The Conductance of Sodium Perchlorate in Water-sulfolane Mixtures at 35 °C

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Measurements on the conductance of dilute solutions of sodium perchlorate, at 35 °C, in water-sulfolane mixtures over the entire solvent composition range are reported. Experimental data were analyzed by the 1965 Fuoss-Onsager-Skinner equations.

No detectable ion association was found for this electrolyte, unlike sodium chloride in the same solvent mixtures. The association order $K_A(Cl^-) > K_A(ClO_4^-)$ is in contrast with that observed in protic solvents $[K_A(ClO_4^-) > K_A(Cl^-)]$ and is similar to that found in aprotic solvents. This shows that in water-sulfolane mixtures, association phenomena are mainly controlled by sulfolane.

The lack of transport numbers for water-sulfolane mixtures precludes unambiguous explanations for Walden products $\Lambda_0 \eta$.

Introduction

Earlier studies from this laboratory indicate that the ion association of lithium[1], sodium[2] and potassium[3] chlorides in water-sulfolane mixtures is higher than expected on the basis of simple electrostatic theory. Association constants, higher than the Fuoss[4] and Bjerrum[5] equations predict, were also found in several protic solvents by Evans and coworkers[6] and they offered a satisfactory explanation by discussing this anomalous behaviour in terms of a multiple-step association process. The proposed mechanism predicts that perchlorates are more associated than chlorides.

With the purpose of seeing if this association trend also holds good in mixtures of protic with aprotic solvents like water-sulfolane, the conductance of sodium perchlorate was measured in these mixtures over the entire 0 – 100% sulfolane composition range at 35 °C.

Experimental

Water and sulfolane purification has already been described[7].

Sodium perchlorate (Fisher Scientific Company) was recrystallized three times from conductivity water and dried under vacuum at 150 °C.

Conductance cells were of the Erlenmayer type as described by Daggett, Bair and Kraus[8]. Their constants were determined at 25 °C by measuring the conductance of aqueous potassium chloride solutions, as suggested by Ying-Chech Chiu and R. M. Fuoss[9]. Cell constants were 1.0667 ± 0.0001 and $0.21654 \pm 0.00002\ \text{cm}^{-1}$. An Erlenmayer cell with a constant $0.06337 \pm 0.00003\ \text{cm}^{-1}$ was calibrated by comparison.

All conductance measurements on $NaClO_4$ solutions were performed at 35 °C.

Previous experience[10] indicates that cell constants do not significantly change between 25° and 35 °C.

Conductance measurements were performed at 1, 2.5 and 10 kC/sec using a Jones and Dike Bridge (manufactured by Leeds and Northrup Co). The cells were thermostated at 25 °C and 35 °C in a constant temperature oil bath (Leeds and Northrup). The control was within ±0.002 °C and the temperature monitored by an NBS certified resistance thermometer and an L&N Muller Bridge G2.

Density, viscosity and dielectric constant measurements together with experimental procedure have been described elsewhere[7].

Conductance cells were initially filled with a weighed amount of solvent, then working solutions in the concentration range $(10 \div 70) \cdot 10^{-4}$ moles/l were obtained by adding small increments of a concentrated stock solution using a weight buret.

The molarity c of solutions was calculated from the molality m by the equation:

$$c/m = \varrho + k\,m$$

where ϱ is the density of the solvent mixture and k is an empirical constant determined by density measurements.

Results

The properties of the solvent mixtures are summarized in Table 1. The symbols have the following meanings: w_2 and N_2 are sulfolane weight per cent

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Table 1. Properties of water-sulfolane mixtures at 35 °C.

System	w_2	N_2	ϱ (g/ml)	η (cP)	D
1	0.00	0.0000	0.99406	0.7194	74.64
2	12.135	0.02052	1.02176	0.8287	72.30
3	34.257	0.07309	1.07499	1.1445	67.24
4	55.464	0.1589	1.12893	1.6577	61.47
5	74.053	0.3050	1.17932	2.5445	55.09
6	91.286	0.6111	1.22913	4.4414	47.57
7	100	1.0000	1.25752	9.033	42.71

and mole fraction; ϱ, η and D are densities, viscosities and dielectric constants of the solvents.

Table 2 gives equivalent conductances Λ and concentrations c for sodium perchlorate in the different systems which are identified by their dielectric constants. The experimental data were analyzed using the Fuoss-Onsager-Skinner[11] 1965 equations, for associated (1) and unassociated (2) electrolytes:

$$\Lambda = \Lambda_0 - S\, c^{\frac{1}{2}} \gamma^{\frac{1}{2}} + E'\, c\, \gamma \ln \tau^2 \gamma + L\, c\, \gamma - K_{\mathrm{A}}\, c\, \gamma\, \Lambda \exp(-2\, \tau\, \gamma^{\frac{1}{2}}) \,, \tag{1}$$

$$\Lambda = \Lambda_0 - S\, c^{\frac{1}{2}} + E'\, c \ln \tau^2 + L\, c \,. \tag{2}$$

All calculations were performed on an IBM 360/65 computer using the Skinner and Fuoss program. Analysis by Eq. (1) gave for all studied systems negative association constants or very small K_{A} values with standard deviations larger than K_{A}. Then, the data were automatically processed by the two-parameters Equation (2).

The derived parameters Λ_0 and a_{L} are summarized in Table 3 together with standard deviations in each parameter, standard deviations of individual points σ_Λ and Walden products $\Lambda_0 \eta$. The differences $\Delta\Lambda$ between measured and calculated conductance are also included in Table 2.

Table 3. Derived parameters for sodium perchlorate in water-sulfolane mixtures at 35 °C.

System	Λ_0	a_{L}	σ_Λ	$\Lambda_0 \eta$
1	142.15 ± 0.02	2.77 ± 0.06	0.02	1.023
2	120.94 ± 0.04	3.36 ± 0.15	0.04	1.002
3	87.22 ± 0.03	3.58 ± 0.14	0.03	0.998
4	61.791 ± 0.009	4.15 ± 0.07	0.008	1.024
5	42.989 ± 0.007	3.94 ± 0.05	0.008	1.094
6	25.516 ± 0.005	3.36 ± 0.04	0.006	1.133
7	11.740 ± 0.002	2.42 ± 0.02	0.002	1.060

Discussion

Sodium perchlorate does not appear appreciably associated to ion pairs over the entire solvent composition range. On the contrary, previous measurements[2] have shown that sodium chloride in the same solvent mixtures is associated starting from $w_2 \cong 70$ wt% sulfolane ($D \cong 55$). Hence in water-sulfolane sodium chloride is more associated than sodium perchlorate. This association order agrees with that observed in pure sulfolane[12] and in other aprotic solvents like acetone[13], nitrobenzene[14], nitromethane[15], acetonitrile[16], 1,1,3,3 tetramethyl-

Table 2. Equivalent conductance of sodium perchlorate in water-sulfolane mixtures at 35 °C.

10^4 c	Λ	$\Delta\Lambda \cdot 10^3$	10^4 c	Λ	$\Delta\Lambda \cdot 10^3$	10^4 c	Λ	$\Delta\Lambda \cdot 10^3$	10^4 c	Λ	$\Delta\Lambda \cdot 10^3$
	$D = 74.64$			$D = 72.30$			$D = 67.24$			$D = 61.47$	
14.779	138.03	+19	17.679	116.98	−24	19.555	84.09	+27	16.563	59.629	+ 9
24.314	136.90	+12	22.120	116.58	+16	23.499	83.80	+25	19.804	59.437	+ 4
34.839	135.89	−17	25.996	116.21	−10	27.712	83.50	− 6	25.202	59.156	− 4
42.575	135.28	−10	38.296	115.35	+55	30.790	83.29	−28	30.528	58.914	−10
50.595	134.69	−27	49.381	114.57	−37	35.297	83.04	−32	36.547	58.680	− 8
57.964	134.22	−17	64.389	113.82	+ 2	40.959	82.78	− 3	42.934	58.468	+ 3
64.910	133.84	+23				47.691	82.47	− 5	50.804	58.228	+ 8
75.204	133.26	+17				59.962	82.00	+26			
	$D = 55.09$			$D = 47.57$			$D = 42.71$				
14.543	41.477	+16	19.367	24.291	− 8	19.286	11.053	− 2			
18.901	41.258	− 4	24.714	24.147	− 2	23.910	10.977	—			
24.118	41.047	−10	31.341	23.993	+ 4	30.553	10.878	—			
30.608	40.835	− 2	38.172	23.851	+ 7	37.357	10.788	—			
37.218	40.637	− 6	54.120	23.566	+ 3	45.145	10.696	+ 1			
44.516	40.453	− 1	61.789	23.448	—	51.864	10.625	+ 2			
52.201	40.282	+ 5	77.795	23.234	− 5	60.001	10.544	+ 1			
66.508	39.996	+ 2				75.143	10.407	− 3			

urea[17]. It is, on the contrary, the opposite of what is observed in protic solvents[6] where perchlorates are more associated than chlorides.

The association behaviour found in the latter solvents has been interpreted by Evans et al.[6] supposing that the association mechanism for a salt MX in a protic solvent SH is a multiple-step process according to the equations:

$$M^+ + X^-(SH)_n \overset{K_1}{\rightleftharpoons} M^+(SH)_n X^- , \qquad (3)$$

$$M^+(SH)_n X^- \overset{K_2}{\rightleftharpoons} M^+X^-(SH)_{n-1} + (SH) . \qquad (4)$$

Equation (3) predicts the formation of a "solvent-separated ion pair", which rearranges to a "contact ion pair", by losing a solvent molecule as shown in Equation (4).

The experimental association constant is:

$$K_A = K_1(1 + K_2/[SH]) \qquad (5)$$

where K_1 may be calculated from the Fuoss equation[4] and K_2 depends on the strength of anion solvation. Equation (5) accounts for association constants higher than expected on the basis of electrostatics ($K_A > K_1$). Furthermore, as expected on the basis of ionic radii, K_2 is greater for perchlorates than chlorides and this accounts for the observed association behaviour in protic solvents.

In aprotic solvents anions are scarcely solvated[18]; therefore chloride is more associated than perchlorate because the former interacts more strongly with cations, having a higher charge density than the latter.

In water-sulfolane mixtures the sodium chloride association, greater than expected on the basis of the Fuoss equation, could be accounted for by the mechanism suggested by Evans and cow.[6], assuming that anions, which form ion pairs, are preferentially solvated by water. In this case sodium perchlorate should be more associated than chloride. However the order observed, typical of aprotic solvents, shows that association phenomena in our mixtures depend on the fraction of ions interacting with sulfolane. Heat of transfer data[19] show that the chloride ion is less stabilized in sulfolane than in protic solvents. Thus it forms very stable ion pairs in sulfolane, as shown by the high value of the association constant for LiCl[1] ($K_A = 14595$). The conclusion which can be drawn is that the ions interacting with sulfolane form very stable ion pairs even in water-sulfolane mixtures, in spite of the high value of dielectric constants.

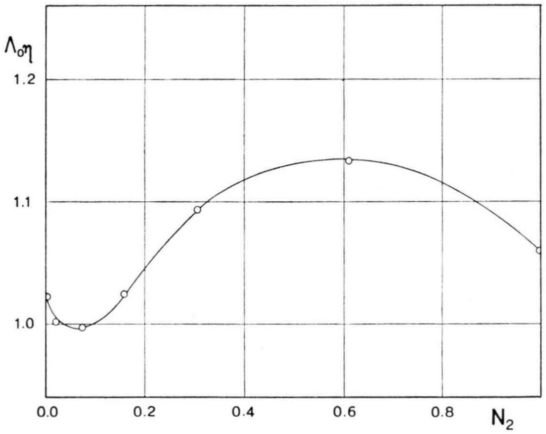

Fig. 1. Walden products for $NaClO_4$, at 35 °C, vs. sulfolane mole fraction in solvent mixtures.

Let us now consider the Walden products. Figure 1 shows a minimum in water-rich mixtures followed by a maximum at about 90 wt% sulfolane. It should be possible to find some explanation for this complex trend in terms of structural changes of solvent mixtures or changes of ion solvation on adding sulfolane to water. Nevertheless, we believe that it is necessary to know the ionic contribution to the total $\Lambda_0 \eta$ products, as also shown by Kay, Cunningham and Evans[20]. Unfortunately, the lack of transport numbers for the water-sulfolane mixtures precludes a correct interpretation.

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