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 $NaClO_4$ 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 $NaClO_4$ in tetrahydrofuran + water have been made by Osinska et al. (*11*). No measurements appear to have been made for $NaClO_4$ in *N,N*-dimethylformamide + water. Taniewska et al. have pointed out that $NaClO_4$ is associated in tetrahydrofuran + water at a tetrahydrofuran concentration of >25 mol %. The present paper reports the molar conductivity of a dilute solution of $NaClO_4$ 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 $LiAlH_4$ 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*). $NaClO_4$ (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 P_2O_5.

(*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 $NaClO_4$ 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 Fouss (1978-80) conductance equation (*16*). The limiting molar conductance, Λ_0, and the association constant, K_A, for the process

$$M^+ + A^- \underset{K_a}{\overset{K_A}{\rightleftharpoons}} M^+A^- \quad (1)$$

were deduced from the set of equations

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

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

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

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

x_1	$\rho/(g\cdot cm^{-3})$	$\eta/(mPa\cdot s)$	ϵ
	N,N-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 $NaClO_4$ Solutions in *N,N*-Dimethylformamide (1) + Water (2) at 298.15 K

	$\Lambda/(S\cdot cm^2\cdot mol^{-1})$						
$10^4c/$ $(mol\cdot dm^{-3})$	$x_1 =$ 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

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

10^4c/(mol·dm^{-3})	Λ/(S·cm^2·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	Λ_0/(S·cm^2·mol^{-1})	K_A/(dm^3·mol^{-1})	R/(10^{-8} cm)	$100\sigma_\Lambda/\lambda_0$
N,N-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, $\sigma(\Lambda)$,

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

by a least-squares analysis, where $\Delta X/X$ is the relaxation field effect, and $\Delta\Lambda_{el}$ 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 Λ_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 Λ_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 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.

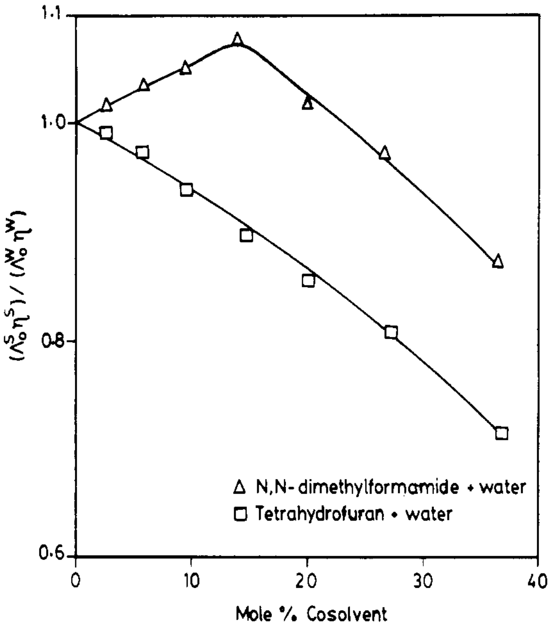

Figure 1. Dependence of the values of normalized Walden products, $(\Lambda_0^s\eta^s)/(\Lambda_0^w\eta^w)$, for $NaClO_4$ on the composition of *N,N*-dimethylformamide + water (△) and tetrahydrofuran + water (□) at 298.15 K.

For tetrahydrofuran + water mixtures, it is found that the Λ_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 Λ_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*-dimethylformamidie + water and tetrahydrofuran + water mixitures, 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 dm^3·mol^{-1} up to solvent composition x_1 = 0.18. Further it is found that K_A values increase to 22 dm^3·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 dm^3·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 Λ was observed. As seen in Table IV, the values of R are from 9.33 to 16.3 Å, for the $Na^+ClO_4^-$ 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)*

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

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:

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

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 Na^+ 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.

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