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Molar Conductance of Sodium Bromide and Sodium Iodide in Methanol + Water at 298.15 K

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The molar conductances of dilute solutions of sodium bromide and sodium iodide at 298.15 K in methanol + water over the entire range of composition are reported. The limiting molar conductances, association constants, and ion size are evaluated by means of the Fuoss−Onsager equation. The results show that no detectable ion association was found for the electrolytes below 80 mass % methanol.

Introduction

Conductance measurements provide useful and sensitive indications of ion−solvent interaction, ion−ion association, and solvent structure. Although numerous conductance measurements have been reported in the literature, such studies in mixed solvents are relatively rare (Janz et al., 1972). Studies on the molar conductance of electrolytes in mixed solvents are useful for the understanding of the theory.

Methanol + water mixtures have many special properties, which are different from that of the other alcohol + water mixtures. Here we report the molar conductance data of NaBr and NaI in methanol + water mixtures at 298.15 K. Combined with the results of NaCl in methanol + water mixtures reported in our previous paper (Zhang et al., 1996), the relationship between the limiting molar conductance and the negative ionic radius is discussed. The limiting molar conductance for the three salts shows a minima around 50 mass % methanol.

Experimental Section

A. R. grade methanol was further purified as described by Butler et al. (1951). The purified methanol had a density of 0.786 62 g cm^{-3} at 298.15 K, slightly above that reported by Bulter et al., (0.786 57 g cm^{-3}); its specific conductance, in general, varied between (3.5 and 6.5) × 10^{-8} S cm^{-1}. Conductivity water was prepared by double-distilling freshly deionized water in the presence of $KMnO_4$, and its specific conductivity generally varied between (5 and 8.5) × 10^{-7} S cm^{-1}. NaBr and NaI were analytic grade regents, and they were twice recrystallized from conductivity water, dried, and stored in a vacuum bottle kept in a vacuum and a no-light box.

Conductance measurements were carried out using the precise alternating current conductance bridge which had been carefully calibrated (Zhang et al., 1993). Suitable corrections were made for the solvent conductivities. Oil thermostats at 298.15 K were regulated to within ±0.003 K, and the temperatures were observed with a periodically calibrated platinum resistance thermometer. A conductance cell, similar to that described by Shedlovsky (1932) with lightly platinized electrodes was used for all the measurements. Electrode polarization errors were eliminated by taking readings at several frequencies and extrapolating to infinite frequency. Cell constants were determined by calibration with aqueous KCl solutions, as recommended by Wu et al. (1987, 1991).

Table 1. Properties of Methanol (1) + Water (2)

$100w_1$	ρ_0/(g cm^{-3})	ϵ	η/(mPa s)	$10^7\kappa_0$/(S cm^2 mol^{-1})
0.000	0.997 05	78.48	0.8949	5.0−8.5
10.00	0.979 73	74.21	1.158	0.8−1.2
20.00	0.964 51	70.01	1.400	0.72−1.0
30.00	0.948 69	65.55	1.531	0.50−0.91
40.00	0.931 34	60.92	1.593	0.48−0.83
50.00	0.911 85	56.35	1.510	0.45−0.78
60.00	0.890 13	51.71	1.403	0.45−0.76
70.00	0.867 06	47.03	1.190	0.41−0.71
80.00	0.842 17	42.60	1.006	0.38−0.67
90.00	0.815 28	37.88	0.767	0.37−0.66
100.0	0.786 62	32.64	0.541	0.35−0.65

All solutions were made up by mass. The electrolyte concentration generally covered a range from (5 to 95) × 10^{-4} mol dm^{-3}. Seven concentrations were measured in each experiment and at least two check experiments were always carried out. Conversions from molality (m) to molarity (c) were made by means of $c/m = \rho_0(1 + Am)$, where ρ_0 denotes the density of mixed solvents. A is constant. The density of mixed solvents and electrolyte-containing solutions were measured by means of a pycnometer with a capacity of 10 cm^3. For each set of measurements, the density of the corresponding mixed solvent and the most concentrated electrolyte solution were determined, and linearity was assumed for the variation of the solution density with electrolyte concentration.

The physical properties of various methanol + water mixtures were given in Table 1. The densities of mixed solvents were measured using a pycnometer. The viscosities and dielectric constants of the solvent mixtures were those used by Shedlovsky and Kay (1956) and Sesta (1967), respectively, except for 50 mass % and 70 mass % methanol, which were obtained by regressing the corresponding data in the literature (Shedlovsky and Kay, 1956, Sesta, 1967).

Results and Discussion

The molar concentration and conductances are summarized in Table 2 for NaBr and Table 3 for NaI. As a check on salt purity and the measurement reliability, aqueous solutions of each salt were also measured.

The conductance data were analyzed with the Fuoss−Onsager equations, (1) for unassociated electrolytes and (2) for associated electrolytes:

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec\log(c) + Jc \qquad (1)$$

$$\Lambda = \Lambda_0 - S(c\gamma)^{1/2} + Ec\gamma\log(c\gamma) + J(c\gamma) - K_A c\gamma\Lambda f^2 \qquad (2)$$

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Table 2. Molar Conductances for NaBr in Methanol (1) + Water (2) at 298.15 K

10^4c/(mol dm^{-3})	Λ/(S cm^2 mol^{-1})	10^4c/(mol dm^{-3})	Λ/(S cm^2 mol^{-1})	10^4c/(mol dm^{-3})	Λ/(S cm^2 mol^{-1})
$w_1 = 0.0000$		$w_1 = 0.0993$		$w_1 = 0.2003$	
9.6252	125.52	7.9070	100.31	7.2474	83.338
22.154	124.19	10.626	100.00	10.018	83.040
27.874	123.72	29.607	98.494	27.818	81.761
46.243	122.53	49.397	97.474	48.541	80.783
57.739	121.93	66.863	96.782	66.487	80.122
79.352	121.04	88.999	95.996	85.633	79.563
98.818	120.29	96.681	95.728	96.612	79.281
$w_1 = 0.3002$		$w_1 = 0.3993$		$w_1 = 0.4996$	
10.368	72.348	9.7200	67.348	8.2431	65.621
19.800	71.652	19.537	66.537	16.493	64.801
29.602	71.122	29.641	65.922	25.466	64.127
38.534	70.719	43.062	65.289	40.098	63.285
58.171	70.033	57.439	64.709	52.653	62.670
75.815	69.534	75.584	64.108	73.799	61.844
94.244	69.111	92.862	63.599	89.853	61.298
$w_1 = 0.5991$		$w_1 = 0.7004$		$w_1 = 0.8000$	
8.3141	65.705	10.037	67.857	9.9780	71.974
16.408	64.804	17.660	66.863	15.492	71.051
27.551	63.892	26.914	65.952	25.330	69.777
40.366	63.089	39.324	64.986	39.336	68.397
53.063	62.420	52.213	64.167	49.305	67.596
72.477	61.553	68.860	63.256	68.622	66.328
88.789	60.957	87.368	62.448	83.750	65.495
$w_1 = 0.9003$		$w_1 = 1.0000$			
7.8059	80.059	8.5480	94.392		
16.605	78.004	17.269	91.416		
25.057	76.562	21.784	90.241		
34.953	75.225	33.648	87.767		
48.990	73.731	46.843	85.673		
65.178	72.339	62.013	83.808		
84.103	71.052	78.291	82.222		

Table 3. Molar Conductances for NaI in Methanol (1) + Water (2) at 298.15 K

10^4c/(mol dm^{-3})	Λ/(S cm^2 mol^{-1})	10^4c/(mol dm^{-3})	Λ/(S cm^2 mol^{-1})	10^4c/(mol dm^{-3})	Λ/(S cm^2 mol^{-1})
$w_1 = 0.0000$		$w_1 = 0.1000$		$w_1 = 0.2000$	
8.6852	124.68	8.2046	99.811	8.6900	82.901
20.445	123.40	9.7961	99.626	9.6326	82.830
32.505	122.43	21.405	98.609	19.833	82.013
46.221	121.65	40.685	97.468	39.237	80.995
59.655	120.97	59.292	96.663	47.921	80.651
79.162	120.16	78.718	96.022	70.598	79.918
98.426	119.49	96.580	95.482	96.804	79.254
$w_1 = 0.2998$		$w_1 = 0.3996$		$w_1 = 0.4997$	
8.6507	72.929	9.4110	67.623	15.725	65.248
10.078	72.780	14.232	67.204	19.632	64.989
18.783	72.114	19.211	66.895	28.622	64.467
28.430	71.539	37.579	65.988	42.009	63.901
40.012	71.015	54.106	65.416	56.756	63.393
65.362	70.094	75.671	64.843	73.020	62.978
95.493	69.301	92.558	64.497	71.958	62.580
$w_1 = 0.5991$		$w_1 = 0.7004$		$w_1 = 0.8000$	
12.582	66.643	9.4060	70.126	7.2458	76.308
18.460	66.075	15.989	69.276	8.4330	76.047
26.860	65.414	21.334	68.756	17.490	74.556
42.660	64.465	33.868	67.776	31.626	72.983
52.406	63.984	49.923	66.821	48.934	71.604
70.439	63.219	69.246	65.984	66.779	70.524
88.411	62.616	86.513	65.373	86.408	69.596
$w_1 = 0.9000$		$w_1 = 1.0000$			
6.7709	85.272	6.3712	101.49		
8.2600	84.835	8.3530	100.58		
18.109	82.642	15.111	98.171		
32.141	80.557	23.974	95.873		
51.112	78.591	30.632	94.528		
65.837	77.457	53.137	91.228		
83.042	76.396	78.927	88.838		

Here all symbols have the usual significance (Fuoss and Accascina, 1959). Using a least squares computer program, the conductance parameters were obtained and listed in Table 4 with the standard deviations of the unknowns. These standard deviations were sufficiently low to analyze the conductance data accurately. No significant association phenomena were observed, as the conductance equation (1) was suitable for treating the conductance data at most compositions of the systems. Only when the methanol percentage was more than 90 mass % for NaBr and more

Table 4. Conductance Parameters for NaBr and NaI in Methanol (1) + Water (2) at 298.15 K

$100w_1$	Λ_0/(S cm^2 mol^{-1})	a^0	K_A
	NaBr + CH_3OH + H_2O		
0.000	128.26 ± 0.013	3.41 ± 0.06	
9.931	102.37 ± 0.010	3.17 ± 0.06	
20.03	85.056 ± 0.006	3.10 ± 0.05	
30.02	74.272 ± 0.003	3.78 ± 0.04	
39.93	69.293 ± 0.006	2.78 ± 0.04	
49.96	67.618 ± 0.004	2.53 ± 0.03	
59.91	67.984 ± 0.007	2.74 ± 0.03	
70.04	70.904 ± 0.007	2.85 ± 0.03	
80.04	75.768 ± 0.005	2.95 ± 0.01	
90.03	84.680 ± 0.032	3.52 ± 0.02	1.31 ± 0.11
100.0	101.76 ± 0.018	3.79 ± 0.01	2.19 ± 0.06
	NaI + CH_3OH + H_2O		
0.000	127.27 ± 0.012	3.66 ± 0.06	
10.00	101.88 ± 0.007	3.53 ± 0.05	
20.03	84.763 ± 0.006	3.70 ± 0.06	
29.98	74.712 ± 0.005	3.31 ± 0.05	
39.96	69.467 ± 0.006	4.29 ± 0.05	
49.97	67.807 ± 0.005	4.67 ± 0.04	
59.92	69.417 ± 0.005	3.15 ± 0.03	
70.01	73.015 ± 0.007	3.95 ± 0.03	
80.00	79.578 ± 0.025	3.91 ± 0.03	1.07 ± 0.08
90.00	89.641 ± 0.033	4.03 ± 0.02	1.46 ± 0.10
100.0	107.98 ± 0.023	4.33 ± 0.01	2.82 ± 0.08

Table 5. Literature Values of Λ_0/(S cm^2 mol^{-1}) for NaBr and NaI in Methanol

NaBr in methanol	NaI in methanol
101.77[a]	107.97[a]
101.76[b]	107.98[c]
101.76[c]	

[a] Harned and Owen, 1958. [b] Robinson and Stokes, 1965. [c] This work.

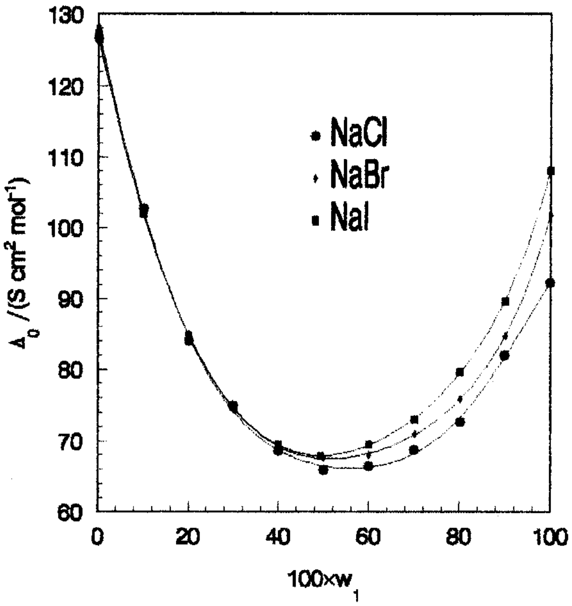

Figure 1. Variance of limiting molar conductance Λ_0.

than 80 mass % for NaI was it necessary to analyze the conductance data with eq 2, and the corresponding K_A were listed in Table 4.

As can be seen from Table 5, for pure methanol, the literature results are in good agreement with our values.

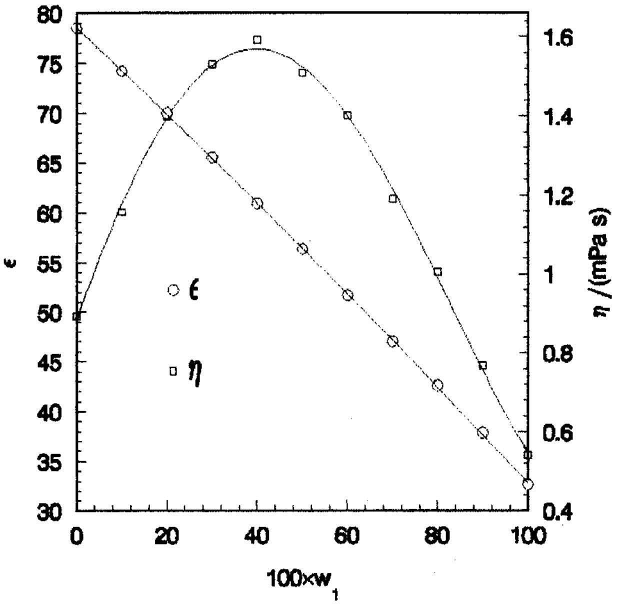

Figure 2. Viscosities and dielectric constants for methanol−water mixtures at 298.15 K.

Figure 1 shows the variation of the limiting molar conductance with the mass % of methanol. Plotted also are the limiting molar conductance of NaCl in methanol + water mixtures at 298.15 K reported previously (Zhang et al., 1996). The limiting molar conductances of each electrolyte show a minimum point around 50 mass % methanol, whereas the viscosity for methanol + water mixtures reached its maximum around 40 mass % methanol, as shown in Figure 2. The ion mobility in methanol + water mixtures is not completely controlled by the bulk viscosity and the dielectric properties. The results cannot be explained by the Stokes law, which would predict Λ_0 to be the reciprocal of the ion size. A more satisfactory interpretation of the Λ_0 minima for these systems is based on the ion sorting effects (Frank, 1955; Kay and Broadwater, 1976; Spivey and Shedlovsky, 1967).

Another feature of the curves in Figure 1 is that the limiting molar conductances for NaCl, NaBr, and NaI have nearly the same value when the percentage of methanol is less than 40 mass % methanol, and the differences incease gradually at higher methanol mass fractions in the order NaI > NaBr > NaCl.

Table 4 shows that no detectable ion association was found for the electrolytes below 80 mass % methanol. It may be due to the larger dielectric constant of the methanol−water mixtures and the smaller ion size.

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