

CHAPTER VI

ELECTRICAL CONDUCTANCES OF SOME ALKALI-METAL SALTS IN *N,N*-DIMETHYLACETAMIDE-WATER MIXTURE AT 298.15K

Studies of the transport properties of electrolytes in different solvent media are of great importance to obtain information on the behaviour of ions in solution. The conductometric method is well-suited to investigate the ion-solvent and ion-ion interactions in electrolyte solutions.^{1,2} In previous chapters, we have reported the conductances of a number of alkali-metal and tetraalkylammonium salts in the pure solvent *N,N*-dimethylacetamide at 298.15K. Now, we have extended the work to study the conductometric behaviour of some alkali-metal salts in *N,N*-dimethylacetamide + water (50% v/v) in an attempt to unravel the nature of various types of interactions prevailing in aquo-organic mixtures.

Experimental

Triply distilled water with a specific conductance of less than 10^{-6} S.cm⁻¹ at 298.15K was used for the preparation of the mixed solvent. The mixed solvent system (50% *N,N*-dimethylacetamide + water v/v) had a density of 0.99877 g.cm⁻³ and a coefficient of viscosity of 0.03318 mPa.s at 298.15K.

The salts were of Fluka's purum or puriss grade. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent.

The relative permittivity of *N,N*-dimethylacetamide + water (50% v/v) mixture ($\epsilon = 59.92$) at 298.15K was obtained using the equations as described in the literature.³

Results and Discussion

The measured molar conductance (Λ) of electrolyte solutions as a function of molar concentration (c) at 298.15K are given in Table 1.

The conductance data have been analyzed by the 1978 Fuoss conductance-concentration equation as described earlier.

The calculations are made by finding the values of Λ^0 and σ which minimize the standard deviation, σ ,

$$\sigma^2 = \sum_{j=1}^n [\Lambda_j(\text{calcd}) - \Lambda_j^0(\text{obsd})]^2 / (n-2) \quad (1)$$

for a sequence of R values and then plotting σ against R ; the best-fit R corresponds to the minimum in σ vs. R curve.

The values of Λ^0 , K_A and R obtained by this procedure are reported in Table 2.

The association constants (K_A) of these electrolytes (*cf.* Table 2) - which are always less than 10 - indicate that these salts are completely dissociated in *N,N*-dimethylacetamide. This implies that these salts remain essentially in the form of free ions in this solvent medium. A comparison of the available association constant

values in pure *N,N*-dimethylacetamide with those obtained in the *N,N*-dimethylacetamide + water system in the present study reveals that the addition of water to pure *N,N*-dimethylacetamide results in a lower level of ionic association. This may be attributed to the increased relative permittivity of the mixed solvent medium compared to the pure *N,N*-dimethylacetamide.

In order to investigate the specific behaviour of the individual ions comprising these electrolytes, it is necessary to split the limiting molar electrolyte conductances into their ionic components. In the absence of accurate transport number data for these systems, we have used the "reference electrolyte" method for the division of Λ^0 into their ionic components. Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) has been used as the "reference electrolyte"⁴ Bu_4NBPh_4 was used as the "reference electrolyte" also by Fuoss and Hirsch⁵ to evaluate the limiting ionic conductances in several organic solvents. We have divided the Λ^0 values of Bu_4NBPh_4 into ionic components using a method similar to that proposed by Krumgalz⁶ for division of viscosity *B* coefficients :

$$\Lambda^0(\text{Bu}_4\text{NBPh}_4) = \lambda^0(\text{Bu}_4\text{N}^+) + \lambda^0(\text{Ph}_4\text{B}^-) \quad (2)$$

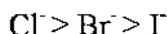
$$\frac{\lambda^0(\text{Bu}_4\text{N}^+)}{\lambda^0(\text{Ph}_4\text{B}^-)} = \frac{r(\text{Ph}_4\text{B}^-)}{r(\text{Bu}_4\text{N}^+)} = \frac{5.35}{5.00} \quad (3)$$

The *r* values have been taken from the works of Gill *et al.*⁷ The relevant limiting molar conductance of the electrolyte tetrabutylammonium tetraphenylborate

Bu_4NBPh_4 was obtained from the limiting molar conductivity values of Bu_4NBr , NaBPh_4 and NaBr by the method of additivity. The limiting ion conductances calculated from the above equations are recorded in Table 3.

The limiting ionic equivalent conductivities of the alkali-metal and halide ions in the present solvent system are substantially lower than those observed in aqueous solutions.⁸ It is generally accepted that the alkali-metal and halide ions possess an excess mobility in aqueous medium owing to their ability to break the hydrogen bonds in their immediate vicinity and thereby reduce the local viscosity.⁹

It is seen from Table 3 that for the halide ions, the λ^0 values decrease in the following order:



i.e., the limiting ionic conductivity values decrease with increasing size of these anions.

This is also found to be true for the molecular anions, *i.e.*, the λ^0 values of these ions decrease in the order:



This observations indicate that all these anions remain unsolvated in *N,N*-dimethylacetamide + water solvent system investigated here. Had these ions been solvated in the mixed solvent medium, their limiting ionic conductivity values would have been in the reverse order since the smaller ions with higher surface

charge density could associate greater number of solvent molecules to form a bigger solvodynamic entity with lower mobility. This is, obviously, not the case here.

The starting point for most evaluations of ionic conductances is Stokes' law that contents that the limiting Walden product (the limiting ionic conductance-solvent viscosity product) for any singly charged, spherical ion is a function only of the ionic radius and thus, under normal conditions, is a constant. In Table 3 we have collected the Stokes' radii (r_s) of the ions in *N,N*-dimethylacetamide + water solvent system. For lithium ion, the Stokes' radius is much higher than its crystallographic radius suggesting that this ion is significantly solvated in this solvent medium. The Stokes' radii of the other ions are, however, found to be either very close to or smaller than their corresponding crystallographic radii¹⁰. This observation indicates that these ions are scarcely solvated in the mixed solvent medium. This also supports our earlier contention derived from the order of the limiting ionic conductivity values (*cf.* the preceding paragraph). Similar behaviour has also been observed in pure *N,N*-dimethylacetamide solutions.¹¹

It may thus be concluded that all these alkali-metal salts, essentially dissociated in *N,N*-dimethylacetamide + water solvent system apparently due to the high relative permittivity of the solvent medium. Lithium ion is found to be significantly solvated in this solvent medium while the other ions remain scarcely solvated.

References

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Table 1. Equivalent Conductances and Corresponding Molarities of Electrolytes in N,N-Dimethylacetamide + Water (50% v/v) at 298.15K

10^4 c/ mol.dm ⁻³	Λ / S.cm ² .mol ⁻¹	10^4 c/ mol.dm ⁻³	Λ / S.cm ² .mol ⁻¹
	LiCl		LiBr
512.95	22.41	470.01	21.01
477.58	22.61	437.59	21.17
442.20	22.79	405.18	21.29
406.83	22.99	372.76	21.43
371.45	23.19	340.35	21.60
336.07	23.40	307.93	21.76
300.70	23.60	275.52	21.93
265.32	23.86	243.10	22.10
	LiI		LiClO ₄
444.92	17.75	433.95	19.18
414.24	17.85	404.02	19.30
383.55	17.93	374.09	19.41
352.87	18.02	344.17	19.54
322.18	18.12	314.24	19.68
291.50	18.22	284.31	19.83
260.82	18.32	254.38	20.00
230.13	18.47	224.46	20.12

Contd...

$10^4 c / \text{mol.dm}^{-3}$	$\Lambda / \text{S.cm}^2.\text{mol}^{-1}$	$10^4 c / \text{mol.dm}^{-3}$	$\Lambda / \text{S.cm}^2.\text{mol}^{-1}$
	LiBF ₄		NaBr
420.05	21.85	438.72	31.41
391.09	21.98	406.60	31.59
362.12	22.13	376.48	31.78
333.15	22.24	346.36	31.95
304.18	22.39	316.24	32.14
275.21	22.56	286.12	32.33
246.24	22.70	256.01	32.55
217.27	22.88	225.89	32.78
	KBr		RbBr
437.36	35.34	472.68	36.01
407.20	35.48	440.08	36.12
377.03	35.59	407.48	36.22
346.87	35.70	374.88	36.35
316.71	35.82	342.29	36.47
286.55	35.99	309.69	36.60
256.38	36.10	277.09	36.71
226.22	36.26	244.49	36.85

contd...

$10^4 \text{ c/ mol.dm}^{-3}$	$\Lambda / \text{S.cm}^2.\text{mol}^{-1}$	$10^4 \text{ c/ mol.dm}^{-3}$	$\Lambda / \text{S.cm}^2.\text{mol}^{-1}$
	CsBr		NaBPh ₄
432.99	35.06	436.50	20.00
403.13	35.22	406.40	20.10
373.27	35.41	376.29	20.20
343.40	35.59	346.19	20.29
313.54	35.79	316.09	20.40
283.68	36.00	285.98	20.50
253.82	36.20	255.88	20.62
223.96	36.43	225.78	20.75
	Bu ₄ NBr		
435.90	21.14		
405.84	21.33		
375.78	21.55		
345.72	21.77		
315.65	21.98		
285.59	22.13		
255.53	22.42		
225.47	22.68		

Table 2. Conductivity Parameters of Electrolytes in N,N-Dimethylacetamide + Water (50% v/v) at 298.15K

Salt	$\Lambda^0 / \text{S-cm}^2\text{-mol}^{-1}$	$K_A / \text{dm}^3\text{-mol}^{-1}$	R/A^0	$\sigma\%$
LiCl	26.61 ± 0.03	5.19 ± 0.06	14.0 ± 0.5	0.04
LiBr	24.40 ± 0.03	4.58 ± 0.06	9.5 ± 0.5	0.04
LiI	20.25 ± 0.03	2.47 ± 0.08	12.5 ± 0.5	0.05
LiClO ₄	22.30 ± 0.03	4.77 ± 0.10	6.5 ± 0.5	0.06
LiBF ₄	25.19 ± 0.03	4.47 ± 0.10	6.5 ± 0.5	0.04
NaBr	35.76 ± 0.02	3.88 ± 0.04	8.0 ± 0.5	0.02
NaBPh ₄	25.52 ± 0.01	3.12 ± 0.03	6.0 ± 0.5	0.03
KBr	38.50 ± 0.03	1.99 ± 0.04	8.5 ± 0.5	0.04
RbBr	38.81 ± 0.02	1.68 ± 0.02	12.0 ± 0.5	0.02
CsBr	39.50 ± 0.01	3.45 ± 0.02	8.0 ± 0.5	0.01
Bu ₄ NBr	25.54 ± 0.08	6.86 ± 0.19	16.0 ± 0.5	0.01

**Table 3. Limiting Ionic Conductances, Walden products and Stokes radii in
N,N- Dimethylacetamide + Water (50% v/v) at 298.15K**

ion	$\lambda_{\pm}^0 / \text{S cm}^2 \text{ mol}^{-1}$	$\lambda_{\pm}^0 \eta_0 / \text{S cm}^2 \text{ mol}^{-1} \cdot \text{Pa.s}$	$r_s / \text{\AA}$
Li ⁺	6.76	0.022	3.66
Na ⁺	18.13	0.060	1.36
K ⁺	20.87	0.069	1.18
Rb ⁺	21.18	0.070	1.17
Cs ⁺	21.87	0.072	1.13
Bu ₄ N ⁺	7.81	0.026	3.12
Cl ⁻	19.85	0.066	1.24
Br ⁻	17.63	0.058	1.40
I ⁻	13.49	0.044	1.83
ClO ₄ ⁻	15.53	0.051	1.59
BF ₄ ⁻	18.42	0.061	1.34
BPh ₄ ⁻	7.39	0.024	3.35