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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 ($\mathrm{Bu^iOH}$) at 303·1°K at pressures up to 3 kbar. Similar measurements were made on solutions of sodium iodide in $\mathrm{Bu^iOH}$ 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 ($\mathrm{Bu^iOH}$) 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 $\mathrm{Bu^iOH}$ 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 ($\mathrm{Pr_4NI}$) in acetone. The measurements on sodium iodide in $\mathrm{Bu^iOH}$ 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 $\mathrm{MgSO_4}$. 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[1] Ewald, A. H., and Scudder, J. A., unpublished data.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.)

Aust. J. Chem., 1970, **23**, 1939–45

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.

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

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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* We thank Dr W. H. F. Sasse of the Division of Applied Chemistry, CSIRO, for preparing the compound for us.

[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.

parameter $\mathring{a}$, and an arbitrary but reasonable value (5 Å)[12] was assumed for this in the parameter fit. The molar association constant, K_γ, was then calculated from equation (2) and was found to be relatively insensitive to the choice of $\mathring{a}$.

$$K_\gamma = (1-\gamma)/\gamma^2 c f^2 \tag{2}$$

If $\mathring{a}$ was treated as an additional adjustable parameter the value of K_A in equation (1) was found to approach the value of K_γ after lengthy iteration.

Equation (2) was evaluated at each experimental concentration and the values of K_γ were found to have a spread of $\pm 10\%$; the average value is given in Table 2. The other rows in Table 2 give values of Λ^0, accurate to ± 2 in the last figure.

TABLE 2

CONDUCTANCE PARAMETERS

Λ^0 in cm^2 Ω^{-1} mol^{-1}, $K\gamma$ in l. mol^{-1}

Salt	T (°K)	Parameter	Value of Conductance Parameters for P (bar)				
			1	506	1013	2026	3040
			Acetone				
mmpI	293·1	Λ^0	198	162	124	90	68
		K_γ	596	487	242	162	133
	303·1	Λ^0	209	170	140		74
		K_γ	638	451	313		210
	313·1	Λ^0	262	215	168	127	93
		K_γ	1010	782	469	384	277
NaI	298·1	Λ^0	184[a]				
		K_A	170[a]				
			Bu^{i}OH				
mmpI	303·1	Λ^0	16·2	11·1	8·20	4·84	3·20
		K_γ	4795	3212	2670	2203	2402
NaI	298·1	Λ^0	11·8	8·50	6·20	3·62	2·30
		K_γ	858	599	440	281	219
	308·1	Λ^0	14·3	10·5	7·90	4·87	3·20
		K_γ	914	647	483	313	245

[a] Ref. 12.

Some measured conductances are plotted against $\sqrt{c}$ in Figure 1. The solid curves are drawn through values calculated from equation (1) and the straight lines give the Onsager tangents. The dashed interpolations follow the pattern of a type III phoreogram.[3] The conductances measured by Detoit and Duperthuis[13] and the Λ^0 values obtained from them by Walden[14] are higher than those found by extrapolating our values. Doubts about their reliability were already expressed by Walden.[15]

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[12] Janz, G. J., and Tait, M. J., *Can. J. Chem.*, 1967, **45**, 1101.

[13] Detoit, P., and Duperthuis, H., *J. Chim. phys.*, 1908, **6**, 726.

[14] Walden, P., in "Landolt–Börnsteins Tabellen", 5th Edn, Suppl. Vol. 1, p. 632. (Springer: Berlin 1961.)

[15] Walden, P., *Z. phys. Chem.*, 1911, **78**, 257.

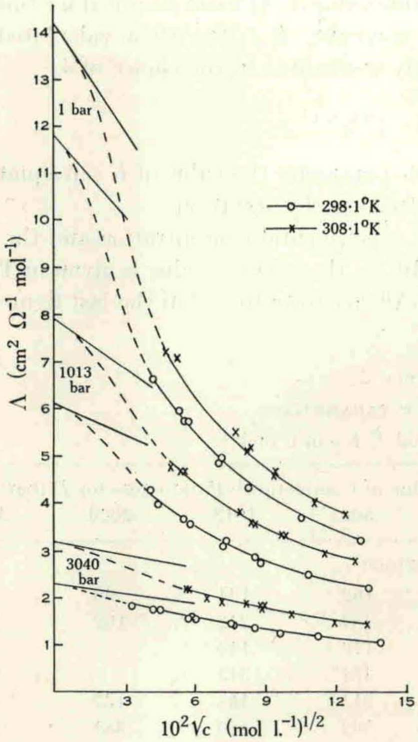

Fig. 1.—Conductance of NaI in Bu^{t}OH as a function of concentration at 1, 1013, and 3040 bar. The solid curves are calculated from equation (1).

Table 3

THERMODYNAMIC QUANTITIES FOR ION ASSOCIATION

ΔG and ΔH in kJ mol^{-1}; ΔS in J mol^{-1} K^{-1}; ΔV in cm^3 mol^{-1}

Quantity[a]	Thermodynamic Quantities at 303·1°K for P (bar) 1	506	1013	2026	3040
	mmpI in Acetone				
ΔG	−22·8	−22·1	−21·2	−20·8	−20·5
ΔH	+19	+16	+24	+32	+27
ΔS	+140	+130	+150	+170	+150
ΔV		+16	+16	+4	+3
	mmpI in Bu^{t}OH				
ΔG	−27·2	−26·6	−26·1	−25·7	−26·0
ΔV		+17	+8	+4	0
	NaI in Bu^{t}OH				
ΔG	−23·0	−22·3	−21·6	−20·6	−20·0
ΔH	+4·2	+5·0	+6·3	+7·1	+7·9
ΔS	88	+92	+92	+92	+92
ΔV		+17	+13	+10	+6

[a] Errors: ΔG $\pm0\cdot3$ kJ mol^{-1}; ΔH $\pm0\cdot6$ kJ mol^{-1}; ΔS $\pm3\cdot5\%$; ΔV ±1 cm^3 mol^{-1}.

The thermodynamic quantities for ion association at 303·1°K are given in Table 3. They were derived from the mole fraction equilibrium constant ${}^{x}K_{\gamma}$, which is related to the molar equilibrium constant through the molar volume V of the solution by ${}^{x}K_{\gamma} = K_{\gamma}/V$, found at various temperatures and pressures.

The limiting molar conductance of an ion can be expressed in terms of the transition state theory[4] by the equation:

$$\lambda_{\mathrm{i}}{}^{0} = (z e\boldsymbol{F}/6\boldsymbol{h})L^{2}\exp(-\Delta G^{\ddagger}/\boldsymbol{R}T) \tag{3}$$

in which L is the jump distance through which an ion moves when it passes through the transition state, and the other symbols have their usual significance. The equation can be used to calculate $\Delta G^{\ddagger}$ if one assumes[16] that $L = (V/\boldsymbol{N})^{1/3}$ (where V is the molar volume of the solvent and $\boldsymbol{N}$ is Avogadro's number), and uses experimental values of Λ^{0} in place of the unknown ionic conductance $\lambda_{\mathrm{i}}{}^{0}$.[4,5]

Differentiation of (3) with respect to temperature and pressure leads to equations (4) and (5)

$$\Delta H^{\ddagger} = \boldsymbol{R}T^{2}(\delta \ln \lambda_{\mathrm{i}}{}^{0}/\delta T)_{P} - \tfrac{2}{3}\boldsymbol{R}T^{2}\alpha \tag{4}$$

$$\Delta V^{\ddagger} = -\boldsymbol{R}T(\delta \ln \lambda_{\mathrm{i}}{}^{0}/\delta P)_{T} - \tfrac{2}{3}\boldsymbol{R}T\beta \tag{5}$$

in which α is the isobaric thermal expansivity and β the isothermal compressibility of the solvent. Values of the activation parameters evaluated from (3), (4), and (5) are given in Table 4.

TABLE 4

ACTIVATION PARAMETERS FOR CONDUCTANCE

$\Delta G\ddagger$ and $\Delta H\ddagger$ in kJ mol^{-1}; $\Delta S\ddagger$ in J mol^{-1} K^{-1}; $\Delta V\ddagger$ in cm^{3} mol^{-1}

Parameter	Activation Parameters at 303·1°K for P (bar)				
	1	506	1013	2026	3040
		mmpI in Acetone			
$\Delta G^{\ddagger}$	+9·37	+9·75	+10·3	+10·9	+11·6
$\Delta H^{\ddagger}$	+11·3	+13·0	+12·6	+12·1	+7·1
$\Delta S^{\ddagger}$	+6·7	+10·9	+7·9	+4·6	−14·6
$\Delta V^{\ddagger}$		+9·1	+8·4		+6·8
		mmpI in Bu$^{\mathrm{i}}$OH			
$\Delta G^{\ddagger}$	+16·4	+17·4	+18·1	+19·3	+20·3
$\Delta V^{\ddagger}$		17·7	14·3	12·4	9·8
		NaI in Bu$^{\mathrm{i}}$OH			
$\Delta G^{\ddagger}$	+16·8	+17·8	+18·5	+19·7	+20·7
$\Delta H^{\ddagger}$	+6·7	+7·9	+8·4	+10·9	+11·7
$\Delta S^{\ddagger}$	−33	−33	−33	−30	−29
$\Delta V^{\ddagger}$		+15·0	+13·5	+12·8	+10·3

The volume change, ΔV, accompanying the formation of ion pairs can be calculated from the values of ΔG given in Table 3. The values of ΔV given in Table 3

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[16] Brummer, S. B., *J. chem. Phys.*, 1965, **42**, 1636.

are estimated to be accurate to ±1 $cm^3\ mol^{-1}$. The increase in volume is due to the decrease in electrostriction of the solvent around the ions as these join to form ion pairs, and the effect rapidly decreases with rising pressure as the free solvent itself is compressed.

The decrease in K_γ with rising pressure means that the number of free ions in the solution increases, but Table 2 shows that the conductance of the solution decreases nonetheless. This is illustrated by Figure 2 in which the relative conductance, Λ_P/Λ_1, and for comparison, the relative fluidity of the solvent, η_1/η_P, are plotted as a function of pressure. The decrease in the relative conductance is smaller, and this shows that the increase in viscosity is partly compensated by the increase in the concentration of charge carrying ions. The degree of dissociation γ increases with pressure but at the lowest concentration (about 10^{-3} mol l.$^{-1}$) and highest pressure (3000 bar) it still only reaches 0·9 for NaI in Bu^{i}OH and 0·82 for mmpI in acetone.

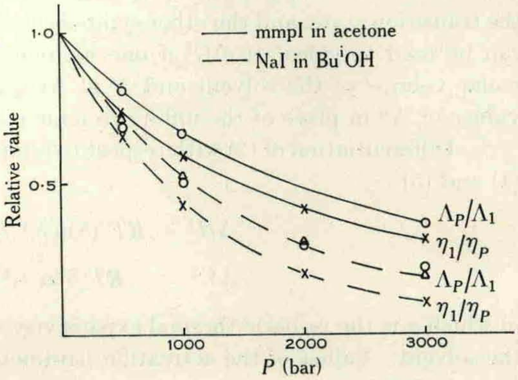

Fig. 2.—Relative conductance of solutions and relative fluidity of solvents as a function of pressure.

The decrease in relative conductance with pressure is more pronounced in Bu^{i}OH than in acetone and Figure 2 shows that this is due to a greater increase in the already large viscosity of Bu^{i}OH (see Table 1). The large viscosity also accounts for the low Λ^0 and large $\Delta G^\ddagger$ (Table 4) of mmpI in Bu^{i}OH.

Sodium iodide is less associated than mmpI in Bu^{i}OH but at the same time has a lower limiting conductance. This indicates that Na^+ has a lower mobility than mmp^+, presumably due to more extensive solvation of the smaller ion.

The conductances of some quaternary ammonium iodides in acetone were recently measured by Adams and Laidler[5] over a range of pressures and temperatures and were used to find limiting conductances, association constants K_A (equation (1)), and activation parameters (equations (3)–(5)). Their values for Pr_4NI are compared with our values for mmpI in Table 5 and show close agreement in Λ^0, ΔV, and $\Delta V^\ddagger$ in spite of the difference in association constant. Values of $\Delta H^\ddagger$, on the other hand, are different for the two electrolytes but show little pressure dependence.

Reynolds and Kraus[17] derived a value for the limiting ionic conductance of I^- in acetone at 298°K from measurements on $R_4N^+FBPh_3^-$ and RN^+I^- (R = n-butyl) and one can use this value to find the limiting conductance of the mmp$^+$ cation

[17] Reynolds, M. B., and Kraus, C. A., *J. Am. chem. Soc.*, 1958, **70**, 1709.

from Λ^0 values determined under the same conditions. From the limiting conductance one can in turn calculate Stokes radii for the ions. The $\lambda^0(\mathrm{I}^-)$ value was adjusted to 303°K by assuming the transport number to remain constant, and the limiting ionic conductances for mmpI in acetone at 303°K found by this method are $\lambda^0(\mathrm{mmp}^+) = 95 \cdot 7$ and $\lambda^0(\mathrm{I}^-) = 113 \cdot 9$ cm^2 Ω^{-1} mol^{-1}. The Stokes radii calculated from these are $2 \cdot 32 \times 10^{-10}$ m for I^- and $2 \cdot 84 \times 10^{-10}$ m for mmp^+. The Stokes radius of I^- is in good agreement with the value of Hughes and Hartley[18] and of Savedoff[19] and agrees with that of Adams and Laidler[5] when the latter is corrected for the difference in η_0 values.

TABLE 5

COMPARISON OF CONDUCTANCE AND ACTIVATION PARAMETERS OF Pr_4NI AND mmpI IN ACETONE

K in l. mol^{-1}; ΔV in cm^3 mol^{-1}; ΔH in kJ mol^{-1}

Parameter	Pr_4NI		mmpI	
	298·7°K	318·1°K	293·1°K	313·1°K
Λ^0 (1 bar)	190·6	224·4	199	262
Λ^0 (1 kbar)	119·6	142·5	124	168
K (1 bar)	156[a]	200[a]	596[b]	1010[b]
K (1 kbar)	94[a]	134[a]	242[b]	469[b]
ΔV (1–500 bar)	+15		+16	
$\Delta V^\ddagger$ (1–500 bar)	+9·3		+9·1	
$\Delta H^\ddagger$ (1 bar)	6·3		11·3	
$\Delta H^\ddagger$ (1 kbar)	6·3		12·6	

[a] From equation (1). [b] From equation (2).

ACKNOWLEDGMENT

We wish to thank Mr E. S. Merritt for assistance with the high pressure measurements.

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[18] Hughes, O. L., and Hartley, G. S., *Phil. Mag.*, 1933, **15**, 610.

[19] Savedoff, L. G., *J. Am. chem. Soc.*, 1966, **88**, 664.