Electrolyte–Solvent Interaction. VIII. Tetrabutylammonium Salts in Nitrobenzene–Carbon Tetrachloride Mixtures at 25°[1,2]

BY ERNEST HIRSCH[3] AND RAYMOND M. FUOSS

Conductances at 25° of tetrabutylammonium picrate, iodide and nitrate in mixtures of nitrobenzene and carbon tetrachloride, covering the approximate range $35 \geq D \geq 5$, were measured over the concentration range up to $c \approx 2 \times 10^{-4} N$. The data conform to the conductance equation (THIS JOURNAL, 81, 2659 (1959)) for associated ionophores. The association constants satisfy the relation $\log K_A \sim D^{-1}$; the ion size calculated from the slope of this plot agrees with the hydrodynamic value obtained from the limiting conductances for the systems in which D is about 10 or greater. Triple ion formation occurs below this range of dielectric constant.

Introduction

In a recent paper,[4] the conductance of tetrabutylammonium tetraphenylboride in nitrobenzene–carbon tetrachloride mixtures was reported. The two ions of this salt have very nearly the same volume (which is very much larger than the volume of the solvent molecules); consequently, granting the assumption that the transference number of each ion is one half, independent of solvent composition, we have the single ion conductance of the Bu_4N^+ ion as a function of solvent composition for the $PhNO_2$–CCl_4 system. Then measurements of other salts with this cation can in turn evaluate the corresponding anionic conductances. We present in this paper the conductance of tetrabutylammonium picrate, nitrate and iodide in the above solvent system; the range of dielectric constant covered the transition from moderate ion association to pairs to systems in which the pairwise association constant is of the order of 10^6 and where the effects of higher clustering (to triple ions) becomes clearly visible.

The data are analyzed, using the equation[5,6]

$$\Lambda = \Lambda_0 - S(c\gamma)^{1/2} + Ec\gamma \log c\gamma + Jc\gamma - K_A c\gamma f^2 \Lambda - F\Lambda_0 c \quad (1)$$

or appropriate limiting forms of this expression, depending on the dielectric constant. The equation involves three arbitrary constants, Λ_0, J and K_A (assuming F to be known from viscosity measurements) and in the early applications of the equation, the trial-and-error y–x method[7] was used. Subsequent work has shown[8] that the calculation can be much simplified by using a preliminary extrapolation of the data to evaluate Λ_0 approximately, and then using an electrostatic

correction[9] to Walden's rule to evaluate a (and hence J) from the limiting conductances. This procedure reduces equation 1 to the linear form

$$\Lambda_K = \Lambda_0 - K_A Z \quad (2)$$

where Λ_K is defined by the equation

$$\Lambda_K \equiv \Lambda + S(c\gamma)^{1/2} - Ec\gamma \log c\gamma - Jc\gamma + F\Lambda_0 c \quad (3)$$

and the independent variable is

$$Z \equiv c\gamma f^2 \Lambda \quad (4)$$

There are several advantages inherent in the method based on (2): aside from the simpler arithmetic involved, the evaluation of a from Λ_0 avoids the extreme sensitivity of the y–x method to experimental error and sidetracks futile speculation about apparently systematic trends in a-values derived from J which, in solvents of moderate and low dielectric constant, becomes a small difference between two much larger quantities.

Experimental

Materials.—Tetrabutylammonium bromide was prepared from tri-n-butylamine and n-butyl bromide and recrystallized from benzene[10]; m.p., 118°. Tetrabutylammonium picrate was prepared from tetrabutylammonium hydroxide (from the bromide and freshly precipitated silver oxide) and picric acid and was recrystallized from alcohol (4 ml./g. salt plus 10% water); m.p. 89.5°. Tetrabutylammonium nitrate was prepared by charging an Amberlite anion exchange column with sodium nitrate (analytical grade), washing and then passing a solution of tetrabutylammonium bromide through the column. The effluent (bromide-free) was evaporated to dryness; yield, 98.5%. The salt was recrystallized from benzene (9 ml./g. salt); m.p. 119°. Tetrabutylammonium iodide was from laboratory stock; m.p. 145°.

Nitrobenzene (Matheson, C.P. grade) was distilled from activated alumina at 6.5–8 mm. (84–86.5°) at a very slow rate into a receiver from which it was pumped by dry air pressure into the mixing vessel. Carbon tetrachloride was also distilled from alumina. Solvent mixtures were made up by weight; their properties (at 25°), summarized in Table I, were interpolated from the values previously determined by Sadek.[11] The symbols have the usual meanings: w_2 = weight fraction of carbon tetrachloride, D = dielectric constant, η = viscosity, ρ = density and c_{max} = concentration corresponding to $\kappa a = 0.2$, with $\mathring{a} \approx 6$. Solvents 1–12 were used in the picrate determinations, 13–16 for the iodide and 17–21 for the nitrate.

Method.—Solutions were made up by weight and calculated to c = equivalents per liter, using the solvent densities. Both dilution and concentration runs were made. The cell[12] had a constant of 0.022262 ± 0.000006. A Shedlovsky bridge[13] was used to measure the cell resistances. The ex-

(1) Office of Naval Research Project NR 051-002; Technical Report No. 62. This paper may be reproduced in whole or in part for any purpose of the United States Government.

(2) Presented at the International Symposium on Electrolytes, Congresso della Società Italiana per il Progresso delle Scienze, Trieste, 4–10 June 1959.

(3) This paper is abstracted from a thesis presented by Ernest Hirsch to the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1959.

(4) R. M. Fuoss and E. Hirsch, THIS JOURNAL, 82, 1013 (1960).

(5) Symbols used in this paper are defined by (a) R. M. Fuoss and F. Accascina, "La Conducibilità Elettrolitica," Edizione dell' Ateneo, Rome, 1959; (b) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959, and (c) R. M. Fuoss, ibid., 81, 2659 (1959).

(6) Ref. 5c, equations 18 and 27.

(7) R. M. Fuoss, ibid., 79, 3301 (1957).

(8) R. M. Fuoss and F. Accascina, Proc. Natl. Acad. Sci. U. S., 45, 1383 (1959).

(9) R. M. Fuoss, ibid., 45, 807 (1959).

(10) F. Accascina, S. Petrucci and R. M. Fuoss, THIS JOURNAL, 81, 1301 (1959).

(11) H. Sadek and R. M. Fuoss, ibid., 76, 5905 (1954).

(12) J. C. Nichol and R. M. Fuoss, J. Phys. Chem., 58, 696 (1954).

(13) T. Shedlovsky, THIS JOURNAL, 52, 1793 (1930); H. Eisenberg and R. M. Fuoss, ibid., 75, 2914 (1953).

perimental results are summarized in Tables II–IV; the code numbers refer to the solvents listed in Table I.

TABLE I
PROPERTIES OF SOLVENT MIXTURES

No.	w_2	D	$100\,\eta$	ρ	$10^2\,c_{max}$
1	0.0000	34.69	1.839	1.1977	4.54
2	.1291	30.11	1.692	1.2383	3.94
3	.2493	26.17	1.559	1.2783	3.43
4	.2908	24.82	1.515	1.2928	3.25
5	.4145	20.71	1.385	1.3374	2.71
6	.5495	16.20	1.249	1.3889	2.12
7	.6760	12.09	1.136	1.4400	1.58
8	.7695	9.07	1.056	1.4798	1.19
9	.8163	7.57	1.018	1.5001	0.99
10	.8363	6.94	1.003	1.5089	.91
11	.8600	6.19	0.985	1.5196	.81
12	.9005	4.955	0.957	1.5377	.65
13	.2985	24.56	1.506	1.2956	4.63
14	.4604	19.17	1.337	1.3545	3.62
15	.6624	12.53	1.148	1.4345	2.36
16	.7992	8.12	1.032	1.4926	1.53
17	.2009	27.76	1.611	1.2621	5.24
18	.2961	24.68	1.509	1.2947	4.65
19	.4681	18.90	1.330	1.3574	3.56
20	.6570	12.70	1.153	1.4323	2.40
21	.8286	7.18	1.009	1.5056	1.35

TABLE II
CONDUCTANCE OF Bu₄NPi IN PhNO₂-CCl₄ MIXTURES

No. 1 10^4c	Λ	No. 5 10^4c	Λ	No. 9 10^4c	Λ
0.4546	27.367	0.4347	32.383	0.1940	16.205
1.1295	27.107	0.9629	31.815	0.4401	12.116
1.9746	26.871	1.8288	31.110	1.3617	7.721
3.0254	26.641	2.9148	30.412	2.6232	5.937
4.1322	26.443	4.1152	29.773	5.2261	4.528

No. 2 10^4c	Λ	No. 6 10^4c	Λ	No. 10 10^4c	Λ
1.0121	28.509	0.4499	33.377	0.1853	11.594
1.9998	28.171	0.8762	32.453	.2746	9.950
2.9788	27.905	1.4657	31.436	.7968	6.420
4.2027	27.626	2.4345	30.140	1.6137	4.776
		3.6215	28.912	3.4161	3.487
				4.9623	2.999

No. 3 10^4c	Λ	No. 7 10^4c	Λ	No. 11 10^4c	Λ
1.1235	29.970	0.5253	30.981	0.1881	6.583
2.2059	29.487	0.6596	30.162	.2624	5.695
3.6504	28.991	1.3089	27.288	.8476	3.377
4.3720	28.778	2.6293	23.825	1.3432	2.763
		5.9699	19.616	2.3309	2.185

No. 4 10^4c	Λ	No. 8 10^4c	Λ	No. 12 10^4c	Λ
0.5958	30.790	0.4243	21.375	0.0723	2.410
1.3287	30.336	0.7006	18.553	.1338	1.808
2.2256	29.907	1.4487	14.770	.4165	1.058
3.1442	29.543	3.8141	10.531	1.1039	0.678
		8.4479	7.938	1.9910	0.521

TABLE III
CONDUCTANCE OF Bu₄NI IN PhNO₂-CCl₄ MIXTURES

No. 1 10^4c	Λ	No. 14 10^4c	Λ	No. 16 10^4c	Λ
1.2782	31.900	0.3570	35.539	0.0000	(37.9)
1.8843	31.688	.6314	34.967	.2164	15.652
3.3798	31.271	.9632	34.370	.5533	11.060
7.3373	30.428	1.3465	33.762	1.0536	8.568
				1.4854	7.455

No. 13 10^4c	Λ	No. 15 10^4c	Λ	No. 16 10^4c	Λ
0.4149	34.485	0.2080	34.053	1.7951	6.903
0.7969	34.119	.5132	30.847		
1.2402	33.761	.8382	28.542		
1.8335	33.331	1.1206	27.027		
		1.4290	25.695		

TABLE IV
CONDUCTANCE OF Bu₄NNO₃ IN PhNO₂-CCl₄ MIXTURES

No. 1 10^4c	Λ	No. 18 10^4c	Λ	No. 20 10^4c	Λ
1.1133	33.486	0.9096	34.923	0.1524	34.923
1.6338	33.292	1.3187	34.638	.3231	32.339
2.6393	32.970	1.6642	34.432	.6994	28.640
4.9029	32.375			1.1244	25.975
				1.5139	24.225

No. 17 10^4c	Λ	No. 19 10^4c	Λ	No. 21 10^4c	Λ
0.4111	35.544	0.2566	37.144	0.2201	7.554
0.7122	35.302	0.6542	36.112	.5553	5.050
1.2929	34.904	1.1852	34.982	.8880	4.109
1.8121	34.595	1.7882	33.921	1.1737	3.636
		2.2450	33.233	1.4391	3.326

Discussion

The data of Tables II–IV were analyzed by the following procedure. First, preliminary extrapolations were made using equation 5 for the systems of higher dielectric constant and equation 6 for those with $D < 25$; temporarily, the data for $D < 10$ were disregarded at this stage because (6) does not sharply separate the quantity K_A/Λ_0^2 into its two factors when association is marked. These equations are

$$\Lambda_\eta' \equiv \Lambda + Sc^{1/2} - Ec\log c + F\Lambda_0 c \qquad (5)$$

$$\Lambda = \gamma(\Lambda_0 - Sc^{1/2}\gamma^{1/2}) \qquad (6)$$

The first equation 5 defines a quantity Λ'_η which is linear in concentration for negligible or slight association and readily extrapolates to Λ_0; the second is the modified form of the Ostwald dilution law which neglects the higher terms in mobility involving E and J. From our earlier work[4] on Bu₄NBPh₄ in PhNO₂-CCl₄, we obtained the result

$$R^+ = 3.55 + 15/D \qquad (7)$$

for the apparent hydrodynamic radius of the Bu₄N⁺ ion in this solvent system; hence we could calculate $\lambda_0^+\eta$ from the Walden–Stokes relation

$$\lambda_0^+\eta = Fe/1800\,\pi\eta R^+ \qquad (8)$$

for each of the solvent mixtures of Table I. Then subtraction of these values from the preliminary values of $\Lambda_0\eta$ gave $\lambda_0^-\eta$ for each system, and values of R^- for the picrate, nitrate and iodide were thus determined for the solvents in which they were measured. Finally, R–D–D plots were constructed; these were linear[14] and gave the values summarized in Table V, where the symbols are defined by the equation

$$R^- = R^-_\infty + s^-/D \qquad (9)$$

The last column gives the values of $å_A$, obtained by adding 3.55, the value for the Bu₄N⁺ ion to the radius of the corresponding anion. In further calculations, we shall use these values to calculate

(14) Ref. 9, Fig. 3.

TABLE V

EVALUATION OF ION SIZE

Ion	R^-_∞	s^-	$\mathring{a}A$
Pi$^-$	2.36	13.0	5.91
NO$_3^-$	1.37	19.5	4.92
I$^-$	1.61	20.5	5.16

the $J(a)$ term in the conductance equation 1. (If the smaller nitrate and iodide ions penetrate between the alkyl chains of the Bu$_4$N$^+$ ions, these values are of course an over-estimate. But since the J-term is essentially a correction term and since it arises from contacts which presumably do not lead to pairing, we believe that the approximation is justified.)
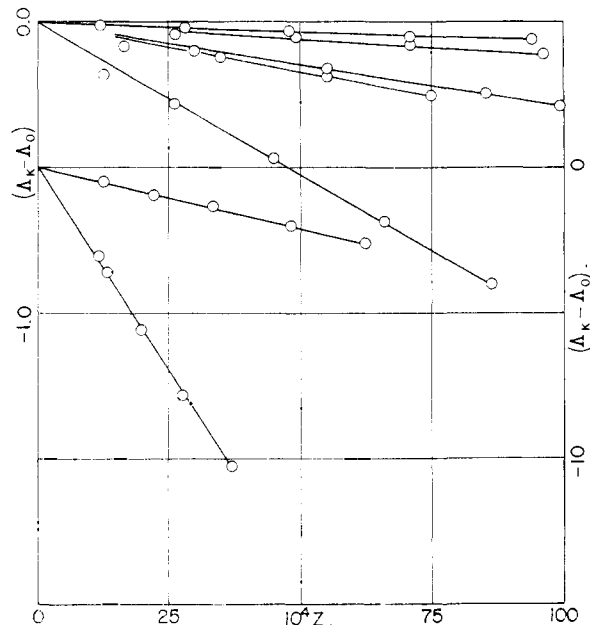
Fig. 1.—Determination of limiting conductance and association constant for Bu$_4$NPi in PhNO$_2$–CCl$_4$: systems 1–5, ordinates left; systems 6–7, ordinates right; sequence of plots, 1–7 from top to bottom.

Next, final values of limiting conductances were determined, using equation 1 of the introduction for Systems 1–7 (picrate), 13–15 (iodide) and 17–20 (nitrate) and also for the iodide and nitrate in pure nitrobenzene. Values of γ were calculated using equations 34 and 35 of ref. 5c; the various constants were computed, using the preliminary values of Λ_0, the coefficients of Table I of ref. 5c and the values of D and η from Table I of this paper. The values of S, E and J are summarized in Table VI.

The resulting Λ_K vs. Z plots are linear, within an experimental error of less than 0.01 Λ unit for concentrations above about 10^{-4} N; at lower concentrations, the deviations are somewhat larger (as much as 0.03) due to uncertainty in the solvent correction. The limiting conductances and association constants, obtained as intercepts and slopes of these plots, are summarized in Table VI. The increase of association with decreasing dielectric constant is shown in Fig. 1 where (Λ_K − Λ_0) is plotted against Z for the picrate systems; the slope is proportional to K_A and rapidly increases as D decreases. These graphs (which are, of course,

the Λ_K vs. Z plots normalized by subtracting the corresponding Λ_0 values in order to permit compact presentation) also serve to show the relative magnitudes of the various terms in (1). The ordinate Λ_K is the observed conductance, corrected for all the (theoretically known) effects of interionic forces on mobility, and the deviation of the Λ_K vs. Z plots from the horizontal is therefore a measure of ionic association. In nitrobenzene, for example, the point at highest concentration (4.132 × 10^{-4}) gives (Λ_K − Λ_0) = −0.069, with Λ = 26.443; clearly association is slight; also we note that K_A is determined by only 0.26% of the total observed conductance, and its numerical value is therefore extremely sensitive to any source of error, either in the conductance data themselves or in the theoretical constants appearing in (1) which depend on viscosity and dielectric constant. As the dielectric constant decreases, the precision in K_A improves; at D = 20.71, for example, (Λ_K − Λ_0) = −0.907 at the highest concentration (4.115 × 10^{-4}) and is 3.04% of the observed conductance.

TABLE VI

DERIVED CONSTANTS

No.	S	$10^{-3} E$	$10^{-3} J$	$\log K_A$	Λ_0
1	65.8	0.1198	0.495	0.87	27.83
2	79.8	.2015	0.742	1.07	29.37
3	97.0	.339	1.135	1.47	31.12
4	104.1	.409	1.300	1.54	31.71
5	132.3	.773	2.284	2.02	33.48
6	181.2	1.777	4.95	2.63	35.24
7	261	4.60	12.35	3.45	36.15
8	357	10.84	28.68	4.44	(35.4)
9	433	18.27	48.6	5.13	(34.3)
10	474	23.38	62.5	5.52	(33.6)
11	532	32.14	86.5	6.07	(32.6)
12	661	58.66	160.9	7.33	(30.2)
1^a	69.6	0.1497	0.514	1.43	32.80
13	110.3	0.486	1.389	1.82	35.31
14	151.6	1.109	2.929	2.42	36.79
15	254.4	4.324	10.85	3.70	38.10
16	396	14.54	36.45	5.12	(33.9)
1^b	70.9	0.1595	0.517	1.38	34.34
17	95.9	.343	0.985	1.79	36.29
18	110.7	.492	1.357	1.63	36.16
19	157.4	1.222	3.100	2.71	38.52
20	254	4.267	10.34	3.78	38.84
21	460	21.49	53.1	5.91	(34.3)

^{a} Constants for iodide. ^{b} Constants for nitrate.

For the systems with dielectric constants below about 10, the Λ_K vs. Z plots began to show progressively greater curvature, in the direction which suggested that 3-ion clusters[15] were beginning to be stable. The data for Systems 8–12, 16 and 21 were therefore treated as follows. First, $\Delta c^{1/2}$ g (c) was computed and plotted against $c(1$ − $\Lambda/\Lambda_0)$, using Λ_0 values calculated by equation 9 and the appropriate constants from Table V. The slope evaluates $\lambda_3 k_3/K_A^{1/2}$ and the intercept gives $\Lambda_0/K_A^{1/2}$; then the contribution of triple ions to the conductance can be estimated by the equation

$$\Delta_3 \equiv \lambda_3 k_3 c \gamma (1 - \Lambda/\Lambda_0) \tag{10}$$

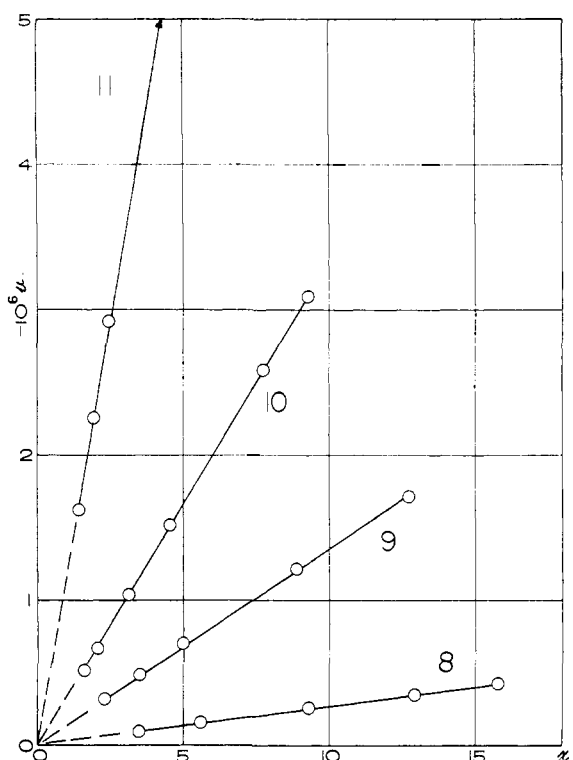(15) Ref. 5, Chapter XVIII, equations 8–28.

Fig. 2.—Determination of association constants for Bu₄NPi in PhNO₂–CCl₄, systems 8–11, by equation 12.

Fig. 3.—Dependence of association on dielectric constant: O, picrate, abscissa top; ◑ iodide, ◐ nitrate, abscissa bottom.

Finally, Λ_K is corrected by subtracting Δ_3 to give Λ'_K

$$\Lambda'_K \equiv \Lambda_K - \Delta_3 \qquad (11)$$

and a plot of

$$v = (\Lambda'_K - \Lambda_0)/c\gamma \qquad (12)$$

against $x = \Lambda f^2$ is made. The slope of the resulting straight line through the points and the origin gives the association constant. (The origin, where $x = 0$, of course has no physical reality; when $c = 0$, $x = \Lambda_0$. But the mathematical origin $x = 0$ is a convenient aid in drawing the lines.) Several examples of v–x plots are shown in Fig. 2. As in Fig 1, increasing steepness indicates increasing association. In Table VI, for the systems enumerated above, the association constants are the values obtained from the slopes of the v–x plots, and the limiting conductances are those computed by (9) from the constants given in Table V, which summarize the Λ_0 values determined by direct extrapolation of Λ_K–Z plots in systems of higher dielectric constant. In general, there was good agreement between these values of K_A and those determined from the intercepts of the triple ion plots at zero concentration; requiring this agreement was a useful criterion when some points were uncertain on the triple ion plot, the slope of which is naturally extremely sensitive to experimental error when k_3 is small.

Fig. 3 summarizes the dependence of association on dielectric constant for the three salts. According to simple theory,[16,17] the association constant

(16) J. T. Denison and J. B. Ramsey, THIS JOURNAL, **77**, 2615 (1955).
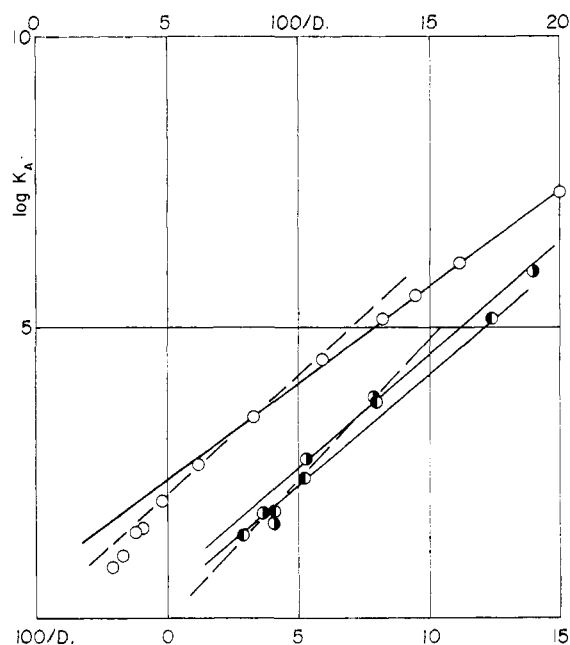
(17) R. M. Fuoss, *ibid.*, **80**, 5059 (1958).

should be a linear function of the reciprocal of the dielectric constant of the solvent medium. As seen in the figure, this relation is a good first approximation over about six decades in K_A. A better representation of the points shown for the three salts, however, would be a curve which is slightly concave down, but it is pertinent to speculate a bit at this point. It is easy to make plausible *ad hoc* assumptions to account for curvature: for example, if the more polar component of the solvent tended to accumulate near the ions as the average dielectric constant decreased, then the association constants would be less than expected at small dielectric constants, either because the "local" dielectric constant was higher than the macroscopic value or because the "effective" ion size was larger on account of "selective solvation." On the other hand, in the systems for which $D < 10$. the K_A values depend explicitly on the values used here for Λ_0, and these depend on the semi-empirical extrapolation (9). Actually, the data (at low dielectric constants) only determine K_A/Λ_0^2, and errors in Λ_0 obviously are reflected in the association constants. Until a theoretical derivation of the explicit function for which (9) is an approximation becomes available, it therefore seems premature to suggest "explanations" of the curvature.

This caution is warranted on other grounds. Consider the picrate first. The solid line of Fig. 3 gives an excellent fit over the range $4.96 \leqslant D \leqslant 16.20$, but the value of a_K calculated from the slope is 7 51, which is considerably larger than $\mathring{a}_A = 5.91$, which was obtained from data in the high D range where there is no ambiguity in the values of Λ_0. The dashed line of Fig. 3 is drawn with a slope corresponding to $\mathring{a} = 5.91$; it fits the observed points quite well over the range $34.69 \geqslant D \geqslant 9.07$. Similarly for the nitrate and iodide, with $\mathring{a}_A =$

4.92 and 5.16, respectively, the dashed line in Fig. 3 with slope corresponding to $\mathring{a} = 5.00$ interpolates the data for these salts in the higher range of dielectric constant but overshoots the points for the two systems at $D \approx 7\text{-}8$. For two systems at least[4,10] ($Bu_4N \cdot BPh_4$ in $MeCN\text{-}CCl_4$ and in $PhNO_2\text{-}CCl_4$ over the range $36 \geqslant D \geqslant 4.8$), the values of a_K and a_A agree with each other and also with the value a_J derived from the coefficient J of the linear long range term. We therefore prefer to give more weight at present to our data which give agreement with the simple model for which $a_A = a_K = a_J$ and leave to future decision, based on more experimental and theoretical work, the question whether the curvature in Fig. 3 is real or whether it is an artifact introduced by the method of computation.

NEW HAVEN, CONN.

Kinetic Studies of Urea Derivatives. I. Methylurea

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Kinetic data on the dissociation of methylurea in aqueous solutions at elevated temperatures are presented. This compound dissociates by two different processes. Initial products are: (1) methyl isocyanate and ammonia and (2) isocyanic acid and methylamine. These initial products undergo further reaction making it impossible to determine individual rate constants in acid solution. By observing reaction rate as a function of pH this difficulty has been overcome, and first order rate constants for both reactions have been determined. These constants are reported. The effect of temperature and ionic strength also has been studied. The experimental findings are discussed.

Introduction

The kinetic behavior of urea,[1] thiourea[2] and the methylated thioureas[3-5] in aqueous solutions has been examined previously in this Laboratory. Conclusions based on these studies have been reported.[6] From a consideration of this earlier work it became apparent that the collection of comparable data for the methylated ureas would be desirable. Such data, in addition to their intrinsic interest, could be used to evaluate more critically several of the mechanistic interpretations that had been proposed.[6]

Methylthiourea dissociates by two different processes.[3] By analogy with this compound and in accordance with the general mechanism[6] postulated for urea and thiourea derivatives, two parallel reactions would be anticipated for methylurea, viz.

$$CH_3NHCONH_2 \begin{cases} \nearrow CH_3NCO + NH_3 & (1) \\ \searrow HNCO + CH_3NH_2 & (2) \end{cases}$$
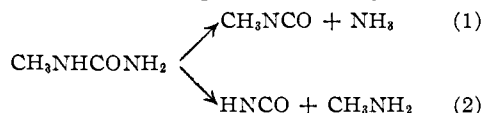
Consequently four different reaction products would be expected. In acid solution, however, a rapid and quantitative hydrolytic conversion of cyanate ion to ammonium ion occurs.[7,8] Methyl isocyanate is also unstable in media of low pH and, in such solutions, the nitrogen-containing end products of both reactions (eqs. 1 and 2) should be $CH_3NH_3^+$ and NH_4^+. These two products should be formed at equal rates. The rate of production of either might be used to measure the total rate of dissociation of methylurea by both reaction one (eq. 1) and reaction two (eq. 2), but no information what-

ever concerning individual rates for these reactions could be gleaned from such measurements. In fact without some a priori mechanistic reason the very possibility that two distinctly different processes leading to the same reaction products could exist, might go unrecognized. This appears to have been true of the pioneering work of Fawsitt.[9] This investigator was the first and, unless we have overlooked some publications, the only other researcher to present quantitative data on the rate of dissociation of methylurea in aqueous solutions.

Fawsitt concluded that the reaction in acid solution could be represented by

$$CH_3NHCONH_2 + 2H^+ + H_2O \longrightarrow$$
$$CO_2 + NH_4^+ + CH_3NH_3^+ \quad (3)$$
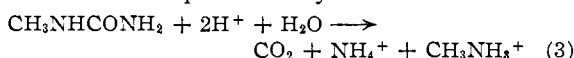
and calculated first order rate constants based on his experiments in HCl, HBr and H_2SO_4 solutions. Limited data for the reaction in water and in basic media also were reported. The reaction was followed by conventional acid-base titration techniques. Although salts of methylamine and ammonia were identified as reaction products and the evolution of CO_2 noted, the individual rates of formation of these substances were not determined.

The present investigation was undertaken in the hope that the existence of the two reactions (eqs. 1 and 2) could be established and corresponding rate constants evaluated. It was felt that this information might be obtained by observing the rate of formation of cyanate, methylamine and ammonia under a variety of experimental conditions.

Experimental

General experimental techniques previously have been described.[1,2,7] The reactions were studied using the method of initial rates and, as before, empirical first order rate constants[2,3] were employed in analyzing the data. The constants k_c, k_a and k_m used in the discussion are based on the rate of production of cyanate, ammonia and methylamine, respectively.

Spectrophotometric analyses were used throughout. Cyanate was determined by the usual procedure.[7] In the

(1) W. H. R. Shaw and J. J. Bordeaux, THIS JOURNAL, 77, 4729 (1955).

(2) W. H. R. Shaw and D. G. Walker, ibid., 78, 5769 (1956).

(3) W. H. R. Shaw and D. G. Walker, ibid., 79, 2681 (1957).

(4) W. H. R. Shaw and D. G. Walker, ibid., 79, 3683 (1957).

(5) W. H. R. Shaw and D. G. Walker, ibid., 79, 4329 (1957).

(6) W. H. R. Shaw and D. G. Walker, ibid., 80, 5337 (1958).

(7) W. H. R. Shaw and J. J. Bordeaux, Anal. Chem., 27, 136 (1955).

(8) A. R. Amell, THIS JOURNAL, 78, 6234 (1956).

(9) C. E. Fawsitt, J. Chem. Soc., 85, 1581 (1904).