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THE EFFECT OF PRESSURE ON THE CONDUCTANCE OF SOME IODIDES IN ACETONE AND 2-METHYLPROPAN-1-OL

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Abstract

The conductance of 4-methoxycarbonyl-*N*-methylpyridinium iodide was measured in acetone at 293·1, 303·1, and 313·1°K and in 2-methylpropan-1-ol (Bu^iOH) at 303·1°K at pressures up to 3 kbar. Similar measurements were made on solutions of sodium iodide in Bu^iOH at 298·1 and 308·1°K. Limiting conductances and ion pair association constants are derived and show incomplete dissociation of the salts at all concentrations.

The conductance of solutions of 4-methoxycarbonyl-*N*-methylpyridinium iodide (mmpI) in acetone and 2-methylpropan-1-ol (Bu^iOH) was measured over a range of temperatures and pressures in order to determine the activity coefficient and association constants of this salt in connection with a study of the effect of pressure on the charge-transfer complexes formed by it.[1] Similar measurements on sodium iodide in Bu^iOH were of interest in a study of charge-transfer complexes formed by iodide ions with neutral molecules.[2] The limiting equivalent conductance, the association constant, and the activity coefficient were calculated from the measurements by means of the Fuoss conductance equation,[3] and the activation parameters for conductance were evaluated in terms of the transition state theory.[4]

The results for mmpI parallel those recently obtained by Adams and Laidler[5] for tetra-n-propylammonium iodide (Pr_4NI) in acetone. The measurements on sodium iodide in Bu^iOH show that this salt is only partly dissociated in this solvent.

Experimental

Acetone (BDH Analar) was purified by the method recommended by Weissberger,[6] fractionally distilled, and stored in dark bottles over $MgSO_4$. Immediately before use it was redistilled (b.p. 329·0–329·2°K), degassed in a vacuum, and subsequently handled only under dry nitrogen. Density and viscosity data required in the calculations were taken from

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[1] Ewald, A. H., and Scudder, J. A., unpublished data.

[2] Scudder, J. A., M.Sc. Thesis, University of Sydney, 1970.

[3] Fuoss, R. M., and Accascina, F., "Electrolytic Conductance." pp. 195, 235 *et seq.*, 268. (Interscience: New York 1959.)

[4] Brummer, S. B., and Hills, G. S., *Trans. Faraday Soc.*, 1961, **57**, 1816.

[5] Adams, W. A., and Laidler, K. S., *Can. J. Chem.*, 1968, **46**, 1977.

[6] Weissberger, A., "Techniques of Organic Chemistry." Vol. 7. (Interscience: New York 1956.)

Timmermans[7] and their pressure dependence was calculated from the data of Bridgman.[8] The values of the dielectric constants at appropriate temperatures and pressures were calculated by the Owen–Brinkley equation[9] for which the parameters were obtained from the data of Hartmann *et al.*[10]

2-Methylpropan-1-ol (Unilab Laboratory Reagent) was dried over K_2CO_3 and fractionally distilled. The fraction boiling between 380 and 381°K was stored over molecular sieves and was redistilled immediately before use and handled under dry nitrogen. The dielectric constant values were calculated as for acetone using the data of Danforth[11] and Owen and Brinkley.[9] Density and viscosity data were obtained from Timmermans[7] and Bridgman.[8]

The atmospheric pressure values of the solvent properties and the parameters for the Owen–Brinkley equation for the dielectric constant are given in Table 1.

TABLE 1

SOLVENT PROPERTIES (1 bar)

A and B are the constants in the Owen–Brinkley equation $1-D_1/D_P = AD_1 \log\{(B+P)/(B+1)\}$

Solvent	Temp. (°K)	Mol. Vol. (l. mol^{-1})	Viscosity (cP)	Diel. Const. D	10^2A	B (bar)
Bu^iOH	298·1	0·0927	3·39	18·0	1·398	1148
	303·1	0·0932	2·88	17·3	1·457	1048
	308·1	0·0936	2·44	16·6	1·522	949
Acetone	293·1	0·0735	0·326	21·22	1·123	674
	303·1	0·0745	0·301	20·23	1·218	637
	313·1	0·0756	0·277	19·26	1·277	575

4-Methoxycarbonyl-*N*-methylpyridinium iodide was prepared by esterifying isonicotinic acid with methanol and quaternizing the ester with MeI.* The crude product was recrystallized from ethanol–benzene. NaI was recrystallized from conductance water and dried in vacuum.

Solutions were made up by weighing, using a microbalance where necessary. The high pressure conductivity apparatus has been described.[1] The conductivity of the solvents was negligible compared with that of the solutions.

RESULTS

The equivalent conductance at infinite dilution Λ^0, the activity coefficient f, and the degree of dissociation γ, were found by a parameter fit of equation (1) to conductances Λ measured at various concentrations, c. These ranged from 2×10^{-5} to 2×10^{-2} mol l.$^{-1}$ for mmpI and 1×10^{-4} to 2×10^{-2} for NaI.

$$\Lambda = \Lambda^0 - Sc_i^{\frac{1}{2}} + Ec_i \log c_i + J'c_i - K_A c_i f^2 \Lambda \quad (1)$$

Equation (1), a method of using it, and definitions of the parameters, are given by Fuoss and Accascina.[3] The parameters E and J' are functions of the ion size

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[7] Timmermans, J., "Physico-chemical Constants of Pure Organic Compounds." (Elsevier: New York 1950.)

[8] Bridgman, P. W., "The Physics of High Pressure." (Bell: London 1949.)

[9] Owen, B. B., and Brinkley, S. R., *Phys. Rev.*, 1943, **64**, 32.

[10] Hartmann, H., Neumann, A., and Rink, G., *Z. phys. Chem.*, N.F., 1965, **44**, 204.

[11] Danforth, W. E., *Phys. Rev.*, 1931, **38**, 1224.