v = linear crystal growth rate, m/s
$\bar{v}$ = mean overall linear growth rate, m/s
η = viscosity (N s/m^2) 1 cP = 10^{-3} N s/m^2
η_S = viscosity of saturated solution, N s/m^2
θ = temperature, °C
ρ_C = crystal density, kg/m^3
ρ_S = density of saturated solution, kg/m^3

Subscripts (100) and (001) refer to the (100) and (001) crystal axes, respectively.

Literature Cited

(1) Mullin, J. W., "Crystallization," 2nd ed. pp 174-207, Butterworths, London, 1972.
(2) Mullin, J. W., Amatavivadhana, A., *J. Appl. Chem. Lond.*, **17**, 151 (1967).
(3) Mullin, J. W., Chakraborty, M., Mehta, K., *J. Appl. Chem. Lond.*, **20**, 367 (1971).
(4) Mullin, J. W., Garside, J., *Trans. Inst. Chem. Engrs., Lond.*, **45**, 285 (1969).
(5) Mullin, J. W., Gaska, C., *Canad. J. Chem. Eng.*, **47**, 483 (1969).
(6) Mullin, J. W., Nienow, A. W., *J. Chem. Eng. Data*, **9**, 526 (1964).

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Conductivities and Densities of Aqueous Solutions of Quaternary Ammonium Iodides Containing Pentyl and Ethoxyethyl Groups

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The conductivities and densities of dilute aqueous solutions of the salts $R_3NR'I$ (R′ = pentyl or ethoxyethyl, R = Me or Et) have been measured at 25°C. Analysis of the molar conductivities with the Fuoss-Hsia and Pitts equations shows that all four salts form ion pairs and that the association constants of the ethoxyethyl compounds are lower than those of their pentyl analogs. The higher limiting molar ionic conductivities observed for the ethoxyethyl salts are correlated with their smaller volumes.

In a previous investigation *(10)* it was shown that the limiting molar conductivities of small quaternary ammonium iodides depend primarily on the size rather than the shape of the cation, and it was also shown that these salts form ion pairs to an extent which increases with increasing cation size. The purpose of the work reported here was to establish whether these relationships still hold when a methylene group in the cation is replaced by an ether oxygen.

Conductance measurements were made at 25°C on aqueous solutions of the iodides of pentyltrimethylammonium, ethoxyethyltrimethylammonium, pentyltriethylammonium, and ethoxyethyltriethylammonium cations, and their densities *(1)* were redetermined with a commercial density meter.

Experimental

The apparatus and procedure for the conductance measurements have been described *(10)*. The cell was rebuilt and had a cell constant of 0.48644 cm^{-1}, determined with potassium chloride solutions for which resistances were calculated using the equation of Lind et al. *(9)*. The solvent conductivity was allowed for. Temperature fluctuations in the oil thermostat bath did not exceed ±0.01°C.

Densities of solutions with concentrations in the range 0.02-0.2 mol kg^{-1} were measured with an Anton Parr DMA 02C density meter. The sample temperature was controlled to ±0.05°C with a Haake-type FE thermostat. The density meter was calibrated daily with at least three sodium chloride solutions with molalities in the range 0-0.9 mol kg^{-1}. The densities of these solutions were calculated from the equation,

$$d = 0.997046 + 0.0416600m - 0.0014972m^{3/2} - 0.0009876m^2 \quad (1)$$

which is based on densities calculated from the smoothed apparent molal volumes [The value of $\phi_v{}^\circ$ for m = 0.3 mol kg^{-1} is 17.62(1) cm^3 mol^{-1} *(18)*] for $m \le$ 0.9 mol kg^{-1} of Vaslow *(17)*. It represents these densities to within 1.4 × 10^{-6} g cm^{-3} and those of Millero *(12)* for $m \le$ 0.51 mol kg^{-1} to within 12 × 10^{-6} g cm^{-3}. All solutions were prepared with boiled distilled water, and vacuum corrections were applied to all weights. The procedure was tested with potassium chloride solutions and the apparent molal volume derived from these measurements was 26.8(2) ± 0.2 (standard error) cm^3 mol^{-1} which is in excellent agreement with the literature *(13)* values (26.8 − 26.9 cm^3 mol^{-1}).

The salts were prepared and purified as described previously *(1)* and were dried in vacuo at 100°C for at least 24 hr before use. All samples had analyses for iodide which showed that they were at least as pure as those used in earlier work *(1)*.

Results

The experimental errors in the density measurements arise from the uncertainty in the sample temperature (±0.05°C) and from the solution handling procedures. The maximum error in the values given in Table I is estimated to be 3 × 10^{-5} g cm^{-3}. The densities can be represented to within this experimental error by the empirical equation

$$d = d_0 + a_1m + a_2m^2 \quad (2)$$

in which d_0 is the density of pure water (0.997046 g cm^{-3}) and a_1 and a_2 have the values given in Table II. The molarities, c, calculated from the observed densities are related to the molalities, m, by the equation

$$c = m\,(d_0 + A_1m + A_2m^2) \quad (3)$$

in which A_1 and A_2 are empirical constants given in Table II. The apparent molal volumes ϕ_v calculated from the observed densities were fitted to the equation *(1, 2)*

$$\phi_v = \phi_v{}^\circ + S_vc^{1/2} + jc \quad (4)$$

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Table I. Densities at 25°C

Pent-NMe$_3$I		EtOCH$_2$CH$_2$NMe$_3$I	
$10^3\,m$/mol kg^{-1}	d/g, cm^{-3}	$10^3\,m$/mol kg^{-1}	d/g, cm$^{-3\,a}$
33.585	0.999300	57.507	1.001597 ± 1
61.279	1.001147	82.189	1.003527 ± 2
161.68	1.007667	109.09	1.005610 ± 2
		192.44	1.011938 ± 6

Pent-NEt$_3$I		EtOCH$_2$CH$_2$NEt$_3$I	
$10^3\,m$/mol kg^{-1}	d/g, cm$^{-3\,a}$	$10^3\,m$/mol kg^{-1}	d/g, cm$^{-3\,a}$
63.866	1.001243 ± 1	25.554	0.999057
134.77	1.005754 ± 3	49.127	1.000874 ± 4
143.65	1.006315 ± 4	73.344	1.002719 ± 7
215.67	1.010775 ± 6	97.810	1.004574 ± 15
		184.74	1.011023 ± 2

[a] Errors are in ppm and represent the deviation from the mean of duplicate measurements on different samples of the same solution.

Table II. Constants for Equations 2, 3, and 4[a]

Salt	$\phi_v^{\circ\,b}$	j^b	a_1	a_2	A_1	A_2
Pent-NMe$_3$I	189.66 ± 0.12	−3.8 ± 1.0	0.067550	−0.011397	−0.188787	0.035317
Pent-NEt$_3$I	232.91 ± 0.06	−4.1 ± 0.4	0.066515	−0.013537	−0.231585	0.051450
EtOCH$_2$CH$_2$NMe$_3$I	179.16 ± 0.04	−3.2 ± 0.3	0.079911	−0.013071	−0.178346	0.031073
EtOCH$_2$CH$_2$NEt$_3$I	222.68 ± 0.12	−3.2 ± 0.9	0.078776	−0.017414	−0.221412	0.046104

[a] The units of ϕ_v°, j, a_1, a_2, A_1, and A_2 are consistent with ϕ_v in cm^3 mol^{-1}, d in g cm^{-3}, c in mol dm^{-3}, and m in mol kg^{-1}. [b] Errors are standard errors; the maximum errors in ϕ_v° and j are estimated to be ±0.5 cm^3 and ±3 cm^3 dm^3 mol^{-2}, respectively.

in which ϕ_v° is the limiting apparent molal volume, S_v is a theoretical constant (= 1.868 cm^3 mol$^{-3/2}$ dm$^{3/2}$) *(16)* and j is an empirical constant. The values of ϕ_v° and j given with their standard errors in Table II were obtained by a least-squares procedure in which the points were weighted in proportion to their concentrations so as to allow for the dependence of errors in ϕ_v on the reciprocal of the concentration *(11)*. The maximum errors in the values of ϕ_v° and j are estimated to be ±0.5 cm^3 mol^{-1} and ±3.0 cm^3 dm^3 mol^{-2}, respectively. All of the ϕ_v° values agree with those obtained by pycnometry *(1)* to within experimental error.

The observed molar conductances Λ are given in Table III. The values were fitted to the equation,

$$\Lambda = \alpha[\Lambda^\infty - (B_1\Lambda^\infty + B_2)(c\alpha)^{1/2} + E(c\alpha)\ln(c\alpha) + J_1(c\alpha)^{1/2} - J_2(c\alpha)^{3/2}] \quad (5)$$

using expressions *(5, 6)* for J_1 and J_2 (which are functions of the ion size parameter a) based on the treatments of Pitts [P] *(14, 15)* and Fuoss and Hsia [F-H] *(7, 8)*. The degree of dissociation of the ion pairs, α, is related to their association constant, K_A, by the expression

$$K_A = (1 - \alpha)/c\alpha^2 y_\pm^2 \quad (6)$$

where $y_\pm$ is the molar activity coefficient given by the Debye-Hückel equation,

$$\log_{10} y_\pm = -A(c\alpha)^{1/2}/[1 + Ba(c\alpha)^{1/2}] \quad (7)$$

The best fit values of the molar conductivity at infinite dilution Λ^∞ and the association constant K_A were obtained for fixed values of a which were chosen on the basis of the ϕ_v° values so as to be consistent with those used in earlier work *(4, 11)*. The values obtained for Λ^∞ (Table IV) did not change by more than 0.01 ohm^{-1} cm^2 mol^{-1} when $10^{10}\,a/m$ was increased from 3 to 7 or when the F-H or the P versions of Equation 5 were used. The maximum uncertainty in the Λ^∞ values based on the errors from all identified sources is ±0.2 ohm^{-1} cm^2 mol^{-1}. The duplicate runs with pentyltriethylammonium iodide give Λ^∞ values which agree to well within this error limit. As expected *(3, 10)* the values obtained for K_A depend on that chosen for the ion size parameter, a. This is shown in Figure 1 for association constants calculated with the F-H equation. Those obtained with the P equation lie above those in Figure 1 at low a values and slightly below them for high a values. The P and F-H equations give identical K_A values when $10^{10}\,a \simeq 6m$. The error in the association constants given in Table IV other than that arising from the choice of conductance equation and ion size parameter is probably ±0.5 dm^3 mol^{-1}. Table IV also contains the standard deviations σ_Λ

Table III. Molar Conductivities at 25°C

Pent-NMe$_3$I		EtOCH$_2$CH$_2$NMe$_3$I	
$10^3\,c$/mol dm^{-3}	Λ/ohm^{-1} cm^2 mol^{-1}	$10^3\,c$/mol dm^{-3}	Λ/ohm^{-1} cm^2 mol^{-1}
0.5321	106.38	0.6567	107.25
1.1619	105.28	1.2518	106.35
1.8410	104.45	1.8497	105.60
2.4984	103.77	2.3690	105.06
3.2287	103.12	2.8944	104.61
3.8674	102.60	3.5314	104.09
4.9840	101.80	4.0710	103.70

Pent-NEt$_3$I (Run 1)		EtOCH$_2$CH$_2$NEt$_3$I	
$10^3\,c$/mol dm^{-3}	Λ/ohm^{-1} cm^2 mol^{-1}	$10^3\,c$/mol dm^{-3}	Λ/ohm^{-1} cm^2 mol^{-1}
0.2714	101.69	0.6967	101.55
0.5122	101.12	0.9909	101.05
0.7535	100.68	1.3033	100.64
0.9755	100.34	1.5993	100.29
1.1739	100.03	1.8708	99.99
1.4122	99.75		
1.6253	99.50		

Pent-NEt$_3$I (Run 2)

$10^3\,c$/mol dm^{-3}	Λ/ohm^{-1} cm^2 mol^{-1}
0.3531	101.63
0.7314	100.88
1.1168	100.27
1.5002	99.75
1.8506	99.34
2.1886	99.00
2.4367	98.72

Table IV. Parameters Derived from Molar Conductivities

Salt	10^{10} a/m	Λ^{∞}/ohm^{-1} cm^2 mol^{-1}	K_A/dm^3 mol^{-1}		10^2 σ_Λ/ ohm^{-1} cm^2 mol^{-1}
			F-H	P	
Pent-NMe_3I	5.64	108.4_1	3.3_5	3.3_6	2.4
Pent-NEt_3I (Run 1)	5.99	103.1_2	3.5_3	3.5_8	1.1
Pent-NEt_3I (Run 2)	5.99	103.2_9	3.9_2	3.9_5	1.0
$EtOCH_2CH_2NMe_3I$	5.55	109.5_1	2.8_4	2.8_7	2.8
$EtOCH_2CH_2NEt_3I$	5.91	103.8_6	3.2_3	3.2_7	1.9

Table V. Limiting Ionic Molar Conductivities and Apparent Molal Volumes

Salt	λ_+^{∞}/ohm^{-1} cm^2 mol^{-1} [a]	ϕ_+°/cm^3 mol^{-1} [b]	q[c]
Pent-NMe_3I	31.4	147.5	877.4
Pent-NEt_3I	26.2	190.7	868.7
$EtOCH_2CH_2NMe_3I$	32.5	137.0	864.5
$EtOCH_2CH_2NEt_3I$	26.9	180.5	858.5

[a] Limiting molar ionic conductivity based on $\lambda^{\circ}(I^-) = 76.98$ ohm^{-1} cm^2 mol^{-1}. [b] Limiting ionic partial molal volume based on $\phi_-^{\circ}(I^-) = 42.2$ cm^3 mol^{-1}. [c] $q = \lambda_+^{\infty}(\phi_+^{\circ})^{2/3}$; mean value = 867.3 ± 7.9.

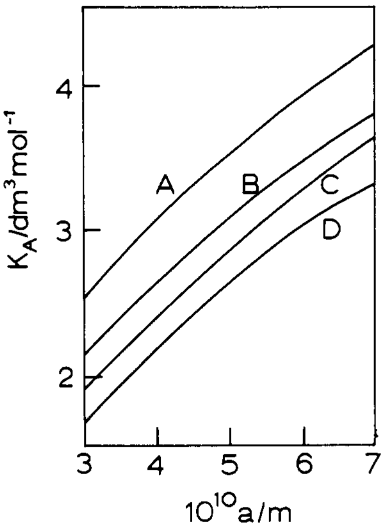

Figure 1. Association constants obtained with Fuoss-Hsia conductance equation for different values of the ion size parameter a

A, Pent-NEt_3I (Run 2); *B*, Pent-NMe_3I; *C*, $EtOCH_2CH_2NEt_3I$; *D*, $EtOCH_2CH_2NMe_3I$

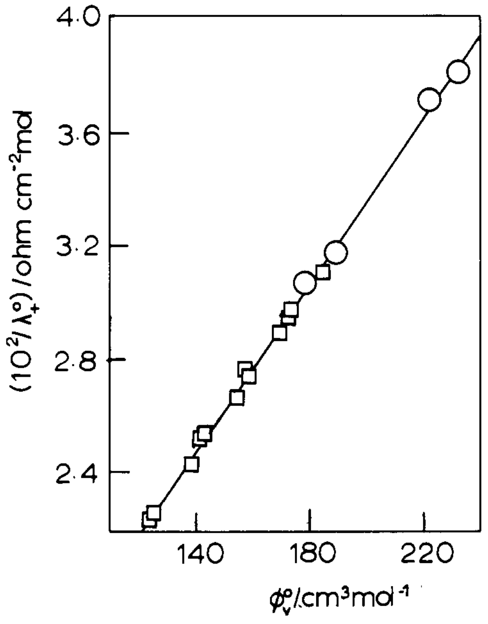

Figure 2. Reciprocal of the ionic conductivity plotted against the apparent molal volume of the iodide

□, results (*10, 11*) for small straight chain and cyclic quaternary ammonium iodides; ○, this work

based on the observed Λ and that calculated with the best fit values of Λ^{∞} and K_A. The differences between σ_Λ values obtained with the F-H and P equations and with ion size parameters between $3 \times 10^{-10} - 7 \times 10^{-10}$ m were always less than 0.01 ohm^{-1} cm^2 mol^{-1} and could not be used to choose between the equations or the a-parameters.

Discussion

The replacement of —CH_2— by —O— leads to an increase in Λ^{∞} and it is clear from Figure 2 in which the limiting ionic resistivity $1/\lambda_+^{\infty}$ is plotted against ϕ_v° that a substantial part of this increase arises from the decrease in cation volume. This is also borne out by the values obtained for $q[= \lambda_+^{\infty}(\phi_+^{\circ})^{2/3}]$ given in Table V, which are all within experimental error of the value 868.4 ± 10.1 (standard deviation) obtained for cyclic and straight chain cations with sizes between those of Me_4N^+ and Et_4N^+ (*10*).

The association constants obtained for the two ethoxyethyl compounds are both lower than those of their pentyl analogs by 0.50 dm^3 mol^{-1}. This decrease in K_A although only just significant is larger than would be expected simply from the change in cation size (about 0.1 dm^3 mol^{-1}) and probably reflects a difference in the solute-solvent interactions of the pentyl and ethoxyethyl groups. The decrease (about 0.40 dm^3 mol^{-1}) in K_A consequent on the replacement of —NEt_3 by —NMe_3 is the same for both pentyl and ethoxyethyl compounds.

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Nomenclature

A = theoretical constant in Equation 6
A_1, A_2 = empirical constants in Equation 3
a = ion size parameter
a_1, a_2 = empirical constants in Equation 4
B = theoretical constant in Equation 6
B_1, B_2 = theoretical constant in Equation 5
c = molarity, mol dm^{-3}
d = density, g cm^{-3}
E = theoretical constant in Equation 5
J_1, J_2 = ion size dependent constants in Equation 5
j = empirical constant in Equation 4

K_A = association constant, $dm^3\ mol^{-1}$
m = molality, $mol\ kg^{-1}$
S_v = theoretical constant in Equation 4
$y_\pm$ = molar activity coefficient
α = degree of dissociation
Λ = molar conductivity, $ohm^{-1}\ cm^2\ mol^{-1}$
ϕ_v = apparent molal volume
σ_Λ = standard deviation between observed and calculated values of Λ

Literature Cited

(1) Barlow, R. B., Lowe, B. M., Pearson, J. D. M., Rendall, H. M., Thompson, G. M., *Molec. Pharmacol.*, **7**, 357, (1971).
(2) Conway, B. E., Verall, R. E., Desnoyers, J. E., *Trans. Faraday Soc.*, **62**, 2738 (1966).
(3) Duer, W. C., Robinson, R. A., Bates, R. G., *J. Chem. Soc. Faraday I*, **68**, 716, (1972).
(4) Fernandez-Prini, R., *Trans. Faraday Soc.*, **64**, 2146 (1968).
(5) Fernandez-Prini, R., *ibid.*, **65**, 3311, (1969).
(6) Fernandez-Prini, R., Prue, J. E., *Z. Phys. Chem* (Leipzig), **228**, 373, (1965).
(7) Fuoss, R. M., Hsia, K.-L., *Proc. Nat. Acad. Sci.*, **59**, 1550 (1967).
(8) Hsia, K.-L., Fuoss, R. M., *J. Amer. Chem. Soc.*, **90**, 3055, (1968).
(9) Lind, J. E., Zwolenik, J. J. Fuoss, R. M., *ibid.*, **65**, 1242, (1961).
(10) Lowe, B. M., Rendall, H. M., *J. Chem. Soc. Faraday I*, **68**, 2191, (1972).
(11) Lowe, B. M., Rendall, H. M., *Trans. Faraday Soc.*, **67**, 2318, (1971).
(12) Millero, F. J., *J. Phys. Chem.* **74**, 356 (1970).
(13) Millero, F. J., in "Water and Aqueous Solutions," Ed., R. A. Horne, P. 576, Wiley, New York, N.Y., 1972.
(14) Pitts, E., *Proc. Roy. Soc. A.*, **217**, 43, 1953.
(15) Pitts, E., Tabor, B. E., Daly, J., *Trans Faraday Soc.*, **65**, 849 (1969).
(16) Redlich, O., Meyer, D. M., *Chem. Rev.*, **64**, 221 (1964).
(17) Vaslow, F., *J. Phys. Chem.*, **70**, 2286 (1966).
(18) Vaslow, F., Oak Ridge National Research Laboratory, Oak Ridge, Tenn., private communication, 1972.

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Isothermal Vapor-Liquid Equilibrium Data for System Heptane–2-Pentanone at 90°C

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Isothermal equilibrium vapor and liquid composition measurements have been made for the heptane–2-pentanone system at 90.0°C, using equilibrium samples produced with the aid of a vapor-recirculation equilibrium still. Vaporization equilibrium constants (*K* values) and activity coefficients were calculated from the equilibrium compositions, and the thermodynamic consistency was checked by two methods.

Isothermal vapor–liquid equilibrium data at low pressures are useful for studying the thermodynamics of nonideal solutions and desirable for establishing the vaporization equilibrium constants (*K*-values) used for the design of equilibrium stage processes.

A survey of the literature indicates that no such isothermal data have been published for the system heptane–2-pentanone. Because of this, the equilibrium compositions reported here were determined.

Experimental

A detailed description of the experimental equipment, procedures, and methods has been given by Lodl and Scheller (*5*) and by Scheller et al. (*10*).

Briefly, a modification of the vapor-recirculation equilibrium still described by Hipkin and Myers (*3*) was used. Pressure in the still was controlled by a Cartesian manostat of the type described by Gilmont (*2*) and measured with a mercury manometer to ±0.1 mm.

Temperature was measured with an iron-constantan thermocouple to ±0.1°C, using a Model 320 Data Technology Corp. digital voltmeter which could be read to the nearest microvolt. The thermocouple was calibrated at the solid-state transition point of sodium sulfate decahydrate (32.384°C) and also against the boiling point of water. Distilled water was placed in the equilibrium still, the pressure was adjusted to the desired value with the aid of the Cartesian manostat, and the system was allowed to operate until a constant millivolt reading was obtained on the potentiometer. The temperature was determined from the measured pressure and the steam tables. Twenty-three experimental points between 85.6 and 690.3 mm of Hg (48.44° and 97.33°C) were used in the calibration. A linear equation of temperature as a function of voltage was fitted to these 23 points by the method of least squares. The absolute average deviation between the experimental and calculated temperatures is 0.13°C. Spot checks of the calibration were made using pure benzene, acetone, and toluene.

Compositions of equilibrium samples were obtained with the aid of a Perkin-Elmer 880 gas chromatograph with a hot-wire detector, a 194B printing integrator, an L&N Speedomax G strip chart recorder, and a stationary phase of diisodecyl phthalate on 80/90 mesh ABS Anakrom packed in a stainless steel tube ⅛ in. by 10 ft. long. Helium was used as the elution gas. The chromatograph was calibrated with 12 mixtures of heptane–2-pentanone of known composition by relating the area fraction of the heptane peak to the mole fraction of heptane. The overall precision of the composition analyses was 0.2 mol %.

The heptane and 2-pentanone were obtained from Phillips Petroleum Co. and Eastman Kodak Co., respectively. Because chromatographic analysis indicated small secondary peaks, the reagents were distilled at high reflux in a glass distillation column about 5 ft 6 in. high. A heart cut representing approximately the center 40% of each reagent was collected and displayed no secondary peaks on the chromatograph. Densities, refractive indexes, and normal boiling points were measured and are compared with literature values in Table I.

Discussion of Results

Table II contains the experimental *x, y, P* equilibrium data obtained at 90.0°C. The vaporization equilibrium constants ($k = y/x$) and activity coefficients were calculated and are also tabulated in Table II. The liquid phase

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