J. Chem. Eng. Data 1993, *38*, 527–530

Conductivities and Thermodynamic Dissociation Constants for Chloroacetic Acid in Binary Mixed Solvent Systems at 298.15 K

M. Sadiq Khan Niazi

Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan

Electrolytic conductivities of dilute solutions of chloroacetic acid in binary mixtures of methanol, ethanol, 1-propanol, *N,N*-dimethylformamide, acetone, and acetonitrile with water have been measured at 298.15 K. The results were fitted to the Lee–Wheaton conductance equation for the derivation of thermodynamic dissociation constants and limiting molar conductivities. The results are compared with literature values pertaining to this acid in analogous media with mainly derived potentiometric measurements.

Introduction

Chloroacetic acid is a moderately strong acid with a $\mathrm{p}K_a$ value of 2.86. Such a carboxylic acid and its alkali-metal salt have been of particular use as buffers for the calibration of pH meters both in aqueous as well as in mixed solvent systems (*1–3*). The $\mathrm{p}K_a$ (thermodynamic dissociation constant) values of chloroacetic acid are known in aqueous methanolic and ethanolic and a few *N,N*-dimethylformamide + water mixtures mainly derived potentiometrically (*4–9*). The literature survey shows that no such values are available for this acid in solvent systems like binary mixtures of water with 1-propanol, acetone, and acetonitrile. The present paper reports molar conductivities of dilute solutions of chloroacetic acid in alcohol + water, *N,N*-dimethylformamide + water, acetone + water, and acetonitrile + water mixtures ranging in composition from 0 to 70 mass % cosolvent at 298.15 K. The thermodynamic dissociation constant, $\mathrm{p}K_a$, and limiting molar conductivity, Λ_0, values for the acid have been derived from the conductance–concentration results. The results are compared with those available in the literature derived potentiometrically.

Experimental Section

Chloroacetic acid (from Merck, extra pure) was recrystallized from ethanol + water, dried under vacuum over P_2O_5, and stored in a desiccator. The melting point of the acid was 60–62 °C.

The solvents were the same as used in previous studies, and their purification has been detailed previously (*10–14*). The fractionally distilled solvents had specific conductivities within (1–3) × 10^{-8} S·cm^{-1}. Triply distilled water with a specific conductivity of less than 10^{-6} S·cm^{-1} was used for the preparation of binary mixtures and as an aqueous medium. Conductance measurements were carried out using an automatic Microprocessor conductivity meter Model LF 2000 (Germany) which works at 1 kHz. The conductance cell was the same as detailed earlier (*10–14*). Two platinized platinum electrodes with cell constants 0.998 ± 0.001 and 0.685 ± 0.001 cm^{-1} were used. Dry nitrogen was used to prevent the admission of air into the cell when solvent or stock solution was added. The cell was calibrated following the method of Wu and co-workers (*15*), using aqueous KCl solution. The concentrations for the acid were kept constant for each solvent mixture, and no buoyancy corrections were made while calculating the molar conductivities of acid solutions. Weighing of the acid had an accuracy of ±0.0001 g, and the electrolytic conductivities were accurate up to ±0.1%. All the glass apparatus were calibrated with triply distilled water, and the variation in volume of the flask was within ±0.01 cm^3. The measurements were made at a temperature of 25 ± 0.01 °C.

The density ρ, viscosity η, and dielectric constant ϵ values for solvent mixtures were taken from the literature (*10–14*). Other procedures were the same as detailed earlier (*10–14*).

Results and Discussion

The values of the molar conductances for solutions of different concentrations of the acid in different solvent mixtures are given in Tables I and II. The experimental results were analyzed with the Lee and Wheaton conductance equation in series form as suggested by Pethybridge and Taba (*16–18*). The limiting molar conductance Λ_0 and association constants $K_A = 1/K_a$ for the process

$$\mathrm{H^+ + A^- \underset{K_a}{\overset{K_A}{\rightleftharpoons}} H^+A^-} \qquad (1)$$

were deduced from the set of equations

$$\Lambda_0 = \alpha[\Lambda_0(1 + \Delta x/x) - \Delta\Lambda_{el}] \qquad (2)$$

$$K_A = (1 - \alpha)\alpha^2\gamma^2 C \qquad (3)$$

$$-\ln \gamma = bk/2(1 + kR), \quad b = e^2/\epsilon KT \qquad (4)$$

which minimize the standard deviation, σ_A:

$$\sigma_A^{\,2} = \sum_j [\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^2/(n - 2) \qquad (5)$$

where n is the number of data points. All the symbols have been described in previous papers (*10–14*).

In the case of carboxylic acids no minimum is observed in a R–σ_A (%) plot (*19*). The R (ion pair distance) values were varied from 3 to 10 Å. The values of R used for these acids were from 4 to 8 Å in different solvent mixtures. These values are the Bjerrum distance (q) (*20*) as selected by some other researchers according to the suggestion of Justice *et al.* (*21*). The conductance parameters of the acid in different solvent mixtures are given in Table II.

(**a**) ***Limiting Molar Conductances.*** The Λ_0 value for aqueous chloroacetic acid is 382.00 ± 0.05 S·cm^2·mol^{-1}. The literature values are 382 (*4*) and 391 S·cm^2·mol^{-1} (*8*). Table II shows that the limiting molar conductances for the acid decreased with the increase in concentration of the cosolvent in the water. This decrease in the Λ_0 values may be attributed to the relative increase in the viscosity values of water + cosolvent mixtures and respective solvations of the ions. Similar results were found for benzoic, nitrobenzoic, and

0021-9568/93/1738-0527$04.00/0

Table I. Molar Conductivities, Λ, for Monochloroacetic Acid Concentration *C* in Cosolvent (1) + Water (2) at 298.15 K[a]

	Λ/(S·cm^2·mol^{-1})						Λ/(S·cm^2·mol^{-1})	
10^4c/(mol·dm^{-3})	$x_1 = 0$	$x_1 = 10$	$x_1 = 20$	$x_1 = 30$	$x_1 = 40$	$x_1 = 50$	10^4c/(mol·dm^{-3})	$x_1 = 60$	$x_1 = 70$
				Methanol (1) + Water (2)					
1.923	308.68	281.26	209.63	166.92	123.90	79.50	1.191	57.28	38.86
3.703	285.45	248.91	182.47	142.19	103.10	63.66	2.273	45.94	30.34
5.355	268.90	228.15	162.82	127.7	91.54	55.51	3.261	40.15	26.20
6.896	256.28	213.46	154.24	117.96	83.92	50.33	4.167	36.50	23.65
8.333	246.28	203.34	145.60	110.80	78.40	46.67	5.006	33.94	21.89
9.677	238.03	193.53	138.84	105.24	74.19	43.93	5.769	32.02	20.58
10.937	231.18	186.38	133.38	100.80	70.86	41.77	6.482	30.52	19.57
12.121	225.31	180.41	128.84	97.14	68.13	40.03	7.143	29.32	18.76
13.235	220.26	175.36	125.02	94.08	65.84	38.58	7.759	28.32	18.09
14.285	215.85	170.99	121.75	91.46	63.39	37.37	8.333	27.48	17.53
15.277	211.94	167.19	118.90	89.18	62.23	36.32	8.871	26.76	17.05
16.216	208.46	163.85	116.39	87.19	60.76	35.41	9.375	26.14	16.64
17.105	205.35	160.88	114.17	85.45	59.48	34.61	9.849	25.59	16.28
17.948	202.53	158.21	112.20	83.89	58.34	33.90	10.294	25.11	15.96
18.750	199.99	155.82	110.41	82.49	57.32	33.27	10.714	24.68	15.68
				Ethanol (1) + Water (2)					
1.923		269.50	206.76	155.53	112.18	76.15	1.911	59.51	42.58
3.703		243.53	179.21	128.06	91.01	60.47	2.273	47.07	33.28
5.355		226.11	162.52	113.16	79.84	52.52	3.261	40.89	28.74
6.896		213.35	150.95	103.42	72.63	47.50	4.167	37.04	25.53
8.333		203.48	142.36	96.45	67.52	43.97	5.006	34.36	23.98
9.677		195.56	135.66	91.15	63.66	41.33	5.769	32.37	22.54
10.937		189.03	130.25	86.94	60.61	39.26	6.482	30.81	21.42
12.121		183.53	125.76	83.54	58.15	37.59	7.143	29.56	20.53
13.230		178.95	121.99	80.68	56.10	36.22	7.759	28.53	19.79
14.285		174.77	118.75	78.28	54.36	34.93	8.333	27.67	19.17
15.277		171.20	115.94	76.20	52.86	34.04	8.871	26.93	18.64
16.216		168.04	113.48	74.38	51.56	33.18	9.375	26.30	18.18
17.105		165.23	111.28	72.78	50.42	32.48	9.849	25.73	17.78
17.948		162.70	109.35	71.37	49.41	31.75	10.294	25.24	17.43
18.750		160.42	107.59	70.10	48.50	31.15	10.714	24.80	17.14
				1-Propanol (1) + Water (2)					
1.923		263.30	187.90	132.54	92.25	57.45	1.191	44.25	29.69
3.703		234.89	164.59	112.98	76.32	46.55	2.273	35.59	23.45
5.355		216.44	150.12	101.55	67.57	40.77	3.261	31.17	20.37
6.896		203.16	139.98	93.81	61.84	37.06	4.167	28.38	18.45
8.333		193.06	132.38	88.13	57.72	34.44	5.006	26.41	17.12
9.677		185.04	126.42	83.76	54.59	32.47	5.769	24.94	16.13
10.937		178.48	121.59	80.25	52.12	30.99	6.482	23.79	15.36
12.121		172.99	117.59	77.37	50.09	29.66	7.143	22.87	14.74
13.235		168.34	114.20	74.94	48.40	28.62	7.759	22.10	14.23
14.285		164.32	111.29	72.88	46.92	27.73	8.333	21.46	13.80
15.277		160.79	108.75	71.09	45.74	26.31	8.871	20.90	13.43
16.216		157.69	106.52	69.52	44.67	25.79	9.375	20.42	13.12
17.105		154.93	104.55	68.14	43.72	25.53	9.849	20.00	12.84
17.948		152.46	102.79	66.91	42.12	25.21	10.294	19.63	12.60
18.750		150.21	101.19	65.71	42.12	24.75	10.714	19.31	12.38
				N,*N*-Dimethylformamide (1) + Water (2)					
1.923		258.04	188.31	131.69	79.97	52.48	1.191	45.25	31.85
3.703		233.63	168.89	117.35	70.37	44.62	2.273	38.61	26.32
5.355		217.17	156.12	108.09	64.34	40.05	3.261	34.77	23.33
6.896		205.06	146.84	101.42	60.04	36.95	4.167	32.19	21.35
8.333		195.69	140.72	96.33	56.88	34.68	5.006	30.32	20.01
9.677		188.15	134.04	92.35	54.35	32.93	5.769	28.13	18.96
10.937		181.93	129.39	88.99	52.30	31.53	6.482	27.72	18.13
12.121		176.70	125.49	86.32	50.60	30.38	7.143	26.78	17.46
13.235		172.22	122.16	83.88	49.15	29.41	7.759	25.99	16.90
14.285		168.33	119.29	81.86	47.92	28.59	8.333	25.31	16.43
15.277		164.94	116.78	80.09	46.83	27.88	8.871	24.73	16.02
16.216		161.90	114.56	78.35	45.88	27.26	9.375	24.23	15.67
17.105		159.21	112.58	77.14	45.03	26.71	9.849	23.78	15.36
17.948		156.79	110.80	75.90	44.28	26.21	10.294	23.39	15.09
18.750		154.60	109.20	74.78	43.60	25.77	10.714	23.04	14.84
				Acetone (1) + Water (2)					
1.923		268.50	195.30	141.06	87.92	51.06	1.191	37.70	24.76
3.703		241.49	168.96	116.97	70.44	40.03	2.273	29.58	19.11
5.355		223.59	153.03	103.71	61.44	34.57	3.261	25.60	16.41
6.896		210.53	142.04	94.98	55.71	31.15	4.167	23.14	16.07
8.333		200.50	133.90	88.70	51.68	28.79	5.006	21.43	13.63
9.677		192.48	127.56	83.92	48.64	26.96	5.769	20.16	12.80
10.937		185.89	122.45	80.12	46.26	25.61	6.482	19.17	12.15
12.121		180.36	118.23	77.02	44.33	24.49	7.143	18.38	11.63

Table I (Continued)

$10^4c/(\mathrm{mol{\cdot}dm^{-3}})$	$\Lambda/(\mathrm{S{\cdot}cm^2{\cdot}mol^{-1}})$						$10^4c/(\mathrm{mol{\cdot}dm^{-3}})$	$\Lambda/(\mathrm{S{\cdot}cm^2{\cdot}mol^{-1}})$	
	$x_1 = 0$	$x_1 = 10$	$x_1 = 20$	$x_1 = 30$	$x_1 = 40$	$x_1 = 50$		$x_1 = 60$	$x_1 = 70$
				Acetone (1) + Water (2)					
13.235		175.63	114.67	74.43	42.73	23.58	7.759	17.73	11.21
14.285		171.55	111.62	72.23	41.38	22.80	8.333	17.18	10.85
15.277		167.97	108.98	70.34	40.22	22.13	8.871	16.72	10.55
16.216		164.81	106.66	68.69	39.22	21.56	9.375	16.32	10.29
17.105		161.98	104.60	67.24	38.34	21.05	9.849	15.96	10.06
17.948		159.47	102.77	65.95	37.55	20.61	10.294	15.65	9.86
18.750		157.15	101.13	64.79	36.85	20.21	10.714	15.38	9.68
				Acetonitrile (1) + Water (2)					
1.923		269.16	209.00	150.34	102.71	63.59	1.191	46.35	30.63
3.703		244.24	182.86	125.84	89.91	50.09	2.273	36.78	23.87
5.355		227.27	166.70	112.10	72.56	43.34	3.261	31.98	20.59
6.896		214.79	155.35	102.97	65.89	39.11	4.167	18.98	18.56
8.333		205.08	146.85	96.32	61.19	36.16	5.006	26.88	17.17
9.677		197.29	140.18	91.22	57.64	33.94	5.769	25.32	16.13
10.937		190.86	134.78	87.18	54.85	32.20	6.482	24.11	15.33
12.121		185.44	130.28	83.86	52.58	30.82	7.143	23.13	14.68
13.235		180.80	126.48	81.09	50.70	29.65	7.759	22.32	14.15
14.285		176.78	123.22	78.74	49.11	28.69	8.333	21.67	13.71
15.277		173.25	120.38	76.73	47.74	27.86	8.871	21.07	13.33
16.216		170.12	117.89	74.92	46.55	27.14	9.375	20.57	13.00
17.105		167.24	115.68	73.36	45.50	26.51	9.849	20.19	12.72
17.948		164.73	113.70	71.97	44.58	25.94	10.294	19.74	12.47
18.750		162.43	111.92	70.75	43.75	25.44	10.714	19.40	12.24

[a] x_1 = mass % cosolvent.

Table II. Conductance Parameters for Chloroacetic Acid in Cosolvent (1) + Water (2) at 298.15 K

cosolvent mass %	$\Lambda_0/(\mathrm{S{\cdot}cm^2{\cdot}mol^{-1}})$	$10^{-3}K_A/(\mathrm{dm^3{\cdot}mol^{-1}})$	$100\sigma_A/\Lambda_0$	cosolvent mass %	$\Lambda_0/(\mathrm{S{\cdot}cm^2{\cdot}mol^{-1}})$	$10^{-3}K_A/(\mathrm{dm^3{\cdot}mol^{-1}})$	$100\sigma_A/\Lambda_0$
	Methanol (1) + Water (2)				*N,N*-Dimethylformamide (1) + Water (2)		
0	382.00 ± 0.05	0.724 ± 0.001	0.020	10	301.65 ± 0.01	1.017 ± 0.001	0.008
10	347.39 ± 0.06	1.509 ± 0.001	0.031	20	224.87 ± 0.04	1.197 ± 0.001	0.021
20	270.48 ± 0.02	1.956 ± 0.001	0.007	30	159.64 ± 0.09	1.330 ± 0.001	0.015
30	231.05 ± 0.02	2.79 ± 0.002	0.007	40	100.77 ± 0.02	1.632 ± 0.001	0.009
40	188.24 ± 0.02	4.152 ± 0.002	0.005	50	73.15 ± 0.02	2.859 ± 0.002	0.005
50	148.30 ± 0.06	8.532 ± 0.002	0.021	60	62.62 ± 0.02	7.079 ± 0.003	0.007
60	108.11 ± 0.07	14.235 ± 0.014	0.009	70	50.43 ± 0.03	16.255 ± 0.013	0.006
70	91.38 ± 0.23	27.053 ± 0.035	0.016		Acetone (1) + Water (2)		
	Ethanol (1) + Water (2)			10	318.55 ± 0.06	1.143 ± 0.001	0.036
10	316.39 ± 0.05	1.056 ± 0.001	0.030	20	256.20 ± 0.14	2.142 ± 0.004	0.059
20	270.24 ± 0.02	2.104 ± 0.001	0.006	30	216.32 ± 0.20	4.314 ± 0.005	0.050
30	246.99 ± 0.12	4.941 ± 0.002	0.046	40	163.12 ± 0.20	8.386 ± 0.010	0.027
40	193.92 ± 0.04	6.679 ± 0.003	0.006	50	112.54 ± 0.16	13.996 ± 0.015	0.014
50	152.26 ± 0.26	10.568 ± 0.010	0.028	60	84.96 ± 0.05	24.003 ± 0.024	0.008
60	125.02 ± 0.18	19.850 ± 0.023	0.016	70	67.10 ± 0.10	39.272 ± 0.031	0.005
70	45.93 ± 0.37	41.634 ± 0.028	0.018		Acetonitrile (1) Water (2)		
	1-Propanol (1) + Water (2)			10	312.12 ± 0.06	0.979 ± 0.001	0.038
10	318.20 ± 0.15	1.309 ± 0.002	0.008	20	265.54 ± 0.03	1.786 ± 0.001	0.013
20	238.04 ± 0.15	1.767 ± 0.004	0.028	30	222.03 ± 0.05	3.684 ± 0.002	0.013
30	182.84 ± 0.12	2.761 ± 0.006	0.040	40	182.58 ± 0.04	7.250 ± 0.004	0.006
40	143.86 ± 0.14	4.633 ± 0.007	0.031	50	134.36 ± 0.08	12.320 ± 0.010	0.007
50	100.74 ± 0.16	7.043 ± 0.009	0.023	60	94.80 ± 0.05	18.003 ± 0.012	0.005
60	81.79 ± 0.14	13.528 ± 0.015	0.022	70	73.99 ± 0.39	28.582 ± 0.021	0.025
70	62.97 ± 0.20	20.635 ± 0.027	0.018				

salicylic acids in these solvent mixtures (*10–13, 24*). Due to the differences of solvent mixture compositions, the present results could not be compared with those reported by Chakravorty *et al.* (*8*), in methanol + water.

(***b***) ***Thermodynamic Dissociation Constants.*** The pK_a value found for chloroacetic acid is 2.859 ± 0.003. This value is in good agreement with those reported in the literature, *i.e.*, 2.86 and 2.91 (*4–9, 22*), derived either potentiometrically or conductometrically. The pK_a values reported by Grunwald *et al.* (*7*) in 20.3 and 50.1 mass % ethanol + water mixtures are 3.26 and 3.95. Presently derived values in 20 and 50 mass % mixtures of the same solvents are 3.32 and 4.02. Since other solvent mixtures differ, a comparison could not be made. Chakravorty *et al.* (*8*) have reported pK_a values for chloroacetic acid in some methanol + water mixtures (different from those of ours), and for their solvent mixtures of compositions 0, 25.2, 34.4, 44.7, 54.2, and 64.1, the pK_a values are 2.85, 3.39, 3.56, 3.75, 3.99, and 4.18, respectively. The pK_a values found in the present work in methanol + water mixtures of compositions 0, 10, 20, 30, 40, 50, 60, and 70 mass % are 2.859, 3.178, 3.291, 3.445, 3.618, 3.931, 4.153, and 4.443. These values are slightly higher than those of Chakroverty *et al.* (*8*).

Tables II shows that the pK_a values increased with the addition of cosolvent in water. This increase may be attributed to decrease in the values of the dielectric constant of water + cosolvent mixtures. The pK_a values found for chloroacetic acid for alcohol + water mixtures decrease in the

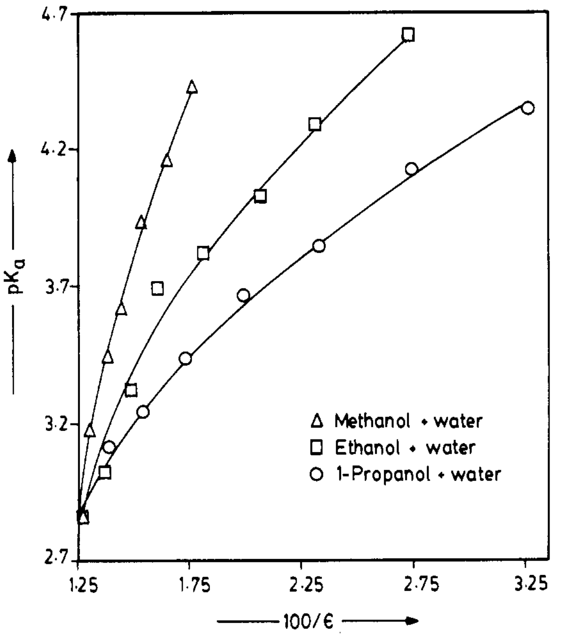

Figure 1. Dependence of thermodynamic dissociation constant, pK_a, values for salicylic acid on the inverse of the dielectric constant (100/ϵ) values of cosolvent + water at 298.15 K.

order ethanol + water > methanol + water > 1-propanol + water. This order is not in accordance with the order of the dielectric constant values of these solvent mixtures. In the case of the other three solvent mixtures, the pK_a values for the acid in *N,N*-dimethylformamide + water are lower than those in acetonitrile + water which are lower than those in acetone + water. This may be due to higher dielectric constant values for the former mixtures than those of the latter mixtures. The dependence of pK_a values on the inverse of permittivity (1/ϵ) of water + cosolvent mixtures is shown in Figures 1 and 2. The figures indicate that, for the isodielectric solvent mixtures, different pK_a values for this acid have been found. It means that the dielectric constant is not the sole parameter for the solvent which determines the extent of the dissociation of electrolyte in the solution. The nonlinearity of these plots (Figures 1 and 2) indicates that in addition to simple electrostatic interactions some specific solute–solvent interactions are taking place.

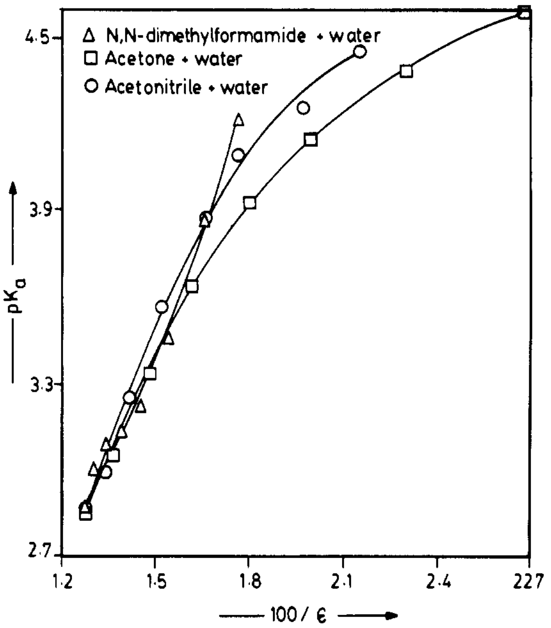

Figure 2. Same as in Figure 1.

Literature Cited

(1) Aleksandrov, V. V.; Burakhovich, A. A. *Russ. J. Phys. Chem.* **1970**, *44*, 1158.
(2) Rondinini, S.; Mussini, P. R.; Mussini, T. *Pure Appl. Chem.* **1985**, *57*, 865.
(3) Mollin, J. Measurement of pH in Mixed and Non-aqueous Solvents. *Chem. Listy* **1988**, *82*, 785.
(4) Wright, D. D. *J. Am. Chem. Soc.* **1934**, *56*, 314.
(5) Saxton, B.; Langer, T. W. *J. Am. Chem. Soc.* **1933**, *55*, 3638.
(6) Shedlovsky, T.; Brown, A. S.; MacInnes, D. A. *Trans. Electrochem. Soc.* **1934**, *66*, 165.
(7) Grunwald, E.; Berkowitz, B. J. *J. Am. Chem. Soc.* **1951**, *73*, 4939.
(8) Chakrovorty, S. K.; Maity, S. K.; Lahiri, S. C. *Z. Phys. Chem. (Leipzig)* **1985**, *266*, 1194.
(9) Petrov, S. M.; Umanskii, Yu. I.; Golikova, N. D.; Khabibova, F. S.; Safiullina, L. A. *Russ. J. Phys. Chem.* **1969**, *43*, 1670.
(10) Niazi, M. S. K.; Shah, S. S.; Ali, J.; Khan, M. Z. I. *J. Solution Chem.* **1990**, *19*, 623.
(11) Niazi, M. S. K.; Ali, J. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3619.
(12) Niazi, M. S. K.; Ali, J. *J. Chem. Eng. Data* **1992**, *37*, 235.
(13) Niazi, M. S. K.; Khan, M. Z. I.; Hassan, A.; Shah, S. S.; Ali, J. *J. Chem. Eng. Data* **1992**, *37*, 470.
(14) Niazi, M. S. K.; Fischer, O.; Fischerova, E. *J. Solution Chem.* **1986**, *15*, 957.
(15) Wu, Y. C.; Koch, W. F. *J. Solution Chem.* **1991**, *20*, 391.
(16) Lee, W. H.; Wheaton, R. J. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, *743*, 1456.
(17) Lee, W. H.; Wheaton, R. J. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 1128.
(18) Pethybridge, A. D.; Taba, S. S. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 368.
(19) Fuoss, R. M. *J. Phys. Chem.* **1978**, *82*, 2427.
(20) Bjerrum, N.; Idensk, K. D. *Selk* **1926**, *7*, 1–46.
(21) Justice, J.-C. *Electrochim. Acta* **1971**, *16*, 701.
(22) Minnick, L. J.; Kilpatric, M. *J. Phys. Chem.* **1939**, *43*, 259.
(23) Larsson; Adell *Z. Phys. Chem.* **1931**, *A157*, 342.
(24) Niazi, M. S. K.; Shah, S. S.; Khan, M. Z. I. *J. Chem. Eng. Data* **1993**, *38*, 288.

Received for review December 1, 1992. Revised March 25, 1993. Accepted April 26, 1993. Financial support from the University Research Fund (URF) is acknowledged gratefully.