THE CONDUCTANCE BEHAVIOUR OF NaI AND NaBPh₄ IN ACETONE AND IN ISOPROPANOL AT 10, 15, 20, 25, AND 30°C

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Molar conductivities at the limit of zero concentration have been evaluated for NaI and NaBPh₄ in acetone and in isopropanol at 10, 15, 20, 25, and 30°C. The experimental data have been analysed by means of the Lee–Wheaton equation. The thermodynamic parameters of the non--coulombic interaction have been evaluated.

The degree of ion association of an electrolyte in a solvent is mainly influenced by the radii of the ions, the dielectric constant of the solvent, and specific solvent effects. The electrostatic forces between ions cause ions of unlike charges to attract each other and for any pair of ions the mutual potential energy is given as a function of distance by Coulomb's law. However, besides electrostatic forces, solvation forces also exist which are completely system specific and cannot be predicted from the electrostatic theory. Conductometry is the most direct and accurate technique available for determining the extent to which ions associate in solution[1].

Most of the experimental work that exists in the literature has been carried out in solvent systems of high dielectric constant, where ion association is negligible, in order to test various conductance equations. In this work the conductances of NaI and NaBPh₄ in acetone and in isopropanol are reported in the range 10−30°C at 5° intervals. Acetone and isopropanol belong to solvents of medium dielectric constant where considerable ion association occurs. Study of the ionic equilibria over a temperature range permits us to determine the heats and the entropies of the respective ion pairs.

EXPERIMENTAL

NaBPh₄ (Merck p.a.) was recrystallized from acetone and dried under vacuum over P₂O₅. NaI (Merck suprapure) was used as received. Acetone (Fluka p.a.) and isopropanol (Merck p.a.) were passed through 3Å molecular sieves and fractionally distilled. Conductivity of both solvents was better than $5 \cdot 10^{-3}$ S cm^{-1}.

All solutions were maintained in a thermostated Leeds and Northrup oil bath. Resistance measurements were carried out using a Jones and Joseph type (Leeds and Northrup) AC bridge. The cells used were similar to those proposed by Daggett, Bair and Kraus[2]. All solutions were prepared by weight. Details of the experimental procedure have been reported previously[3,4].

TABLE I

Equivalent conductance of NaI and $NaBPh_4$ in acetone and isopropanol at 10, 15, 20, 25, and 30°C (c, mol l^{-1}; Λ, S cm^2 mol^{-1}; η, P)

10°C		15°C		20°C		25°C		30°C	
$c \cdot 10^4$	Λ	$c \cdot 10^4$	Λ	$c \cdot 10^4$	Λ	$c \cdot 10^4$	Λ	$c \cdot 10^4$	Λ

NaI in acetone

($D = 22\cdot2$; $\eta = 0\cdot00351$)		($D = 21\cdot7$; $\eta = 0\cdot00334$)		($D = 21\cdot2$; $\eta = 0\cdot00318$)		($D = 20\cdot7$; $\eta = 0\cdot00302$)		($D = 20\cdot5$; $\eta = 0\cdot002295$)	
4·586	152·36	4·563	159·37	4·534	166·51	4·500	173·82	4·467	181·12
14·366	139·43	14·293	145·26	14·201	151·04	14·097	156·98	13·995	162·72
19·001	135·70	18·903	141·19	18·782	146·72	18·782	152·22	18·509	157·51
26·222	130·66	26·088	135·72	25·921	140·78	25·921	145·77	25·544	150·51
38·128	124·66	37·932	129·23	37·689	133·76	37·689	138·14	37·141	142·28
49·199	120·27	48·947	124·53	48·534	128·66	48·634	132·69	47·927	136·42
56·864	117·75	56·574	121·78	56·211	125·68	56·211	129·45	55·394	132·94

$NaBPh_4$ in acetone

4·656	109·53	4·625	115·27	4·593	121·16	4·558	127·26	7·102	130·73
7·311	107·40	7·262	112·97	7·211	118·77	7·156	124·71	10·884	127·25
11·204	104·59	11·129	110·02	11·051	115·63	10·967	121·39	15·651	124·17
16·109	102·11	16·001	107·44	15·889	112·86	15·769	118·46	19·446	122·23
20·016	100·47	19·882	105·79	19·742	111·12	19·593	116·56	21·995	121·12
22·639	99·491	22·488	104·829	22·329	110·13	22·161	115·58		

NaI in isopropanol

($D = 21\cdot5; \eta = 0\cdot0285$)		($D = 20\cdot87; \eta = 0\cdot285$)		($D = 20\cdot05; \eta = 0\cdot0244$)		($D = 19\cdot3; \eta = 0\cdot0272$)		($D = 18\cdot3; \eta = 0\cdot0179$)	
2·720	11·764	2·703	13·700	2·689	15·825	2·657	18·291	2·644	20·743
5·134	11·093	5·103	12·838	5·077	14·698	5·016	16·862	4·991	19·015
8·133	10·131	8·083	12·061	8·041	13·753	7·944	15·680	7·904	17·578
10·334	10·131	10·269	11·635	10·217	13·229	10·065	15·085	10·015	16·854
12·851	9·793	12·772	11·220	12·701	12·728	12·525	14·459	12·463	16·107
15·428	9·506	15·333	10·873	15·256	12·301	15·044	13·929	14·969	15·472
18·627	9·192	18·512	10·487	18·412	11·212	18·171	13·371	18·080	14·811

NaBPh$_4$ in isopropanol

12·899	11·84	12·834	12·640	12·763	14·630	12·698	16·851	12·635	19·320
16·551	11·629	16·466	12·374	16·378	14·301	16·292	16·499	16·211	18·897
18·048	11·496	18·950	12·219	18·851	14·142	18·750	16·271	18·656	18·629
22·188	11·345	22·017	12·034	21·958	13·927	21·841	16·038	21·732	18·359
26·178	11·186	26·045	11·853	25·098	13·711	25·770	15·781	25·641	18·057
29·374	11·075	29·223	11·716	29·070	13·544	28·915	15·596	28·770	17·829
32·546	9·966	32·379	11·600	32·209	13·416	32·037	15·432	31·877	17·644
35·717	9·878	35·534	11·484	35·348	13·282	35·183	15·275	34·985	17·463

RESULTS AND DISCUSSION

The measured molar conductances for dilute solutions of NaI and NaBPh$_4$ in isopropanol and acetone at 10°, 15°, 20°, 25° and 30°C are listed in Table I. We treated our experimental results by the method proposed by Pethybridge who uses the Lee––Wheaton conductance equation for the special case of a single symmetrical electrolyte[5]. Previous conductance equations[6] were derived from the so-called primitive model of rigid charged unpolarizable spheres in a dielectric continuum whose properties are those of the bulk solvent. Thus in the primitive model solute–solvent interactions are not taken into account. The Lee–Wheaton equation[7,8] is derived from a model more realistic than the primitive model. Lee and Wheaton envisage three regions around the ion itself, which is treated as a rigid conducting sphere. In region I, all the solvent molecules are aligned by the ion's field and there is dielectric saturation, in region II, the solvent structure is still modified by the ion's field though to a lesser extent, and in region III, the solvent retains its bulk properties.

Conductance data can provide three parameters: The limiting molar conductance Λ_0, at infinite dilution, the association constant of the ions K_A, and the distance of closest approach of the ions R.

The exerimental data are fitted to the conductance equation:

$$\Lambda = \gamma \Lambda_0 \{1 + C_1(\beta\varkappa) + C_2(\beta\varkappa)^2 + C_3(\beta\varkappa)^3\} -$$
$$- (\varkappa\varrho)(1 + \varkappa R)^{-1}\{1 + C_4(\beta\varkappa) + C_5(\beta\varkappa)^2 + \varkappa R/12\},$$

where:

$C_1 = -0.09753 + 0.08185t - 0.044t^2 + 0.01114t^3$

$C_2 = 0.11798 - 0.18737t + 0.09052t^2 - 0.02393t^3 + 0.08358 \ln t$

$C_3 = -0.19454 + 0.39764t - 0.37557t^2 + 0.25118t^3 - 0.07843t^4 - 0.102961 \ln t$

$C_4 = -0.04724 + 0.06445t - 0.07419t^2 + 0.01784t^3 - 0.12428 \ln t + 0.09863t \ln t$

$C_5 = 0.84185 - 0.90051t + 0.07809t^2 - 0.05333t^3 + 0.50097 \ln t + 0.45252t \ln t$

$t = \varkappa R$, $\varrho = |z| Fe/(299.79 . 3\pi\eta)$ and $\beta = e^2/DkT$.

All the other symbols have their usual meanings.

The value of Λ_0 calculated from the experimental data by using the Lee–Wheaton equation does not differ appreciably from the value calculated on basis of the previous conductance equations but the value of K_A calculated from the Lee–Wheaton equation is generally higher. The distance of closest approach of the ions R, calculated from Lee–Wheaton conductance equation is reasonable, (the values of R calculated with equations based on the primitive model were sometimes too high or too low), and the fit of the experimental data on the equation is much better[9,10].

The molar conductances at infinite dilution, association constants and standard deviations calculated from the experimental data for NaI in isopropanol and acetone are given in Table II. The physical constants of the solvents have been taken from the literature[11,12]. In all cases a sharp minimum was observed in the $\sigma\%$–R plot at 8 ± 1 Å for NaI and 10 ± 1 Å for NaBPh$_4$. The center to center distance of NaI is 3·1 Å and of NaBPh$_4$ 5·1 Å (refs[13,14]). The diameter of the isopropanol or acetone molecule is 5·6 Å (ref.[15]). The R values found suggest that the ion pairs that are formed are solvent separated ion pairs.

Isopropanol and acetone have similar dielectric constants at 10°C and ion association of an electrolyte in these solvents should be about the same. However, both electrolytes studied in this work are more associated in isopropanol than in acetone. Alcohols are good hydrogen bond donors and acceptors. Consequently the liquids are extensively self-associated, forming hydrogen bonded solvents. Acetone is a good hydrogen bond acceptor but since it has no donor hydrogen it is unassociated as a pure liquid. The larger values of K_A observed in isopropanol may be attributed to a diminution in the dielectric constant in the vicinity of an ion pair. The magnitude of the bulk dielectric constant is due in large measure to the structures arising from hydrogen bonding. However, in the vicinity of an ion pair extensive hydrogen bonding between the alcohol molecules is unlikely because of the orientation of the alcohol

TABLE II

Conductance parameters

°C	Λ_0	K_A	$\sigma_A, \%$	$K_{A(el)}$	Λ_0	K_A	$\sigma_A, \%$	$K_{A(el)}$
	NaI in isopropanol $R = (8 \pm 1)$ Å				NaI in acetone $R = (8 \pm 1)$ Å			
10	13·416	350	0·017	367	168·63	124	0·031	295
15	15·697	396	0·021	400	176·75	132	0·042	306
20	18·411	489	0·031	472	185·54	144	0·037	319
25	21·595	591	0·051	552	194·01	155	0·052	334
30	24·999	721	0·023	732	202·46	169	0·029	352
	NaBPh$_4$ in isopropanol $R = (10 \pm 1)$ Å				NaBPh$_4$ in acetone $R = (10 \pm 1)$ Å			
10	12·840	67	0·031	94	120·52	41	0·073	83
15	15·004	74	0·034	99	126·73	42	0·069	85
20	17·425	78	0·041	109	133·29	44	0·082	87
25	20·191	84	0·028	120	140·11	46	0·071	90
30	23·597	96	0·034	141	146·86	48	0·068	92

dipoles by the ions. This results in a decreased local dielectric constant thereby enhancing the Coulomb's attraction between ions and increasing ion association.

There exists a number of equations that can be used in order to predict the value of K_A when only coulombic and thermal forces are taken into account[16,17]. However, these equations take only electrostatic effects into consideration and their validity must be looked for only in cases where nonelectrostatic effects are nonexistent. A number of similar but not identical equations have been proposed in order to calculate the noncoulombic part of the free energy of association[18,19]. In this work we have used the "Fuoss 75" equation. The association constant, if only coulombic forces are taken into account, is given by the integral

$$K_A = \frac{4\pi N}{1\,000} \int_a^R r^2 \exp\left(\beta/r\right) \mathrm{d}r \,, \qquad (1)$$

where a is the sum of crystallographic radii of the cation and the anion and $\beta = e^2/DkT$. Ions whose pairwise separation lies between a and $R = a + d$ where d is the distance of a solvent molecule.

Equation (1) does not take into account short range forces. If short range forces are taken into account then a Boltzman factor must be added and K_A is given by the equation

$$K_A = \frac{4\pi N}{1\,000} \exp\left(-\Delta G/RT\right) \int_a^R r^2 \exp\left(\beta/r\right) \mathrm{d}r \,. \qquad (2)$$

The values of $K_{A(el)}$ (e.g. $\Delta G = 0$) are given in Table II. The ΔG values at 25°C calculated from Eq. (2) are for NaI in isopropanol 0, for NaI in acetone 2·4 kJ, for NaBPh$_4$ in isopropanol 1·15 kJ, and for NaBPh$_4$ in acetone 1·8 kJ. The ΔH values found for all cases were about zero. Thus ΔG is due only to entropic effects. A decrease in the entropy of the system suggests that the ion pairs that are formed organize the solvent molecules in their vicinity better than the ions.

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