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Ionic Association and Conductances of Sodium Perchlorate in *N,N*-Dimethylformamide + Water and Tetrahydrofuran + Water at 298 K

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The electrolytic conductivity of NaClO₄ in *N,N*-dimethylformamide + water and tetrahydrofuran + water has been measured at 298.15 K. The limiting molar conductivity, Λ_0 , and association constant, K_A , were derived from concentration-conductivity data with the Fuoss (1978-80) equation. The results are compared with literature values.

Introduction

Alkali-metal perchlorates have been studied conductometrically in pure solvents and binary mixtures of water + organic solvent and nonaqueous solvents (1-10). Electrolytic conductivity measurements of NaClO₄ in tetrahydrofuran + water have been made by Osinska et al. (11). No measurements appear to have been made for NaClO₄ in *N,N*-dimethylformamide + water. Taniewska et al. have pointed out that NaClO₄ is associated in tetrahydrofuran + water at a tetrahydrofuran concentration of >25 mol%. The present paper reports the molar conductivity of a dilute solution of NaClO₄ in tetrahydrofuran + water and *N,N*-dimethylformamide + water ranging in composition from 0 to 70 mass % of the cosolvent at 298.15 K. The values of the limiting molar conductivity, Λ_0 , and association constant, K_A , have been derived and compared with literature values.

Experimental Section

(a) **Chemicals.** Tetrahydrofuran from E. Merck (99.5 mass %) was further treated with LiAlH₄ to remove peroxides and was distilled. The fraction boiling at 66.5 and 67.5 °C was collected. *N,N*-Dimethylformamide was also from Merck (99.5 mass %), and its purification has been detailed elsewhere (12). NaClO₄ (reagent grade) was crystallized from a methanol + water mixture (1:1 by volume) and dried at 150 °C in a vacuum oven. The dried salt was kept in a desiccator containing P₂O₅.

(b) **Conductivity Measurements.** The conductivity measurements were carried out using a Microprocessor Model LF 2000 conductivity meter (Germany). Conductivity cells with cell constants of 0.011 ± 0.001 and 0.775 ± 0.001 cm⁻¹ were used. Platinized black platinum electrodes were used in the cells. The conductivity cell was calibrated using aqueous KCl solutions as recommended by Wu et al. (13). The other procedures and details have been reported in previous papers (14, 15).

The densities, ρ , viscosities, η , and dielectric constants, ϵ , for the solvent mixtures were taken from previous papers (14, 15), and are given in Table I.

Results and Discussion

The molar conductivities of NaClO₄ solutions of different concentrations in *N,N*-dimethylformamide + water and tetrahydrofuran + water are given in Tables II and III, respectively. The conductivity-concentration data were analyzed using the Fuoss (1978-80) conductance equation (16). The limiting molar conductance, Λ_0 , and the association

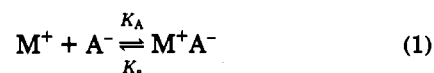
Table I. Densities, ρ , Viscosities, η , and Dielectric Constants, ϵ , for Cosolvent (1) + Water (2) at 298.15 K

x_1	ρ /(g·cm ⁻³)	η /(mPa·s)	ϵ
<i>N,N</i> -Dimethylformamide (1) + Water (2)			
0.00	0.9971	0.8903	78.54
2.7	0.9964	1.153	76.78
5.8	0.9963	1.326	74.65
9.5	0.9971	1.665	72.00
14.1	0.9968	2.042	68.92
19.8	0.9961	2.338	64.96
26.9	0.9934	2.491	60.48
36.5	0.9913	2.580	55.50
Tetrahydrofuran (1) + Water (2)			
2.7	0.9933	1.199	71.76
5.9	0.9876	1.500	64.60
9.7	0.9795	1.710	56.59
14.3	0.9694	1.785	48.20
20.0	0.9572	1.718	39.96
27.3	0.9467	1.529	32.00
36.8	0.9326	1.259	24.62

Table II. Molar Conductivities, Λ , for NaClO₄ Solutions in *N,N*-Dimethylformamide (1) + Water (2) at 298.15 K

$10^4 c$ / (mol·dm ⁻³)	Λ /(S·cm ² ·mol ⁻¹)						
	$x_1 = 0.027$	$x_1 = 0.058$	$x_1 = 0.095$	$x_1 = 0.141$	$x_1 = 0.198$	$x_1 = 0.269$	$x_1 = 0.0365$
9.524	89.76	79.02	63.96	53.99	44.02	39.39	34.92
18.182	89.08	78.37	63.32	53.35	43.34	38.64	34.24
26.087	88.61	77.92	62.85	52.87	42.83	38.08	33.72
33.333	88.24	77.57	62.47	52.48	42.42	37.61	33.30
40.000	87.94	77.29	62.15	52.15	42.07	37.23	32.95
46.154	87.69	77.05	61.89	51.87	41.77	36.89	32.65
51.852	87.47	76.84	61.65	51.62	41.51	36.60	32.39
57.143	87.29	76.66	61.45	51.40	41.28	36.34	32.16
62.069	87.12	76.50	61.27	51.21	41.07	36.11	31.95
66.666	86.97	76.36	61.10	51.03	40.88	35.90	31.77
70.968	86.87	76.26	60.98	50.91	40.75	35.76	31.64
75.000	86.72	76.11	60.82	50.73	40.56	35.55	31.45
78.788	86.62	76.00	60.69	50.60	40.42	35.40	31.32
82.353	86.52	75.91	60.58	50.47	40.29	35.26	31.19
85.714	86.42	75.82	60.47	50.36	40.16	35.13	31.07

constant, K_A , for the process



were deduced from the set of equations

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

$$K_A = (1 - \alpha)/\alpha^2\gamma^2c \quad (3)$$

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

Table III. Molar Conductivities, Λ , for NaClO_4 Solutions in Tetrahydrofuran (1) + Water (2) at 298.15 K

$10^4 c / (\text{mol} \cdot \text{dm}^{-3})$	$\Lambda / (\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1})$						
	$x_1 = 0.027$	$x_1 = 0.059$	$x_1 = 0.097$	$x_1 = 0.143$	$x_1 = 0.200$	$x_1 = 0.272$	$x_1 = 0.368$
4.762	86.21	66.85	56.29	49.46	50.82	52.85	54.83
9.091	85.60	66.22	55.63	48.87	50.07	51.69	53.10
13.044	85.16	65.75	55.16	48.44	49.55	50.84	51.90
16.666	84.81	65.37	54.79	48.10	49.17	50.16	50.98
20.000	84.52	65.05	54.47	47.81	48.76	49.61	50.24
23.077	84.28	64.77	54.20	47.57	48.45	49.13	49.64
25.926	84.06	64.52	53.97	47.35	48.18	48.72	49.13
28.571	83.87	64.30	53.76	47.16	47.94	48.36	48.70
31.034	83.70	64.11	53.58	46.99	47.74	48.04	48.31
33.333	83.55	63.93	53.42	46.84	47.54	47.75	47.98
35.483	83.41	63.77	53.27	46.71	47.37	47.49	47.68
37.500	83.29	63.63	53.13	46.58	47.22	47.26	47.41
39.400	83.17	63.49	53.01	46.46	47.07	47.04	47.17
41.176	83.07	63.37	52.89	46.36	46.94	46.85	46.96
42.857	82.97	63.25	52.79	46.26	46.84	46.67	46.76

Table IV. Conductance Parameters for NaClO_4 in Cosolvent (1) + Water (2) at 298.15 K

x_1	$\Delta_0 / (\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1})$	$K_A / (\text{dm}^3 \cdot \text{mol}^{-1})$	$R / (10^{-8} \text{ cm})$	$100 \sigma_A / \lambda_0$
<i>N,N</i> -Dimethylformamide (1) + Water (2)				
0.000	118.17 ± 0.01	0.60 ± 0.11	13.2	0.01
0.027	91.85 ± 0.02	1.84 ± 0.18	12.3	0.02
0.058	82.33 ± 0.03	2.31 ± 0.21	12.2	0.04
0.095	65.61 ± 0.02	4.59 ± 0.42	10.2	0.03
0.141	55.53 ± 0.04	7.21 ± 1.01	9.4	0.06
0.198	45.51 ± 0.02	11.06 ± 1.52	9.33	0.03
0.269	40.97 ± 0.02	13.80 ± 2.04	9.33	0.05
0.365	36.47 ± 0.03	15.84 ± 2.24	9.33	0.08
Tetrahydrofuran (1) + Water (2)				
0.027	87.78 ± 0.01	4.33 ± 0.21	10.3	0.01
0.059	68.30 ± 0.04	8.29 ± 0.27	9.3	0.06
0.097	57.71 ± 0.02	11.48 ± 1.30	9.3	0.04
0.143	50.93 ± 0.03	14.05 ± 1.91	15.3	0.05
0.200	52.66 ± 0.01	20.69 ± 2.77	16.3	0.04
0.273	55.56 ± 0.06	43.11 ± 6.13	16.3	0.11
0.368	59.03 ± 0.04	64.41 ± 10.8	10.3	0.07

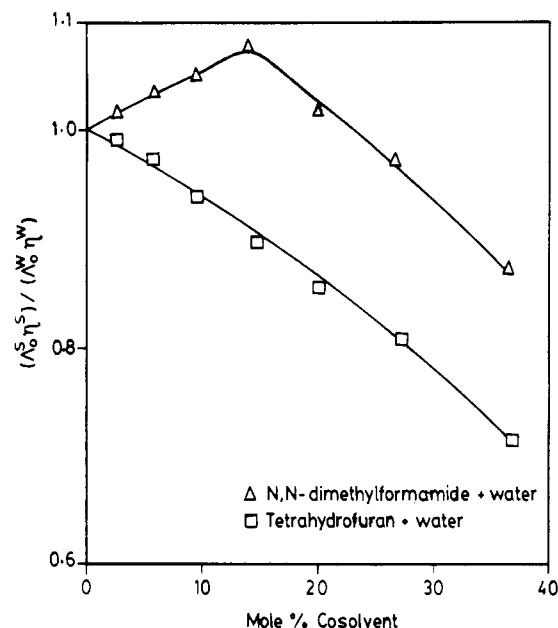
which minimize standard deviation, $\sigma(\Lambda)$,

$$\sigma(\Lambda) = \left\{ \sum_j [\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^2 / (n - 2) \right\}^{1/2} \quad (5)$$

by a least-squares analysis, where $\Delta X/X$ is the relaxation field effect, and $\Delta\Lambda_{\text{el}}$ is the electrophoretic countercurrent. k^{-1} is the radius of the ion atmosphere, ϵ is the dielectric constant of the solvent, e is the electron charge, K is the Boltzmann constant, R is the Gurney-sphere diameter, mostly recognized as an ion-pair distance, α is the fraction of solute present as an unpaired ion, c is the molarity of the solution, γ_c is the activity coefficient, and β is twice the Bjerrum distance (17).

Conductivity measurements can provide at least three parameters: the conductivity at infinite dilution Δ_0 , the ion association constant K_A , and the ion distance parameter R that gives the best fit to the conductance equation (e.g., the lowest standard deviation $\sigma(\Lambda)$). The results are collected in Table IV.

(a) Limiting Molar Conductances. The limiting molar conductivity for NaClO_4 decreased with addition of *N,N*-dimethylformamide to water. The decrease in Δ_0 values may be attributed to a relative increase in the viscosities of *N,N*-dimethylformamide + water mixtures at higher *N,N*-dimethylformamide concentrations. Similar results were also found by other researchers in these solvent mixtures for other electrolytes (18–20). The values of normalized Walden products are plotted against solvent composition in Figure 1. These values pass through a maximum at about $x_1 = 0.15$ of the cosolvent. This maximum does not conform to the

**Figure 1.** Dependence of the values of normalized Walden products, $(\Delta_0^* \eta^5) / (\Delta_0^* \eta^5)$, for NaClO_4 on the composition of *N,N*-dimethylformamide + water (Δ) and tetrahydrofuran + water (\square) at 298.15 K.

maximum in the viscosity–composition curve, which lies at about 25 mol % *N,N*-dimethylformamide. The variation of Walden products with composition is indicative of selective solvation of the ions in these solvent mixtures. *N,N*-Dimethylformamide first dehydrates the ions and then solvates them as its concentration increases in the solvent mixtures.

For tetrahydrofuran + water mixtures, it is found that the Δ_0 values decreased with an increase in the concentration of tetrahydrofuran in water to about 15 mol % tetrahydrofuran and then increase. Similar results were found by Stein for LiClO_4 (7) and Triener et al. (10) for KClO_4 in these solvent mixtures and for NaClO_4 in acetonitrile + water mixtures (5). Due to the difference of solvent composition with that studied by Osinska et al. (11), it is not possible to compare the Δ_0 values. The normalized Walden products are plotted against the solvent mixture composition in Figure 1. No maximum has been found in the plot. The product decreases with an increase in the concentration of tetrahydrofuran in water, indicating selective solvation of ions by tetrahydrofuran. *N,N*-Dimethylformamide is a dipolar aprotic solvent while tetrahydrofuran is an aprotic electron pair donor. The difference in the two solvent mixtures, i.e., *N,N*-dimethylformamide + water and tetrahydrofuran + water mixtures, is that they behave differently toward the same electrolyte.

(b) Association Constants. The values of the association constant, K_A , found for NaClO_4 in *N,N*-dimethylformamide (1) + water (2) mixtures are $<10 \text{ dm}^3 \cdot \text{mol}^{-1}$ up to solvent composition $x_1 = 0.18$. Further it is found that K_A values increase to $22 \text{ dm}^3 \cdot \text{mol}^{-1}$ in pure *N,N*-dimethylformamide (found from reanalysis of conductance–concentration data of Sear et al. (6)).

The K_A values found for NaClO_4 in tetrahydrofuran + water are higher than those observed in *N,N*-dimethylformamide + water (2). As the phenomenon of association is mostly governed by the dielectric constant or polarity of solvent, therefore, K_A values in the former solvent system are higher than those in the latter. As the composition of solvent mixtures varied from pure aqueous to solvent mixtures with more contents of cosolvent, the K_A increased. Though these values are $<10 \text{ dm}^3 \cdot \text{mol}^{-1}$ in water-rich mixtures, appreciable

values have been found for solvent mixtures with $x_1 > 0.2$. The K_A values are highly sensitive to the parameter R , the ion distance parameter. The increase in the values of R increases the K_A value. In Table IV, the values of R are those at which a minimum in the standard deviation of Δ was observed. As seen in Table IV, the values of R are from 9.33 to 16.3 Å, for the $\text{Na}^+\text{ClO}_4^-$ ion pair in different solvent mixtures. The sum of crystallographic ionic radii, a , for NaClO_4 is 3.33 Å. The diameters of water + cosolvent molecule are calculated from the formula (16)

$$d/(10^{-8} \text{ cm}) = 1.183(M/(\text{g}\cdot\text{mol}^{-1}))^{1/3}/(\rho/(\text{g}\cdot\text{cm}^{-3})) \quad (6)$$

where M is the molecular weight of the solvent and ρ its density. For mixed solvents M is replaced by the mole fraction average molecular weight of the mole fractions:

$$M_{av} = M_1M_2/(x_1M_2 + x_2M_1) \quad (7)$$

The values calculated for d are from 3.125 to 3.534 Å for different solvent mixtures. The values of R are higher than $a + d$, which is the maximum 6.864 Å for a solvent mixture of composition $x_1 > 0.368$, indicating clearly that the $\text{Na}^+\text{ClO}_4^-$ ion pair is solvent separated.

Finally it can be concluded that slight association of NaClO_4 is found in N,N -dimethylformamide + water mixtures while for the tetrahydrofuran + water system with composition $x_1 > 0.2$, appreciable values of K_A are found.

Literature Cited

- (1) Barthel, J.; Iberl, L.; Rossmäier, J.; Gores, H. J.; Kankal, B. *J. Solution Chem.* 1990, 19, 321.
- (2) Aprano, A. D. *J. Phys. Chem.* 1971, 75, 3290.
- (3) Aprano, A. D.; Donato, I. D.; Palombo, R. *J. Phys. Chem.* 1972, 76, 2923.
- (4) Gill, D. S.; Sharma, A. N.; Schnieder, H. *J. Chem. Soc., Faraday Trans. 1* 1982, 78, 465.
- (5) Niazi, M. S. K.; Khan, A. *J. Chem. Eng. Data* 1993, 38 (1), 98.
- (6) Ames, D. P.; Sears, P. G. *J. Phys. Chem.* 1955, 59, 16.
- (7) Stein, Z.; Gileadi, E. *J. Electrochem. Soc.* 1985, 132, 2166.
- (8) Janz, G. J.; Tomkins, R. P. T. *Nonaqueous Electrolytes Handbook*; Academic Press: New York, 1972; Vol. I, Chapter III.
- (9) Goffredi, M.; Triolo, R. *Ricerca Sci.* 1967, 37, 1126.
- (10) Bury, R.; Triener, C. *J. Chim. Phys. Phys.-Chim. Biol.* 1968, 65, 1410.
- (11) T.-Osinska, S.; Kozłowski, Z.; Nowicka, B.; Bald, A.; Czeyjis, A. *J. Chem. Soc., Faraday Trans. 1* 1989, 85, 479.
- (12) Niazi, M. S. K.; Ficher, O.; Fischerova, E. *J. Solution Chem.* 1986, 15, 957.
- (13) Wu, Y. C.; Koch, W. F.; Hamer, W. J.; Kay, R. L. *J. Solution Chem.* 1987, 16, 985.
- (14) Niazi, M. S. K.; Ali, J. *J. Chem. Eng. Data* 1992, 37, 235.
- (15) Niazi, M. S. K.; Hassan, A.; Khan, M. Z. I.; Shah, S. S. *J. Chem. Eng. Data* 1992, 37, 470.
- (16) Fuoss, R. M. *J. Phys. Chem.* 1978, 82, 2427; *J. Solution Chem.* 1980, 9, 379.
- (17) Bjerrum, N. K. *Dan. Vidensk. Selsk.* 1926, 7, 1-46.
- (18) Giridher, V. V.; Kalidas, C. *Indian J. Chem.* 1990, 29A, 1050.
- (19) Singh, D.; Bahadar, L.; Ramanamurti, M. V. *J. Solution Chem.* 1977, 6, 703.
- (20) Bahadar, L.; Ramanamurti, M. V. *Can. J. Chem.* 1984, 62, 1051.

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