939. *The Ionic Dissociation of Methyltriethylammonium Iodide in Methylene Dichloride between* 0 *and* −95°.

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The electrical conductivities of solutions of methyltriethylammonium iodide in methylene dichloride between 0 and −95° were measured in a vacuum apparatus over the concentration range 0·26—4·5 × 10^{-4} mole/l. Evaluation of the results by Shedlovsky's method gave Λ_0 and the equilibrium constant K, and hence $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the dissociation of ion-pairs to free ions. The results are only compatible with the Fuoss equation if the interionic distance in the ion pairs is assumed to increase with falling temperature. The same conclusion follows from an examination of the results obtained by other workers with similar systems, and is explicable in terms of changes in the degree of solvation of the ions. The bearing of our results on Gilkerson's theory is discussed.

IN cationic polymerisations the propagating species is known to be an organic cation, but for most systems it is not known whether the free cations, or those associated with an anion in an ion-pair, or both, take part in the reaction. Since in this laboratory much work on the polymerisations of isobutene [1] and styrene [2] has been done with the solvent methylene dichloride between +20 and −95°, we required information on how, in this solvent, the dissociation constant of an ion-pair varies with temperature. As a model compound we chose methyltriethylammonium iodide, and studied the conductivity of its solutions in methylene dichloride.

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[1] Biddulph, Plesch, and Rutherford, International Symposium on Macromolecules, Wiesbaden, **1959**, paper III A 10; Beard, Plesch, and Rutherford, *J.*, 1964, 2566; Biddulph, Plesch, and Rutherford, *J.*, in the press.

[2] Longworth and Plesch, International Symposium on Macromolecules, Wiesbaden, **1959**, paper III A 11; Longworth, Panton, and Plesch, in the press.

EXPERIMENTAL

Materials.—Methylene dichloride,[3] methyl iodide,[4] and triethylamine [4] were purified as described and had the physical constants quoted. Methyltriethylammonium iodide was prepared from the purified reactants in three purified solvents: methylene dichloride, absolute ethanol, and benzene. The salt was recovered from the solvent, and dried over calcium chloride in an evacuated desiccator for a week. The three specimens gave identical conductivity results.

Apparatus and Procedure.—At first, conductivity measurements were made on solutions exposed to the atmosphere, but because the methylene dichloride attained a conductivity which was sufficiently high to interfere with the results, and the reproducibility of these was unsatisfactory, a vacuum technique, similar to that described,[3] was adopted. The methylene dichloride reservoir, the burette, the conductivity cell, and the main vacuum line were separated by all-metal valves.[5]

The conductivity cell, constructed from a 250 ml. Pyrex conical flask, was fitted with bright platinum electrodes, 2 × 2 cm., which were fixed firmly 2 mm. apart by fusing lead-glass beads to their edges. The cell constant did not vary with the volume of the solution, provided that this exceeded 15 ml., and was found by calibration with 0·01D-potassium chloride to be 0·0340.

A sample of the salt (*ca.* $1{\cdot}5 \times 10^{-3}$ g.) was weighed to $\pm 5 \times 10^{-6}$ g., and placed in the cell, which was then attached to the vacuum line and thoroughly evacuated. We avoided testing of the vacuum by Tesla discharge before most of the air had been pumped from the system, because premature testing caused the white salt to become coloured, presumably by oxidation of the iodide by ozone. The method of metering the methylene dichloride into the cell was similar to that described.[3] The methylene dichloride was distilled from a burette (kept in melting ice) into the cell cooled with a mush of ethanol and solid carbon dioxide. The volume of each addition was measured with an accuracy of about 0·5%.

Since the solutions were very dilute, we assumed that they had the same density, viscosity, and dielectric constant as the pure solvent. The concentrations of the solutions were calculated in mole/l. at 0°, and corrections for volume change with temperature were made by means of Morgan and Lowry's [6] values of the density of methylene dichloride. Correction for the solvent present as vapour above the liquid was only required at 0°, and even then only when the total volume of solution was less than about 30 ml. The lowest concentration of solution that could be used in our system was determined by the accuracy of the weighings and by the volume of the cell, and was 10^{-5} mole/l. Different volumes of solutions of the same concentration gave identical conductivities, showing that adsorption or ion-exchange effects of the glass surface were negligible.

The thermostatting substances, used as "mushes," were water–ice, 0°; carbon tetrachloride, −24·2°; chlorobenzene, −47·7°; chloroform, −68·0°; industrial ethanol–solid carbon dioxide, −77·2°; methylene dichloride, −94·7°. The mushes were stirred manually, but the cell contents were stirred magnetically. The temperature of the cell contents was measured to ±0·1° by a thermocouple.

Resistance measurements were made by the method described,[7] which permitted the capacity and resistance to be balanced separately. The smallest measurable specific conductivity was 10^{-9} mho/cm. The resistance of each solution, under vacuum conditions, was taken at the six temperatures.

Errors.—For the Shedlovsky graphical extrapolation method [8] the values of the dielectric constant (D.C.), ε, and the viscosity, η, of the solvents are required over the whole temperature range. Morgan and Lowry's [6] values of ε were used, and η was calculated from an equation given by Weissberger.[9] This is adequate since in the construction of a Shedlovsky plot a large

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[3] Longworth, Plesch, and Rigbi, *J.*, 1958, 451.

[4] Beard and Plesch, *J.*, 1964, 3682.

[5] Biddulph and Plesch, *Chem. and Ind.*, 1956, 569.

[6] Morgan and Lowry, *J. Phys. Chem.*, 1930, **34**, 2413.

[7] Longworth and Plesch, *J.*, 1959, 1887.

[8] (*a*) Shedlovsky, *J. Franklin Inst.*, 1938, **225**, 739; (*b*) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 2nd edn., 1950, p. 128.

[9] Weissberger, "Techniques of Organic Chemistry, Vol. VII, Organic Solvents," Interscience, London, 1955, p. 25, eqn. (28).

TABLE 1.

Specific conductivity, κ, (mho-cm.$^{-1}$) of methyltriethylammonium iodide in methylene dichloride between 0° and −95° (molar concns.).

Temp. 0°

(*a*)	10^4c	4·55	2·93	2·14	1·52	1·126	0·876	0·653	0·512	0·407
	$10^6\kappa$	7·79	6·03	5·02	4·09	3·42	2·93	2·45	2·07	1·80
	$y_\pm$	0·7761	0·8009	0·8172	0·8337	0·8470	0·8578	0·8696	0·8794	0·8874
(*b*)	10^4c	3·80	2·39	1·64	1·173	0·866	0·681	0·507	0·386	
	$10^6\kappa$	7·11	5·37	4·30	3·50	2·91	2·50	2·07	1·73	
	$y_\pm$	0·7852	0·8112	0·8299	0·8455	0·8584	0·8682	0·8794	0·8896	
(*c*)	10^4c	2·73	1·049	0·611	0·427	0·325	0·261			
	$10^6\kappa$	5·75	3·27	2·38	1·85	1·58	1·30			
	$y_\pm$	0·8060	0·8511	0·8722	0·8867	0·8952	0·9042			
(*d*)	10^4c	2·80	1·77	1·119	0·797	0·542	0·420	0·330	0·268	
	$10^6\kappa$	5·82	4·44	3·34	2·73	2·14	1·81	1·53	1·33	
	$y_\pm$	0·8054	0·8283	0·8498	0·8636	0·8786	0·8878	0·8964	0·9031	

Temp. −24·2°

(*a*)	10^4c	4·65	3·00	2·20	1·56	1·161	0·904	0·674	0·528	0·420
	$10^6\kappa$	6·78	5·24	4·41	3·57	3·00	2·57	2·11	1·80	1·56
	$y_\pm$	0·7688	0·7943	0·8100	0·8277	0·8412	0·8525	0·8656	0·8752	0·8835
(*b*)	10^4c	3·89	2·45	1·69	1·21	0·893	0·703	0·523	0·398	
	$10^6\kappa$	6·15	4·66	3·75	3·06	2·53	2·17	1·80	1·50	
	$y_\pm$	0·7787	0·8044	0·8237	0·8399	0·8535	0·8636	0·8754	0·8855	

Temp. −47·7°

(*a*)	10^4c	4·79	3·10	2·26	1·61	1·20	0·931	0·694	0·544
	$10^6\kappa$	5·43	4·21	3·59	2·91	2·41	2·09	1·69	1·46
	$y_\pm$	0·7620	0·7876	0·8025	0·8209	0·8359	0·8466	0·8612	0·8706
(*b*)	10^4c	4·01	2·52	1·74	1·24	0·920	0·724	0·539	0·410
	$10^6\kappa$	4·94	3·76	3·04	2·48	2·05	1·75	1·43	1·20
	$y_\pm$	0·7716	0·7983	0·8171	0·8337	0·8481	0·8388	0·8719	0·8823

Temp. −68°

(*a*)	10^4c	4·91	3·17	2·32	1·65	1·23	0·954	0·711	0·557	0·444
	$10^6\kappa$	4·07	3·16	2·65	2·18	1·81	1·53	1·25	1·061	0·906
	$y_\pm$	0·7534	0·7802	0·7971	0·8147	0·8301	0·8428	0·8572	0·8680	0·8774
(*b*)	10^4c	4·11	2·59	1·78	1·27	0·943	0·742	0·552	0·420	
	$10^6\kappa$	3·72	2·82	2·27	1·85	1·53	1·30	1·075	0·885	
	$y_\pm$	0·7635	0·7914	0·8112	0·8285	0·8431	0·8547	0·8672	0·8788	

Temp. −77·2°

(*a*)	10^4c	4·96	3·21	2·35	1·67	1·24	0·964	0·719	0·563	0·488
	$10^6\kappa$	3·40	2·59	2·22	1·84	1·54	1·29	1·07	0·865	0·750
	$y_\pm$	0·7570	0·7854	0·8002	(i)	(ii)	(iii)	(iv)	0·8714	(v)
(*b*)	10^4c	4·15	2·62	1·80	1·29	0·953	0·750	0·558	0·425	0·342
	$10^6\kappa$	2·90	2·36	1·83	1·54	1·29	1·08	0·898	0·752	0·647
	$y_\pm$	0·7741	0·7941	(i)	(ii)	(iii)	(iv)	0·8692	(v)	0·8882

Some of the experimental points at this temperature coincide within experimental error, and their average values were used to obtain the $y_\pm$ values.

	(i)	(ii)	(iii)	(iv)	(v)
10^4c	1·73	1·26	0·959	0·735	0·437
$10^6\kappa$	1·835	1·54	1·29	1·075	0·751
$y_\pm$	0·8170	0·8312	0·8445	0·8574	0·8789

Temp. −94·7°

(*a*)	10^4c	5·07	3·27	2·40	1·70	1·27	0·985	0·734	0·575	0·458
	$10^6\kappa$	1·92	1·53	1·29	1·14	0·928	0·783	0·667	0·522	0·467
	$y_\pm$	0·7513	(i)	(ii)	0·808	(iii)	(iv)	0·852	(vi)	0·8714
(*b*)	10^4c	4·24	2·67	1·84	1·32	0·973	0·767	0·567	0·434	0·349
	$10^6\kappa$	1·68	1·36	1·14	0·933	0·747	0·651	0·530	0·428	0·377
	$y_\pm$	0·761	0·785	0·8044	(iii)	(iv)	(v)	(vi)	0·8766	0·8839
(*c*)	10^4c	5·21	3·30	2·39	1·73	1·27	0·756	0·585		
	$10^6\kappa$	1·93	1·57	1·33	1·05	0·859	0·651	0·534		
	$y_\pm$	0·7509	(i)	(ii)	0·808	(iii)	(v)	(vi)		

As at −77·2°, average values were used to obtain some of the $y_\pm$ values.

	(i)	(ii)	(iii)	(iv)	(v)	(vi)
10^4c	3·28	2·39	1·29	0·979	0·761	0·576
$10^6\kappa$	1·55	1·31	0·930	0·765	0·651	0·529
$y_\pm$	0·7745	0·7912	0·8219	0·8370	0·8494	0·8636

error in η produces only a negligible error in the parameters obtained from the final plot. The slope and intercept of the Shedlovsky plots were calculated by the method of least squares.

The reproducibility of the values of the dissociation constant was $\pm 2\%$, and was determined by that of the limiting equivalent conductivity, Λ_0, as this was obtained by a rather long extrapolation.

RESULTS

Solvent.—Our methylene dichloride had a specific conductivity of 3×10^{-9} mho/cm. under vacuum conditions; $1{\cdot}5 \times 10^{-8}$ mho/cm. when freshly distilled at atmospheric pressure from calcium hydride; and as high as $3{\cdot}5 \times 10^{-6}$ mho/cm. when left exposed to the atmosphere.

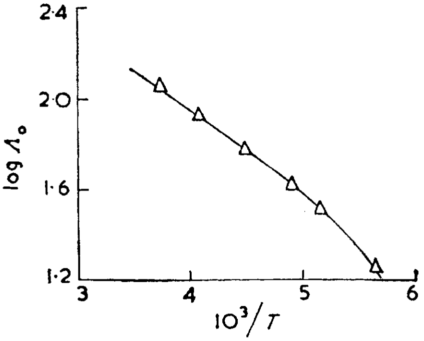

FIG. 1. The variation of log Λ_0 with temperature.

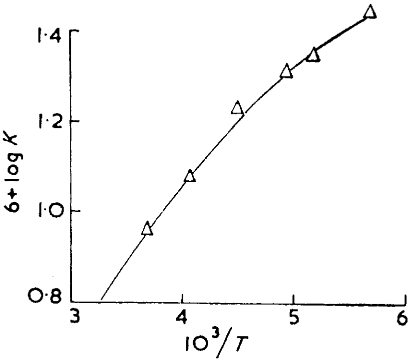

FIG. 2. The variation of log K with temperature.

Solutions.—The series of conductivity measurements are listed in Table 1, which also shows the mean ionic activity coefficients $y_{\pm}$ calculated in the course of constructing the Shedlovsky plots. Under vacuum conditions the conductivity of individual solutions remained constant for more than 48 hr.

The values of the slope, S, the limiting equivalent conductivity, Λ_0, and the dissociation constant, K, derived by Shedlovsky's method [8] are shown in Table 2. The plot of log Λ_0 against $1/T$ is shown in Fig. 1; the corresponding activation energy is found to be $E_{\Lambda} = 1{\cdot}63$ kcal./mole between 0 and $-65°$.

Fig. 2 shows the plot of log K against $1/T$. The values of the standard free energy, $\Delta G°$, enthalpy, $\Delta H°$ and entropy, $\Delta S°$, of dissociation of methyltriethylammonium iodide in methylene dichloride were calculated from the smoothed values of K obtained from Fig. 2, and are in Table 2.

TABLE 2.

Quantities derived from the Shedlovsky plots.

Temp.	ε	Slope, S, of Shedl. plot	Λ_0 (mho cm.^{2})	10^5K (mole l.$^{-1}$)	a (Å)	$\Delta G°$ (kcal. mole^{-1})	$-\Delta H°$	$-\Delta S°$ (e.u.)
0·0°	10·02	8·87	111·8	0·902	4·72	6·30	1·89	30·0
−24·2	11·23	11·4	85·5	1·20	4·74	5·59	1·50	28·5
−47·7	12·62	16·9	59·4	1·68	4·77	4·94	1·17	27·1
−68·0	14·08	30·2	40·5	2·03	4·79	4·40	0·97	26·2
−77·2	14·81	42·0	32·8	2·21	4·81	4·16	0·81	25·4
−94·7	16·44	111·8	18·0	2·76	4·84	3·73		

The plot of $\Delta G°$ against T is very slightly curved convex to the T-axis. $\Delta S°$ at each experimental temperature was obtained from the average of the slopes of the lines joining the corresponding point to its two nearest neighbours. The plot of $\Delta S°$ against temperature is linear. Values of $\Delta H°$ were obtained from the curve in Fig. 2 by the method used for $\Delta S°$, and also from the $\Delta G°$ and $\Delta S°$ values, and in no case did the difference between the values of $\Delta H°$ obtained by the two methods differ by more than 2%. The plot of $\Delta H°$ against T is linear.

DISCUSSION

The Equilibrium Constant.—The values of log K increase linearly with the product εT as the temperature falls, according to the following equation:

$$\log K = (2{\cdot}462 \times 10^{-3} \times \varepsilon T) - 11{\cdot}79 \qquad (1)$$

(least squares method; standard deviation 0·012). For the subsequent computations we prefer to use this empirical equation rather than the theoretically founded correlation between log K and $1/\varepsilon T$ [see eqn. (10)] since eqn. (1) represents our results with the same degree of accuracy, and is much more convenient to handle. Our examination of Morgan and Lowry's results [6] showed that the variation of ε with T is given more accurately by eqn. (2) than by the equation in the literature.[10] The validity of this equation is supported

$$\varepsilon = (3304/T) - 2{\cdot}07 \qquad (2)$$

by the fact that eqn. (3), obtained by combining equations (1) and (2), agrees closely with eqn. (4) obtained from our results (least-squares method).

$$-\log K = 3{\cdot}66 + 5{\cdot}10 \times 10^{-3}T \qquad (3)$$

$$-\log K = 3{\cdot}648 + 5{\cdot}098 \times 10^{-3}T \qquad (4)$$

The Thermodynamic Quantities.—The results in Table 2 show that ΔH° and ΔS° vary considerably over the temperature range used by us. Denison and Ramsey,[11] working between 20 and 35°, and Stern and Martell,[12] between 5·7 and 35°, reported for closely similar systems that over these relatively small temperature ranges no change in ΔH° and ΔS° was detectable.

The negative sign of ΔS° indicates that the solvation of the free ions must involve more solvent molecules than that of the ion-pairs, and the negative sign of ΔH° is consistent with this interpretation.

The Interionic Distance.—Fuoss [13] has derived the equation

$$-\ln K = \ln(4\pi \mathbf{N}a^3/3000) + \mathbf{e}^2/a\varepsilon\mathbf{k}T \qquad (5)$$

where a is the interionic distance in the ion pairs. With a in cm., this takes the form

$$\log K = -3\log a - 21{\cdot}4019 - 7{\cdot}2557 \times 10^{-4}/\varepsilon Ta \qquad (6)$$

Inami, Bodenseh, and Ramsey [14] have derived equation (7)

$$-\ln K = -\ln K^\circ + \mathbf{e}^2/a\varepsilon\mathbf{k}T \qquad (7)$$

from premises which differ from Fuoss's. Their K° represents the hypothetical dissociation constant of "uncharged ions," *i.e.*, it is determined by the non-electrostatic interaction between the components of the solute. Equations (5) and (7) are applicable, strictly, only to salts consisting of symmetrical ions in which the stability of the associated ion pair is determined predominantly by charge–charge interaction; this condition is fulfilled in our system.

If a is constant, equations (5) and (7) both reduce to the form

$$-\log K = A + B/a\varepsilon T \qquad (8)$$

where A and B are constants, and the slope of the plot of log K against $1/\varepsilon T$ is $-B/a$. However, if a did vary with εT, the slope of the plot would be

$$-\frac{d\log K}{d(1/\varepsilon T)} = \frac{dA}{d(1/\varepsilon T)} + B\left(\frac{1}{a} + \frac{1}{\varepsilon T}\frac{d(1/a)}{d(1/\varepsilon T)}\right) \qquad (9)$$

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[10] National Bureau of Standards, Circular 514, 1951.
[11] Denison and Ramsey, *J. Amer. Chem. Soc.*, 1955, **77**, 2615.
[12] Stern and Martell, *J. Amer. Chem. Soc.*, 1955, **77**, 1983.
[13] Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 5059.
[14] Inami, Bodenseh, and Ramsey, *J. Amer. Chem. Soc.*, 1961, **83**, 4745.

The principal point of interest is whether our results, and possibly those obtained by others, can show whether a varies with T; this question, and the significance of a, have been reviewed by Stern and Amis.[15]

Extensive investigations (most of the important ones are quoted by Inami, Bodenseh, and Ramsey[14]) have shown that at constant temperature, for a given salt, log K varies linearly with $1/\varepsilon$, and this led to the conclusion [from eqn. (7)] that a is independent of ε. Since these experiments were done with mixed solvents or a series of different solvents, the same conclusion should hold, *a fortiori*, for a single solvent. For this reason any variation of a with εT which may emerge must be attributed to the effect of changing temperature rather than of the change in ε which accompanies this. We start by considering the plot of log K against $1/\varepsilon T$ for our results which is shown in Fig. 3. It has a slight curvature, but can be represented by the linear equation (10) (least squares method; standard deviation 0·013).

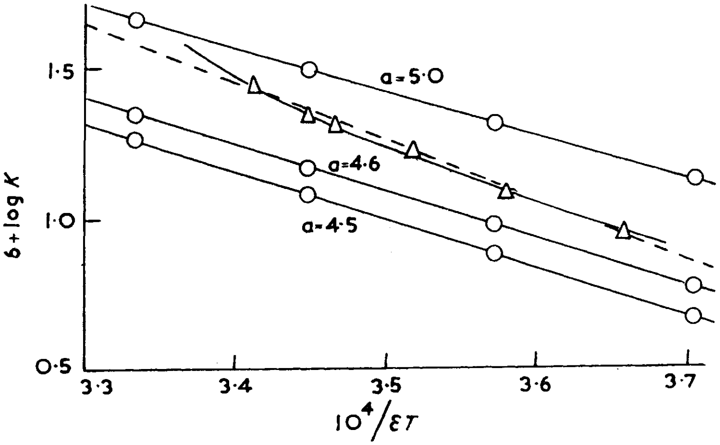

FIG. 3. The variation of log K with $1/\varepsilon T$.
○ Calculated from the Fuoss equation for the values of a (in Å) shown. △ This Paper, eqn. (5).

$$\log K = 2{\cdot}160 - 1{\cdot}974 \times 10^4/\varepsilon T \qquad (10)$$

If, for the present, we accept this linear interpretation, we can compare coefficients for equations (6) and (10). From the temperature-independent term we obtain the quite unrealistic value $a = 1{\cdot}40$ Å, which merely confirms the well-known fact that Fuoss's equation is not valid at very large (infinite) εT. From a comparison of the temperature-dependent terms, we obtain $a = 3{\cdot}68$ Å, a value which molecular models show to be reasonable, though rather low.

However, while the results shown in Fig. 3 are certainly compatible with a linear interpretation, they would be fitted better by a curve. If these were the only results available the matter could not be taken further; however, there are other results which indicate that a change of slope of the log K–$1/\varepsilon T$ plots is a very general phenomenon. Eqn. (9) shows that this necessarily implies that a varies with εT and this, as mentioned above, means that a varies with T.

The manner of this variation can be studied by deriving an explicit expression for a as a function of εT by combining the theoretical equation (5) with our empirical eqn. (1). This gives for a in Å,

$$\varepsilon T = 5{\cdot}869 \times 10^{-3} - (1{\cdot}219 \times 10^{-3} \log a) - 2{\cdot}947 \times 10^3/\varepsilon T a \qquad (11)$$

The values of a obtained from eqn. (11) are in Table 2, and are plotted against εT in Fig. 4.

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[15] Stern and Amis, *Chem. Rev.*, 1959, **59**, 1.

We believe that the increase of a with εT is significant, because a small variation in a causes a large change in K. This may be seen if we substitute the value of $a = 4{\cdot}84$ Å obtained at $-94{\cdot}7°$, back into eqn. (6) to obtain the value of K at 0°; this procedure gives $K = 1{\cdot}18 \times 10^{-5}$, whereas the experimental value is $0{\cdot}90 \times 10^{-5}$, and the difference of 30% is well outside the experimental error.

With the values of a in Table 2 as a guide, we calculated log K as a function of $1/\varepsilon T$ for constant values of $a = 4{\cdot}5$, $4{\cdot}6$, and $5{\cdot}0$ Å (Fig. 3) by means of eqn. (6). The slope of the plots differs considerably from that of the line representing the experimental points which, as was stated above, corresponds to $a = 3{\cdot}68$ Å. Moreover, the position of the experimental curve in the co-ordinate system does not correspond at all to that which would be expected for this value of a from eqn. (6). In other words, the slope and position of the experimental curve are not both compatible with eqn. (6) for the same, constant, value of a. The fact that the slope of the experimental curve is greater than that calculated from eqn. (6) on the assumption that a is constant can be considered as additional evidence that the third term of equation (9) is finite, *i.e.*, that a is not constant.

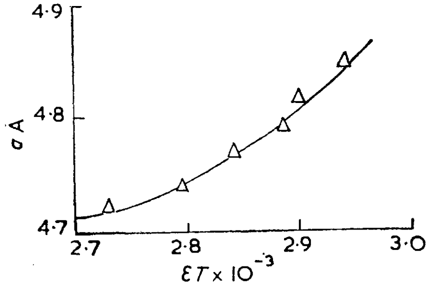

FIG. 4. The variation of the interionic distance a with εT.

Another way of looking at the evidence is to consider that each experimental point lies on a different member of a family of theoretical straight lines of (slightly) different slopes representing eqn. (6) for various values of a.

To sum up, there are two separate lines of evidence that a varies. The (admittedly slight) curvature of the log K–$1/\varepsilon T$ plot, and the magnitude of the slope of that plot and its position in the co-ordinate system in relation to corresponding theoretically calculated lines.

The reason for the increase of the interionic distance a with falling temperature is most probably that as the kinetic energy decreases relative to the solvation energy, the degree of solvation increases, so that the average effective size of both free ions and paired ions, which includes solvating molecules, increases. The fact that the activation energy of the viscosity of methylene dichloride, $E_\eta = -1{\cdot}54$ kcal./mole, is numerically about 6% smaller than E_Λ, over the same temperature range, indicates that Λ_0 is decreasing for reasons other than the increase in η, and thus appears to afford some independent evidence for the increase in the degree of solvation of the free ions with falling temperature.

Other Workers' Results.—Most conductivity measurements with non-aqueous solvents have been restricted to a small temperature range, and therefore there is little information on the dependence of K on temperature. We have examined the results of other workers,[11,12] and have found that, within the experimental error, most of them obey approximately linear relationships similar to eqn. (7), and that such curvature as does occur is always in the same sense as that shown by our results. The results of Sears, Wilhoit, and Dawson,[16] for both potassium thiocyanate and tetra-n-butylammonium iodide in acetone, give nearly linear plots of log K against $1/\varepsilon T$, in the range 25 to $-20°$, but the slope of the plots gradually increases from -20 to $-50°$. Tetra-n-butylammonium iodide consists of electrically symmetrical ions and therefore satisfies the requirement for the applicability of eqns. (5) and (7). The values of a calculated from the slopes increase

[16] Sears, Wilhoit, and Dawson, *J. Phys. Chem.*, 1956, **60**, 169.

with temperature from 0·96 to 2·21 Å, but these values are far too low. We calculated a at 25, -10, and $-50°$ in the same way as for our own results and obtained 3·84, 4·04, and 4·51 Å. As with our system, a calculated in this way increases as εT grows and T decreases. Also, the values are much more realistic than those obtained from the slope of the plots.

The results obtained by French[17] and her co-workers for the dissociation constant of various picrates over a temperature range of 20° in various large-molecule-solvents, show no general correlation of K with εT. This is not surprising because the D.C. is only a macroscopic property of a solvent, and since in the derivation of the Fuoss equation the solvent molecules are assumed to be infinitely small, the inadequacy of ε in this or any similar equation, will become more marked, the larger the solvent molecules.

Gilkerson[18] has studied the variation of dissociation constant with temperature, but his results cover only a relatively small range of εT. While we agree with his view[18b] that " a constant value of a is more satisfying than one which varies in an unpredictable manner," we do not agree, for the reasons given above, with the opinion[18b] that a would be expected to increase monotonically with increasing temperature. It seems to us that it may increase with temperature in a temperature region in which the vibrational energy of the ions in an ion pair dominates the behaviour, because average separation increases with vibrational energy, while at much lower temperatures it may show the variation deduced by us.

We have examined our results according to Gilkerson's theory by means of plots of $\log K - (3/2) \log T + E_s/T$ against $1/\varepsilon T$, with values of E_s equal to $-0{\cdot}4$, 0, 0·4, 1, 2, 4, and 10 kcal./mole. The curve for $E_s = -0{\cdot}4$ had a shallow minimum, that for $E_s = 0$ was nearest to a straight line between 0 and $-68°$, and that for $E_s = 0{\cdot}4$ gave the best straight line between -68 and $-94{\cdot}7°$. The other plots were significantly curved over the whole temperature range. The bearing which these findings have on Gilkerson's theory can be elucidated as follows.

The quantity E_s is the difference between the electrostatic interaction energies of ions and ion pairs with solvent, and according to its definition it must be temperature-dependent. It is thus clear that a single value of E_s will not serve over a large temperature range. Further, E_s can be related to the directly measurable enthalpy of dissociation $\Delta H°$. If $\Delta H_1°$ and $\Delta H_2°$ are the standard enthalpies of solvation of ion-pairs and free ions, and $\Delta H_3°$ is the Coulombic energy of the ion-pair in the gas phase

$$\Delta H° = \Delta \mathrm{H}_1° - \Delta \mathrm{H}_2° + \Delta \mathrm{H}_3°$$

and

$$E_s = \Delta \mathrm{H}_1° - \Delta \mathrm{H}_2°$$

Since $\Delta H°$ varies from $-1{\cdot}89$ kcal./mole at 0° to $-0{\cdot}71$ at $-89°$ and $\Delta H_3°$ is probably almost invariant with temperature, this variation in $\Delta H°$ probably reflects very largely the variation in E_s. Since Gilkerson's treatment ignores the possible variation of E_s with temperature his equation must be defective and it is thus not surprising that it is not compatible with our results covering a wide range of temperature.

Alternative Explanations.—Our results are not compatible with the Bjerrum–Fuoss equation unless the quantity a is assumed to vary with temperature. However, the solute–solvent interaction, and its marked variation with temperature, which our results show, suggest the following alternative interpretation: it may be that the Bjerrum–Fuoss equation is incapable of representing results which cover a wide temperature range because the continuum model and the assumptions concerning energy and entropy changes accompanying dissociation, on which it is based, are too far removed from actuality.

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[17] French and Singer, *J.*, 1956, 1424, 2428; French and Muggleton, *J.*, 1957, 5064.

[18] (*a*) Gilkerson, *J. Chem. Phys.*, 1956, **25**, 1199; (*b*) Curry and Gilkerson, *J. Amer. Chem. Soc.*, 1957, **79**, 4021; (*c*) Gilkerson and Stamm, *ibid.*, 1960, **82**, 5295.

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