrt{\mu} \right)}{1 + \sqrt{\mu}} = E^0 - k\beta\mu \tag{2}$$

where k = 2.303 (RT/F), and A′ = Appropriate Debye-Hückel constant. Since all three electrolytes HCl, NaCl and KCl are completely dissociated, the values of ionic strengths, μ in cells (C-1), (C-2) and (C-3) would be given by m_1, m_1+m_2 and m_1+m_3, respectively. All other terms in Eq. (2) except E^0 and β are known, and the values of k and A are known from Table 1.

E^0 from experiment and m_H and m_{Cl} from molalities of the experimental solution. The left hand side of the Eq. (2) (=Y,say) is plotted against the corresponding values of μ at 308.15, 313.15 and 318.15 K of 2-propanol-water mixture for 10%, 20% and 30%, shown in Figs. 1, 2 and 3. Figures show that the points of HCl alone, mixture of HCl; NaCl and HCl; KCl lie on the line within 0.1 mV. In Figs. 1 to 3, the intercepts of the plots at μ = 0 give the values of E_m^0 and β (the slope), which are recorded in Table 2. The standard electrode potential for the Hg|Hg_2Cl_2, Cl$^-$ electrode in 10%, 20% and 30% of 2-propanol-water mixture is presented by means of a general expression of the method of least-

Table 1. Experimental Parameters of 2-Propanol-Water Mixtures

T (K)	A' (kg$^{-1/2}$ mol$^{-1/2}$)	P$_{soln}$ (mm) Vapour press.	D Dielectric constant	d$_0$ (g cm^{-3})	k
		Percentage of 2-propanol			
		10% 2-Propanol			
308.15	0.5997	60.20	68.10	0.9772	0.061140
313.15	0.6080	80.50	66.40	0.9749	0.062132
318.15	0.6170	101.80	64.72	0.9726	0.063124
		20% 2-Propanol			
308.15	0.7056	73.50	61.10	0.9610	0.061140
313.15	0.7149	97.50	59.56	0.9570	0.062132
318.15	0.7258	125.00	58.08	0.9547	0.063124
		30% 2-Propanol			
308.15	0.8462	86.75	54.13	0.9413	0.061140
313.15	0.8596	103.75	52.71	0.9379	0.062132
318.15	0.8707	133.00	51.44	0.9345	0.063124
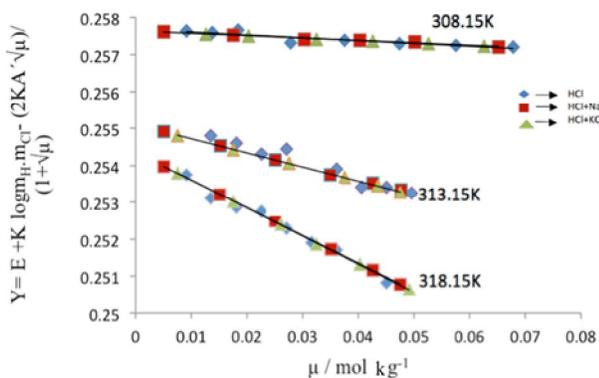
Fig. 1. Plot of Y against μ; X = 10% 2-propanol-water.

Fig. 2. Plot of Y against μ; X = 20% 2-propanol-water.

Fig. 3. Plot of Y against μ; X = 30% 2-propanol-water.

squares to Eq. (3).

$$E_m^0 = a + b (T - 298.15) + c (T - 298.15)^2 \qquad (3)$$

where T is temperature in K. The values of the constants a, b and c for hydrochloric acid in 2-propanol-water are shown in Table 3. The electrode potentials on molal scale (E$_m^0$) were converted to those on molar (E$_c^0$) and mole fractional (E$_N^0$) scale according to these equation,

$$E_C^0 = E_m^0 + 2k \log(d_0/g\ cm^{-3}) \qquad (4)$$

Table 2. Experimental Standard Molal Potential E_m^0 (abs.) volt of the Hg/Hg$_2$Cl$_2$,Cl$^-$ Electrode and β at 308.15 K, 313.15 K and 318.15 K in 10%, n20% and 30% 2-Propanol-Water Solution

	10%		20%		30%	
T (K)	E_m^0 (abs. volt)	β (kg mol^{-1})	E_m^0 (abs. volt)	β (kg mol^{-1})	E_m^0 (abs. volt)	β (kg mol^{-1})
308.15	0.25759± 0.00008	0.090± 0.008	0.24732± 0.00004	0.704± 0.001	0.2301± 0.0002	0.663± 0.004
313.15	0.25551± 0.00009	0.767± 0.003	0.24480± 0.00002	0.460± 0.005	0.2289± 0.0002	0.549± 0.005
318.15	0.25301± 0.00006	0.370± 0.004	0.2428± 0.0003	0.351± 0.002	0.2260± 0.0002	0.303± 0.004

Table 3. Experimental Constant Values of HCl in 2-Proponal Water-Mixture

Wt. % 2-propanol	a = E_{35}^0 (abs. volt)	b (volt K^{-1})	c (volt K^{-2})
10	0.25759	-1.37×10^{-3}	-1.4×10^{-4}
20	0.25551	-1.63×10^{-3}	-1.0×10^{-4}
30	0.25301	-1.40×10^{-3}	-1.36×10^{-4}

and, $E_N^0 = E_m^0 + 2k \log(\text{kg mol}^{-1}/M_{xy})$ (5)

where d_0 is the density of pure solvent mixture at the particular temperature and M_{xy} is the mean molar weight of the solvent defined by the relation,

$\text{kg mol}^{-1}/M_{xy} = 100/M_{xy} = x/M_x + (100-x)/M_y$ (6)

where x is the weight percentage of organic compound, and M_x and M_y are the molar mass of water. All these values are computed and shown in Table 4. The total medium effect on the transfer of an electrolyte from a finite concentration in one solvent to a similar concentration in another solvent is a composite one made up of 'Primary' and 'Secondary' medium effects. The primary medium effect is due to the difference in ion-solvent interaction whereas the secondary medium effect is due to difference in ion-ion interaction in the two solvents and both largely depend on the dielectric constants of each medium.

The values of mole, volume and weight fractional were presented in Table 5. The plots of $^SE_N^0$ against $\ln N_w$, $^SE_C^0$ against $\ln\varphi_w$ and $^SEm^0$ against lnw for 2-propanol-water mixture are found to be linear in nature. All the plots of E_N^0 and E_m^0 against 1/D (D = Dielectric constant of the medium) (Born plot), E_C^0 against $\log\varphi_w$ (φ_w = volume fraction of water in the medium), E_N^0 against $\log N_w$ (N_w = mole fraction of water in the medium) Feakins and French plot [31], and E_N^0-klogN$_w$ against 1/D are similar and curve-linear (not shown here). It is worth noting that deviation from linearity has been observed by Oiwa [32] for HCl in 2-propanol-water and Das [33] for HBr in ethylene glycol-water mixture. Modification of the Born equation,

$$^SE_N^0 - k\, \log N_w = \text{Constant} - \frac{Ne^2}{2F}\frac{1}{D}\sum\frac{1}{r}$$

rested on the assumption that the hydrogen ion is present as the species H$_3$O$^+$. If the concentration of water in the aqueous organic media is high enough, the mole fraction of water can be taken equal to the activity of water in the solvent mixture. The free energy change is assumed to be small particularly in solution of high dielectric constant and can be calculated

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Table 4. Calculated Values of Standard Electrode Potential

$$E_N^0 = E_m^0 + 2k \log(\text{kg mol}^{-1}/M_{xy}) \; ; \; E_C^0 = E_m^0 + 2k \log(d_0/\text{g cm}^{-3})$$

Wt. % of 2-propanol	$E^0_{Hg/Hg2Cl2,Cl^-}$ (abs. volt)	Temp. in K		
		303.15	308.15	313.15
10%	E_m^0	0.25759	0.24732	0.23019
	E_C^0	0.25547	0.24494	0.22637
	E_N^0	0.04810	0.03443	0.01390
20%	E_m^0	0.25551	0.24480	0.22892
	E_C^0	0.25230	0.24134	0.22637
	E_N^0	0.05018	0.03614	0.01693
30%	E_m^0	0.25301	0.24276	0.22601
	E_C^0	0.24979	0.23930	0.22229
	E_N^0	0.05219	0.03868	0.01867

Table 5. Calculated Values of Mole, Volume and Weight Fractional

Wt. % of 2-Propanol	T (K)	$-\log\varphi_w$	$-\log N_w$	$E_N^0 - k \log N_w$	$-\log w$
10	308.15	0.04650		0.04897	
	313.15	0.04653	0.01422	0.03531	0.04576
	318.15	0.04654		0.01479	
20	308.15	0.09989		0.04995	
	313.15	0.10010	0.03136	0.04552	0.09691
	318.15	0.10012		0.04037	
30	308.15	0.16214		0.05540	
	313.15	0.16238	0.05245	0.04194	0.15490
	318.15	0.16257		0.02198	

on the basis of Born equation and thus equation becomes as 7, 8 and 9 for the mole fractional. The volume and weight fractionals scale, respectively.

$$^S E_N^0 = {}^W E_N^0 + nk \; \ln N_w \qquad (7)$$

$$^S E_C^0 = {}^W E_C^0 + nk \; \ln\varphi_w \qquad (8)$$

$$\text{and} \; ^S E_m^0 = {}^W E_m^0 + nk \; \ln w \qquad (9)$$

where n is the solvation number.

The solvation number calculated from the slopes of these plots at different temperatures are reported in the Table 6. 'n' values in this Tableshow wide fluctuations over temperature range as well as among the first, second and third series. The value of 'n' exceeds more than 2 at higher temperature and at lower temperature below than 2. So, the model proposed by Feakins and French does not seem to be applicable in this case. However, Feakins and

Table 6. Values of Hydration Number n, Computed from These Equation

I. $^SE_C^0 = {}^WE_C^0 + nk\ ln\varphi_w$ φ = volume fraction of water

II. $^SE_m^0 = {}^WE_m^0 + nk\ lnw$ w = wt. fraction of water

III. $^SE_N^0 = {}^WE_N^0 + nk\ lnN_w$ N_w = mole fraction of water

T (K)	Values of n for 2-propanol-water mixture		
	From (I)	From (II)	From (III)
308.15	1.56	2.24	1.66
313.15	6.90	3.95	3.56
318.15	16.57	6.91	6.50

Table 7. Mean Molal Activity Coefficient ($\gamma\pm$) of HCl at Various Molalities at Different Temperatures in 2-Propanol-Water Mixtures

Molality of HCl	Mean molal activity coefficient$(\gamma_{\pm})$ $$\log \gamma_i = -\frac{\left(A'Z_i^2\sqrt{\mu}\right)}{1+\sqrt{\mu}} + \beta_i\mu$$		
	308.15 K	313.15 K	318.15 K
	10% 2-Propanol-water		
0.005	0.9138	0.9198	0.9143
0.01	0.8838	0.8962	0.8864
0.02	0.8462	0.8710	0.8530
0.03	0.8207	0.8575	0.8318
0.04	0.7977	0.8499	0.8166
0.05	0.7851	0.8457	0.8050
0.06	0.7716	0.8441	0.7959
	20% 2-Propanol-water		
0.005	0.9056	0.9017	0.8956
0.01	0.8768	0.8701	0.8660
0.02	0.8446	0.8329	0.8262
0.03	0.8259	0.8096	0.8006
0.04	0.8139	0.7929	0.7818
0.05	0.8058	0.7804	0.7673
0.06	0.8006	0.7708	0.7556
	30% 2-Propanal-water		
0.005	0.8860	0.8830	0.8791
0.01	0.8506	0.8459	0.8392
0.02	0.8099	0.8025	0.7910
0.03	0.7852	0.7755	0.7596
0.04	0.7682	0.7563	0.7362
0.05	0.7560	0.7419	0.7179
0.06	0.7469	0.7308	0.7029

French dos not suggest this method as an absolutely reliable method to find 'n' vakues. We may suppose that the 2-propanol is bounded to water hydrates the ion through water end.

Now, the Hg_2Cl_2 present in the Calomel electrode, prepared according to the method suggested by Ives [34], forms a mono molecular film on mercury whose constitution is different from the molecular Hg_2Cl_2. The equilibrium taking place at the surface can be represented by the following equation.

(10)
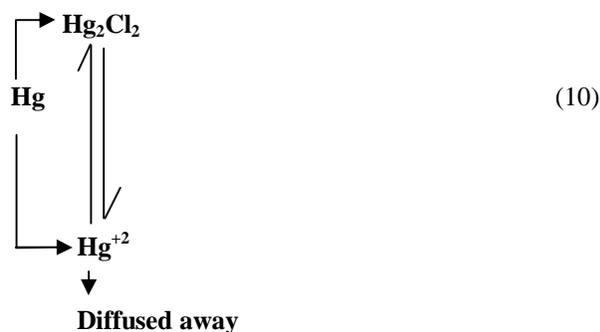
From e.m.f measurement it gives the result of this final equilibrium, which cannot be used here to find the values of ΔG^0, ΔH^0 and ΔS^0 of the individual steps of the above reaction.

To calculate the mean activity coefficient by Bothwell [35], Guggenheim [36] and Davies [37] extended the equation modified by Prasad [38] as below.

$$\log \gamma_i = -\frac{\left(A'Z_i^2\sqrt{\mu}\right)}{1+\sqrt{\mu}} + \beta_i\mu \qquad (11)$$

Now, the value of β_i based on emf data coming from Table 2, and the value of A' Debey Huckel constant coming from Table 1, are utilized to calculate the activity coefficient of hydrochloric acid in 10%, 20% and 30% of 2-propanol-water mixture at different temperatures and at specific ionic strengths, and the related results are reported in Table 7. The value of mean activity coefficient decreases with increasing the molality and percentage of composition due to the effect of more ion solvent interactions.

CONCLUSIONS

In this paper, the activity coefficient of hydrochloric acid in 2-propanol-water mixture has been determined through electromotive force measurement method from 308.15 K to 318.15 K. The value of standard electrode potential (E^0) decreases with increasing the temperature as well as the percentage of composition. Parts of the results extend the temperature range of available literature data of the investigated compounds. The values of the mean molal activity coefficient constants and the thermodynamic parameters are also presented in this work.

ACKNOWLEDGEMENTS

REFERENCES

[1]   A. Hafiz, B. Indhar, A.W.K. Khanzada, J. Chem. Soc. Pak. 22 (2000) 1.

[2]   A. Albert, 6th ed., Selective Toxicity, Chapman and Hall, London, 1979.

[3]   G.B. Barlin, D.D. Perrin, Technique of Organic Chemistry, Wiley Interscience, New York, 1972.

[4]   A. Albert, E.P. Seargent, 3rd ed., The Determination of Ionization Constants, A Laboratory Manual, Chapman and Hall, London, 1979.

[5]   S. Ghosh, M.K. Ghosh, A.K. Ghosh, J. Ind. Coun. Chem. 29 (2012) 44.

[6]   A.G. Asuero, M.J. Navas, J. Trillo, Talanta 33 (1986) 195.

[7]   H. Gampp, M. Maeder, C.J. Mayer, A.D. Zuberbyhler, Talanta 32 (1985) 257.

[8]   P.K. Muhavri, D.K. Hazra, J. Chem. Soc. Faraday Trans. 87 (1991) 3511.

[9]   W.A.E. McBryde, Talanta 21(1974) 187.

[10] O. Budevsky, T. Zikolova, Tanjeheva, Talanta 35 (1988) 899.

[11] R.W. Ramette, J. Chem. Educ. 44 (1979) 647.

[12] A.G. Asuero, M.J. Navas, J.L.J. Trillo, Talanta 33 (1984) 2.

[13]   E.P. Sergeant, Potentiometry and Potentiometric Titration, Wiley, New York, 1984.

[14]   R.C. Das, U.N. Dash, K.N. Panda,Thermochim. Acta 32 (1979) 301.

[15]   R.C. Das, U.N. Dash, K.N. Panda, J. Chem. Soc. Faraday Trans. 1 76 (1980) 2151.

[16]   U.N. Das, M.K Mishra, Thermochim. Acta 115 (1987) 97.

[17]   M.M. Elsemongy, Electrochim. Acta 23 (1978) 957.

[18]   R.N. Roy, W. Vernon, A.L.M. Bothwell, Electrochim. Acta 18 (1973) 81.

[19]   B. Nayak, D.K. Sahu, Electrochim. Acta 16 (1971) 1751.

[20]   B. Nayak, D.K. Sahu, Electrochim. Acta 18 (1973) 271.

[21]   P.K. Das, U.C. Mishra, Electrochim. Acta 22 (1977) 59.

[22]   M.M. Elsemongy, Electrochim. Acta 23 (1978) 881.

[23]   A.A.E. Harakony, H. Sadek, H.A.M. Abdou, Electrochim. Acta 6(1981) 1677.

[24]   B. Nayak, D.K. Sahu, Electrochim. Acta 28 (1983) 1335.

[25]   F.-M. Luis, E. Garcia-Garcia Guillermo, R.R.

Raquel, A. Esteso, J. Electroanal. Chem. 466 (1999) 38.

[26]   A.K. Ghosh, J.C. Ghosh, B. Prasad, J. Ind. Chem. Soc. 57 (1980) 1194.

[27]   G.D. Pinching, R.G. Bates, J. Res. Nat. Bur. Stand. 40 (1948) 405.

[28]   K.S. Pitzer, J. Phys. Chem. 77 (1979) 268.

[29]   K.S. Pitzer, G. Mayorga, J. Phys. Chem. 77 (1973) 2300.

[30]   B. Prasad, J. Ind. Chem. Soc. 54 (1977) 488.

[31]   D. Feakins, C.M. French, J. Ind. Chem. Soc. (1957) 2581.

[32]   I.T. Oiwa, J. Phys. Chem. Ithaca 60 (1956) 754.

[33]   S.K. Banerjee, K.K. Kundu, M.N. Das, J. Chem. Soc. A (1967) 161.

[34]   D.J.G. Ives, G.J. Janz, Reference Electrode, Academic Press, New York, 1961.

[35]   R.N. Roy, W. Vernon, A.L.M. Bothwell, Electrochim. Acta 17 (1972) 1057.

[36]   E. Guggenheim, Phil. Mag. 19 (1935) 588.

[37]   C.W. Davies, J. Chem. Soc. 140 (1938) 2093.

[38]   B. Prasad, J. Ind. Chem. Soc. 54 (1977) 488.