TABLE V

EQUIVALENT CONDUCTANCES OF LITHIUM AND RUBIDIUM IODIDE–IODINE SOLUTIONS AT 25°

Salt	C_{MI} Concn. of stock salt soln., moles/l.	$R = C_I^0/C_{MI}$	Λ_m, ohms^{-1}
LiI	0.185	0.0	94.34
		.1736	92.42
		.2827	90.08
		.4221	87.83
RbI	0.142	.0	143.66
		.0687	142.05
		.4089	136.56
		.6367	132.96

was not studied because R values above 0.5 led to the appearance of an insoluble precipitate thought to be cesium triiodide.

It will be noted that in Fig. 3 there is a small deviation of the experimental curves in the direction of the $j = 3$ curves and that this deviation increases with R. This behavior previously has been observed in the cases of KI and NaI. It cannot be due to the slight amount of iodine existing in solution as I_2 since, in all four cases, the calculations leading to the $j = 2$ curves have had corrections (quite small) made for this based upon the equilibrium $I_3^- = I^- + I_2$ for which the mass law constant, according to Jones and Kaplan,[22] is 1.4×10^{-3}. When the percentage deviations are calculated for the Li, K, Na and Rb salts at a large, and approximately equal, value of R (0.6–0.8), one gets 1.0, 1.2, 0.4 and 0.2%, respectively. One possible explanation may be the failure of the law of independent ion mobilities at these concentrations. However, we think it likely that the effect is due to the presence of traces of higher complexes such as I_5^-. Higher complexes have been discussed by several authors.[23,24]

Acknowledgments.—The authors are indebted to Prof. G. R. Peirce for the development of the speed control, to Prof. R. M. Whitney for his assistance with the conductance measurements, to Mr. A. E. Wood for his advice and for his skill in the construction of the centrifuge and to Dr. E. G. Pickels for the specially straightened shafting for the centrifuge.

[22] G. Jones and B. Kaplan, THIS JOURNAL, **50**, 1845 (1928).

[23] W. C. Bray and G. M. J. McKay, *ibid.*, **32**, 914 (1910).

[24] G. Jones and B. Kaplan, *ibid.*, **50**, 1600 (1928).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARKANSAS]

Thermodynamics of Ion Pair Dissociation. Tetrabutylammonium Picrate in Chlorobenzene, *o*- and *m*-Dichlorobenzene[1]

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The dissociation constant of Bu_4NPi has been measured in chlorobenzene and in *o*- and *m*-dichlorobenzene at 25, 35 and 45°. The corresponding thermodynamic functions have been calculated. The data are used to test the continuum theories of Bjerrum and Denison and Ramsey which are shown to fail in the prediction of ΔS^0 and ΔH^0. The contact distance of the ion-pair is seen to depend on the equation by which it is calculated.

There has been considerable interest in theories of ion-pair dissociation in recent years. The steady accumulation of dissociation constants of salts in a variety of solvents had made it clear that the Bjerrum theory[3] (which considers the electrolyte to exist in a continuous medium distinguished only by its macroscopic dielectric constant D), while adequate for predicting large-scale trends, no longer adequately accounts for all the available data.

It was first suggested by Stern and Martell[4] that a better understanding of electrolyte–solvent interactions might be obtained from a knowledge of the thermodynamic functions for ion-pair dissociation. Shortly thereafter, Denison and Ramsey[5] derived these functions from the Bjerrum theory and also by a simplified treatment which yields essentially the same results for low dielectric constant solvents. For several perchlorates in ethylene chloride and ethylidene chloride the agreement between experimental and calculated values of ΔH^0 and ΔS^0 was very good. Recently, Gilkerson[6] has applied free volume theory to this problem. However, his theory includes several variable parameters and a test of it involves the dipole moment of the solvent. The latter varies considerably with the method of measurement. We shall return to this point later.

The present work was undertaken to provide a further test of the Denison–Ramsey and Gilkerson theories; and to add to the all-too-scanty data in this field. Such a body of data is usually necessary before useful generalizations begin to appear. Tetrabutylammonium picrate (Bu_4NPi) was chosen as the salt because it has been measured in more solvents than any other. The solvents were selected because their chemical similarity makes it likely that any chemical or specific interactions with the salt would be the same for all and because they can be characterized easily by molecular parameters should a theory based on these ever develop; *i.e.*, the molecules are rigid and have well-defined dipole moments and polarizabilities.

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[1] This research was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command under Contract AF 18(600)-960. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] From the M.S. Thesis of P. H. Flaherty.

[3] N. Bjerrum, *Kgl. Danske Videnskab. Selskab*, **7**, No. 9 (1926).

[4] K. H. Stern and A. E. Martell, THIS JOURNAL, **77**, 1983 (1955).

[5] J. T. Denison and J. B. Ramsey, *ibid.*, **77**, 2615 (1955).

[6] W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956).

TABLE I

DIELECTRIC CONSTANT[9] OF *o*-DICHLOROBENZENE AT SEVERAL TEMPERATURES

Temp. (°C.)	5	15	25	35	45	55	65	75
Dielectric constant	10.983	10.504	10.056	9.644	9.253	8.898	8.567	8.258
F.p., °C.	17.12							
Purity (cooling curve), %	99.85							

The dissociation constant K for Bu_4NPi in these three solvents was measured at 25, 35 and 45°.

Experimental

Purification of the Solvents.—Each of the three solvents: chlorobenzene, *o*-dichlorobenzene and *m*-dichlorobenzene (Matheson Chemical Company) was refluxed over anhydrous P_2O_5 for 8 hr., then distilled through an Oldenshaw column at a reflux ratio of 20 to 1. The middle fraction was collected directly in a one-liter round-bottom Pyrex flask equipped with protecting calcium chloride and soda lime tubes and with an outlet tube for delivering the solvent directly into the mixing flask with the least possible exposure of the solvent to the air during the transfer. The solvents were stored over activated aluminum oxide in order to maintain low conductance. To prevent the transfer of Al_2O_3, the delivery tube was fitted with a fine glass filter frit. The conductance of each solvent was never greater than 1×10^{-10} mhos.

Physical Constants.—Because of the inconsistent values of the dielectric constant at 25° for *o*-dichlorobenzene: 9.93 by Smyth[7] and 6.828 by Le Fevre and Le Fevre,[8] the National Bureau of Standards[9] measured our sample of the material. The values are listed in Table I.

The purity of our sample as determined by the Thermochemical Section of the National Bureau of Standards was higher than that previously cited in the literature.

The density and viscosity were obtained from a plot of literature values[10] *vs.* temperature. The dielectric constants for chlorobenzene and *m*-dichlorobenzene were calculated from the values listed in the National Bureau of Standards Circular No. 514 and are shown in Table II.

TABLE II

PHYSICAL CONSTANTS OF THE PURE SOLVENTS

	t, °C.	Dielectric constant	Viscosity (10^2 poise)	Density (g./ml.)
Chlorobenzene	25.00	5.63^{c}	0.758^{a}	1.1008^{a}
	35.00	5.46^{c}	.678^{a}	1.0901^{a}
	45.00	5.30^{c}	.605^{a}	1.0794^{a}
m-Dichlorobenzene	24.80	5.04^{c}	1.0311^{b}	1.2826^{b}
	34.80	4.90^{c}	0.9333^{b}	1.2707^{b}
	45.00	4.77^{c}	0.8443^{b}	1.2585^{b}
o-Dichlorobenzene	24.80	10.06^{d}	1.3262^{b}	1.3000^{b}
	34.80	9.65^{d}	1.1557^{b}	1.2885^{b}
	45.00	9.25^{d}	1.0215^{b}	1.2770^{b}

[a] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, N. Y., 1950. [b] Reference 10. [c] A. A. Maryott, N. B. S. Circular No. 514. [d] Reference 9.

Preparation of the Salt.—Tetrabutylammonium picrate was prepared as follows: picric acid (crystallized three times from anhydrous ethyl acetate) was treated with an excess of silver nitrate; the silver picrate (recrystallized three times from water) was allowed to react in stoichiometric quantities with tetrabutylammonium iodide (recrystallized three times from water) in an alcoholic solution. The silver iodide precipitate was removed by filtration and the remaining solution was evaporated to dryness. The tetrabutylammonium picrate was then recrystallized three times from an alcohol–petroleum ether mixture. The salt was dissolved slowly in boiling alcohol and the petroleum ether added to decrease the solubility of the salt in the alcohol. On cooling, the salt recrystallized. It was dried *in vacuo* for 12 hr. and had a melting point of 89.5°, which agreed with the literature value[11] of 89.5°.

Preparation of Solutions.—Approximately 10 mg. of the salt was weighed to ±2 μg. and introduced into the mixing flask. The desired amount of solvent was added and the flask and its contents were weighed with an accuracy of ±3 mg. The volume concentration was calculated by taking the density of the very dilute solution to be that of the pure solvent. The solution was mixed thoroughly, then pumped with dry, CO_2-free air into the conductance cell. Each successive concentration was prepared in the mixing flask by the dilution method. After each measurement the conductance cell was washed with distilled acetone to remove adsorbed ions from the electrodes and dried for 1 hr. with a water aspirator having a drying tube attachment. Separate solutions were prepared at each temperature measured.

Conductance Measurements.—The experimental measurements of resistance were made with a Jones and Joseph conductance bridge using a frequency of 1000 cycles per second. A Dumont Model 304 H oscilloscope was used to detect the balance point. The bridge resistances were calibrated according to the method of Dike,[12] using a N. B. S. certified resistor.

The cell was constructed so that the platinum electrodes were about 1.5 mm. apart. Mercury was used as a contact between the electrodes and the wire leads to the bridge. The electrodes were lightly platinized, then freed from adsorbed gases and ions by electrolyzing with a 5% sulfuric acid solution and alternating the polarity every 20 seconds. The cell was thereafter steamed and soaked for several days in distilled water.

The cell was standardized using the equivalent conductances which were obtained[13] for tetrabutylammonium picrate in ethylene chloride at various concentrations. The cell constant was calculated to be 0.021203 ± 0.000003 cm.$^{-1}$. Resistance measurements were obtained at 25, 35 and 45°. Each temperature was held constant to ±0.01°.

Results

At least two runs were made in each case which agreed within 0.1%. The conductance data are listed in Table III.

***o*-Dichlorobenzene.**—The ion-pair dissociation constant K and the equivalent conductance at infinite dilution were calculated by Shedlovsky's[14] method. These constants and the thermodynamic functions are listed in Table IV.

Chlorobenzene and *m*-Dichlorobenzene.—Since for solvents of very low dielectric constant the Shedlovsky plots yield very steep slopes, making the intercepts very uncertain, values of Λ_0 were obtained on the assumption that Walden's rule ($\Lambda_0\eta$ = constant) holds in these three solvents. Their chemical similarity makes this appear reasonable. The dissociation constant was then calculated using an equation derived by Fuoss and Kraus.[15]

The thermodynamic functions were calculated in the usual way from the K values. All the results are summarized in Table IV.

Λ_0 and K for Bu_4NPi in $o\text{-}Cl_2C_6H_4$ have been reported previously for 25° by Kraus and co-work-

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[7] C. P. Smyth, THIS JOURNAL, **50**, 1536 (1928).

[8] C. J. Le Fevre and R. J. W. Le Fevre, *J. Chem. Soc.*, 487 (1936).

[9] We would like to express our appreciation to Drs. A. A. Maryott and C. G. Malmberg for these measurements.

[10] V. Griffing, *J. Phys. Chem.*, **58**, 1054 (1954).

[11] J. A. Geddes and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 585 (1936).

[12] P. H. Dike, *Rev. Sci. Instr.*, **2**, 379 (1934).

[13] D. L. Mead, R. M. Fuoss and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936).

[14] T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

[15] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 2387 (1933).

TABLE III

CONDUCTANCE OF TETRABUTYLAMMONIUM PICRATE IN CHLOROBENZENE, o-DICHLOROBENZENE AND m-DICHLOROBENZENE

t (°C.)[a]	Chlorobenzene $C \times 10^4$	Chlorobenzene Λ	m-Dichlorobenzene $C \times 10^5$	m-Dichlorobenzene Λ	o-Dichlorobenzene $C \times 10^4$	o-Dichlorobenzene Λ
25.00	5.2263	0.4296	9.4325	0.2435	8.9794	6.109
	3.6004	.5018	7.0544	.2799	5.5869	7.329
	2.0476	.6482	5.3192	.3188	3.3903	8.873
	1.5400	.7368	4.5578	.3442	2.6904	9.662
	1.1434	.8436	3.8846	.3710	2.0768	10.599
35.00	4.7144	0.5241	18.097	0.2266	4.5731	9.079
	3.8568	.5697	7.1818	.3448	2.6580	11.112
	2.9848	.6370	6.3055	.3667	1.9969	12.336
	1.8044	.7989	5.0551	.4050	1.7269	12.977
	1.3294	.9194	4.0774	.4485	2.5398	11.315
					2.0366	12.268
					1.0260	15.555
					0.9212	16.079
45.00	5.1244	0.5864	15.812	0.2926	5.0450	9.721
	3.5302	.6857	8.1004	.3939	3.8700	10.636
	2.8676	.7492	6.9770	.4208	3.0277	11.652
	2.0077	.8805	5.2286	.4805	2.0682	13.426
			4.1116	.5371	3.8592	10.646
					3.0156	11.610
					2.2723	12.855
					1.8769	13.783

[a] Measurements in o-$Cl_2C_6H_4$ and m-$Cl_2C_6H_4$ were made at 24.80, 34.80 and 45.00°.

TABLE IV

CONSTANTS OF TETRABUTYLAMMONIUM PICRATE IN CHLOROBENZENE, o- AND m-DICHLOROBENZENE

t (°C.)	D	Λ_0	K	ΔF^0 (kcal./mole)	ΔS^0, e.u.	ΔH^0 (kcal./mole)
			m-Dichlorobenzene			
24.80	5.04	44.82	2.53×10^{-9}	11.72		
34.80	4.90	46.68	3.62	11.90	−17.0	6.64
45.00	4.77	46.39	5.16	12.07		
			Chlorobenzene			
25.00	5.63	60.95	2.02×10^{-8}	10.50		
35.00	5.46	64.08	2.48	10.72	−20.2	4.47
45.00	5.30	64.74	3.24	10.90		
			o-Dichlorobenzene			
24.80	10.06	34.85	2.14×10^{-5}	6.36		
34.80	9.65	37.70	2.45	6.50	−11.6	2.91
45.00	9.25	38.34	2.93	6.60		

ers[16] and quite recently by Curry and Gilkerson.[17]

The first group of workers find $\Lambda_0 = 37.3$, $K = 1.71 \times 10^{-5}$, compared with ours (at 24.8°) of 34.85 and 2.14×10^{-5}. Curry and Gilkerson find $K = 1.92 \times 10^{-5}$ at 25°. This agreement is quite satisfactory but Gilkerson's temperature coefficient is much smaller than ours, $K = 2.02 \times 10^{-5}$ at 45°, compared with 2.93×10^{-5}. However, his solvent may contain some isomers of lower dielectric constant. Fuoss[18] has measured the conductance of Bu_4NPi in chlorobenzene at 25°. He estimated Λ_0 from Walden's rule using the conductance in ethylene chloride[13] as standard. He obtained $\Lambda_0 = 60$ and $K = 1.88 \times 10^{-8}$ in good agreement with our results. No previous measurements in m-dichlorobenzene have been reported.

Discussion

There are at present three equations which relate the ion-pair dissociation constant K to properties of the solute and solvent. The Bjerrum theory[3] and the thermodynamic theory of Denison and Ramsey[5] involve an ion size parameter a, temperature T and the dielectric constant D of the solvent. The free-volume theory of Gilkerson contains these as well as the solvation energy E_s and the free volumes and partition functions of the solute particles.

The Bjerrum equation

$$K^{-1} = \left(\frac{4\pi N}{1000}\right)\left(\frac{e^2}{DkT}\right)^3 Q(b) \qquad (1)$$

$$b = e^2/aDkT \qquad (2)$$

has been criticized on two grounds: (a) it yields different a values for the same electrolyte in different solvents. It is thus apparent that a is an arbitrarily variable parameter which probably masks specific solute–solvent interactions. Another way of describing this situation is to say that the theory predicts a linear variation of K with $D^3/Q(b)$, assuming only constant T and a. Figure 1 shows a plot of $-\log K$ vs. $\log Q(b)/D^3$ for $a = 5 \times 10^{-8}$ cm. and 25°. The solid line is the prediction of the Bjerrum theory. The dotted circles represent data for Bu_4NPi in various solvents for which data are available. The experimental values of K and D have been used; $Q(b)$ is calculated for $a = 5 \times 10^{-8}$ cm. It is apparent that the theory provides a description of ion-pair dissociation within one order of magnitude for K. Variations of 1 Å. for, say, Bu_4NPi in different solvents have been reported.

(b) The theory predicts a limiting dielectric constant beyond which no association occurs. This point has been discussed by Fuoss.[19] The Denison–Ramsey theory for low D solvents can be expressed as $K^{-1} = e^b$, where b is defined by equation 2. Fuoss and Kraus[20] have reported linear ΔF^0 vs. $1/D$ plots for several salts in dioxane–water mixtures. This implies a constant a over the entire range of solvent composition. It remains to be seen whether the same a will hold for other mixed solvents. For some solvents for which data are available, a values calculated from the experimental ΔF^0's by the Bjerrum and Denison–Ramsey equations are listed in Table V.

If the model used in the derivation of equation 2 is reasonable the parameter a calculated for Bu_4NPi should be essentially independent of solvent. As the data of Table V show this is approximately so for the three chlorobenzenes as well as ethylidene chloride. (Data for temperatures other than 25° have been omitted). a values in the other solvents are considerably higher. If account is taken of the higher "effective" dielectric constant of ethylene chloride[21,22] and propylene chloride, the a values are lowered to those calculated for the

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(16) F. Accascina, E. L. Swarts, P. L. Mercier and C. A. Kraus, *Proc. Nat. Acad. Sci.*, **39**, 917 (1953).

(17) H. L. Curry and W. R. Gilkerson, THIS JOURNAL, **79**, 4021 (1957).

(18) R. L. McIntosh, D. J. Mead and R. M. Fuoss, *ibid.*, **62**, 506 (1940).

(19) R. M. Fuoss, *ibid.*, **79**, 3301 (1957).

(20) R. M. Fuoss and C. A. Kraus, *ibid.*, **79**, 3304 (1957).

(21) J. B. Ramsey and E. L. Colichman, *ibid.*, **69**, 3041 (1947).

(22) K. H. Stern, F. H. Healey and A. E. Martell, *J. Chem. Phys.*, **19**, 1114 (1951).

TABLE V

a VALUES FOR Bu_4NPi IN SEVERAL SOLVENTS (25°) FROM THE BJERRUM AND DENISON–RAMSEY THEORIES

Solvent	D	a_B (Å.)	a_{DR} (Å.)
Anisole	4.34	4.93	6.25
m-Dichlorobenzene	5.04	4.86	5.58
Chlorobenzene	5.63	4.80	5.58
Propylene chloride	8.78	5.08	6.03
o-Dichlorobenzene	10.06	4.06	5.17
Ethylene chloride	10.23	5.77	6.52
	(11.8)[22]	4.52	5.65
Ethylidene chloride	11.01	4.52	5.56
Pyridine	12.01	7.91	6.72

chlorobenzenes. No similar explanation can be used, however, to account for the much higher a_{DR} values in anisole and pyridine. It is interesting that all the solvents in which the a_{DR} value is constant have substituted chlorines. This suggests again the possibility of specific solute–solvent interaction.

It is interesting that a values calculated from the two theories are usually not the same. With the exception of pyridine the Bjerrum a's are smaller.

A quantitative comparison of the two theories is difficult because $Q(b)$ in the Bjerrum equation is a rather complicated function of b. A good approximation can, however, be derived as follows: according to Bjerrum[3]

$$Q(b) = \int_2^b e^Y Y^{-4} \mathrm{d}Y = \frac{1}{6}\left\{e^2 - Ei(2) + Ei(b) - \frac{e^b}{b}\left(1 + \frac{1}{b} + \frac{2}{b}\right)\right\} \quad (3)$$

and

$$Ei(x) = \int_{\infty}^{-x} e^{-t}\, t^{-1}\, \mathrm{d}t \quad (4)$$

Fuoss and Kraus[23] used the asymptotic expansion

$$Ei(x) = \frac{e^x}{x}\left(1 + \frac{1}{x} + \frac{1.2}{x^2} + \frac{1.2.3}{x^3} + \dots\right) \quad (5)$$

to calculate b. It is then not difficult to show that

$$Q(b) \simeq \frac{e^b}{b^3} \quad (6)$$

If this is substituted into (1) we obtain

$$K^{-1} = \frac{4\pi N a^3}{1000}\, e^b \quad (7)$$

where we have made use of $b = e^2/aDkT$.

Hence the Bjerrum and Denison–Ramsey equations give the same result for K only if $4\pi Na^3/1000 = 1$. This is the case only for $a = 5.1 \times 10^{-8}$ cm. Now this is just in the range of the commonly studied large organic ions. For smaller ions the two theories would differ considerably. Thus, for $a = 4 \times 10^{-8}$ cm. $K^{-1}_{B} \simeq {}^1/_2 K^{-1}_{DR}$. Looked at in another way, this means that even though formally b is defined by (2) in both theories, its value and consequently that of a will in general not be the same. Fuoss[19] has suggested that the difference between the corresponding b_B and b_{DR} is an enthropy term, *i.e.*

$$K^{-1} = \exp\left(b_B + \frac{\Delta S}{R}\right) \quad (8)$$

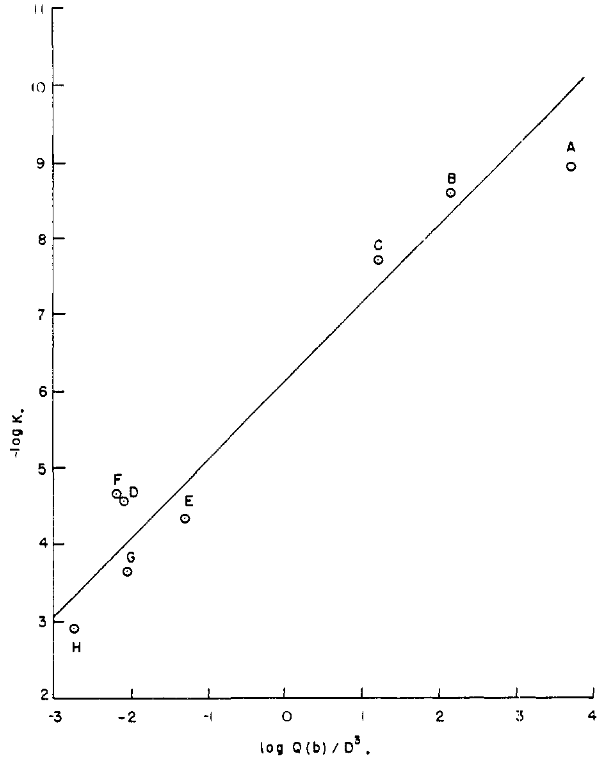

Fig. 1.—Test of the Bjerrum equation: K is the dissociation constant of Bu_4NPi. The solid line represents the theoretical curve for a = 5 Å. The dotted circles represent experimental points calculated for a = 5 Å. A, anisole; B, *m*-dichlorobenzene; C, chlorobenzene; D, *o*-dichlorobenzene; E, propylene chloride; F, ethylene chloride; G, ethylidene chloride; H, pyridine.

The Denison–Ramsey theory also predicts ΔS^0 and ΔH^0. Assuming that a is temperature-independent, they obtain

$$\Delta S^0_{DR} = (\Delta F^0/T)(\mathrm{d} \ln D/\mathrm{d} \ln T) \quad (9)$$

$$\Delta H^0_{DR} = \Delta F^0(1 + \mathrm{d} \ln D/\mathrm{d} \ln T) \quad (10)$$

Even though the assumption regarding a holds well for Bu_4NPi in the three chlorobenzenes, the predicted ΔS^0 and ΔH^0 values differ considerably from those observed. This is also true of these thermodynamic functions calculated from the Bjerrum theory. The equations have been derived previously.[5]

$$\Delta H^0_B = RT[3 + b^{-3}\exp(b/Q(b))]\,[1 + \mathrm{d} \ln D/\mathrm{d} \ln T] \quad (11)$$

$$\Delta S^0_B = R\,\{\ln K + [3 + b^{-3}\exp(b/Q(b))]\,[1 + \mathrm{d} \ln D/\mathrm{d}T]\} \quad (12)$$

Table VI lists these values. The experimental values of ΔF^0 have been used in the calculation.

TABLE VI

EXPERIMENTAL AND THEORETICAL CONSTANTS OF Bu_4NPi IN CHLOROBENZENE, *o*-DICHLOROBENZENE AND *m*-DICHLOROBENZENE AT 25°

Solvent	ΔH^0_B[a]	ΔH^0_{DR}	ΔH^0_{exp}	ΔS^0_B	ΔS^0_{DR}	ΔS^0_{exp}
m-$C_6H_4Cl_2$	2.06	1.85	6.64	−30	−33	−17
C_6H_5Cl	0.93	0.74	4.47	−32	−38	−20
o-$C_6H_4Cl_2$	−1.52	−1.78	2.91	−26	−27	−11

[a] Enthalpies are in kcal./mole, entropies in cal./°mole.

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[23] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, 55, 1019 (1933).

However, Denison and Ramsey in their original paper report good agreement in ethylene chloride and ethylidene chloride.

Gilkerson has derived an equation for K^{-1} in terms of free volume. However, it cannot be used to calculate K from experimental data or present theory because it contains a quantity E_s, the difference in solvation energy between the ion-pair and the free ions. His equation is

$$K^{-1} = \left(\frac{2\pi\mu kT}{h^2}\right)^{-3/2}(gv\sigma)^{-1}\exp(E_s/RT)\exp(\epsilon^2/aDkT) \qquad (13)$$

The terms are defined in the original paper. If we assume $a_G = a_{DR}$, it is apparent that the last exponential term is just $K_{DR}{}^{-1}$.

The entropy change predicted by this theory can be obtained by differentiation of (13) with respect to T. If this is done, assuming g, σ, v, and a temperature independent we obtain

$$\Delta S^0{}_G/R = [\ln(2\pi\mu kT/h^2)^{3/2}(gv\sigma) + 3/2] + (1/R)(\mathrm{d}E_s/\mathrm{d}T) + \frac{\epsilon^2}{ak}\left(\frac{\mathrm{d}(1/D)}{\mathrm{d}T}\right) \qquad (14)$$

This can be compared with the entropy obtained from the Bjerrum and Denison–Ramsey theories. For the former we obtain from equation 7

$$\Delta S^0{}_B/R = \ln(4\pi Na^3/1000) + \frac{\epsilon^2}{ak}\left(\frac{\mathrm{d}(1/D)}{\mathrm{d}T}\right) \qquad (15)$$

while for the latter

$$\Delta S^0{}_{DR}/R = \frac{\epsilon^2}{ak}\left(\frac{\mathrm{d}(1/D)}{\mathrm{d}T}\right) \qquad (16)$$

A comparison of (14), (15) and (16) shows why the entropy obtained from the D–R theory is so bad. Even the first term of (15) amounts to 9 e.u. for large ions. A comparison with (14) is difficult because at the present state of the theory E_s is an adjustable parameter.

One further point needs to be made. The parameter a appears in all three theories, yet methods used for the calculation of a from experimental data yield a different a depending on which theory is used. Arguments used to justify acceptance of an a value (and implicitly of the theory on which it is based) usually have rested on (1) the "reasonableness" of the value and (2) its constancy for a given salt in several solvents. However, if theories are to correspond to events in a real physical system, it would be desirable that the meaning of a be less ambiguous. One way of doing this would be to accept some measurement of dipole moment as yielding a. The dipole moment of Bu_4NPi in benzene[24] is 3.74 Å. The Bjerrum a is 1 Å. and the D–R a 2 Å. larger, whereas Gilkerson's a is 1 Å. smaller. Dipole measurements of the salt in the gas phase would certainly be of interest.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Acid–Base Equilibrium Constants for 2,4-Dinitrophenol and Some Aliphatic Amines in Non-aqueous Solvents

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Equilibrium constants for ion-pair formation determined spectrophotometrically for 2,4-dinitrophenol and some primary, secondary and tertiary amines show that the solvent has a marked effect on the order of basicity. Tertiary amines are the strongest bases in chloroform, chlorobenzene and ethylene dichloride. Secondary amines are the strongest bases in *n*-heptane, benzene and dioxane, while primary amines are the strongest bases of the three types in ethyl acetate. The importance of specific solvation of the acidic protons of an ammonium ion is shown by the effect of small amounts of added substances. It is estimated that each replacement of H by CH_3 in $NH_4{}^+$ leads to a loss of 8 kcal. in the heat of hydration.

Consideration of inductive effects alone would predict that the base strength of aliphatic amines should increase in the order primary, secondary, tertiary, the tertiary being the strongest base. However, it is well known that the base strength of amines, as observed in water, does not follow this order. Trimethylamine is the weakest base in the methylamine series.[2] Diethylamine is a stronger base than triethylamine and, in general, secondary amines are the strongest bases.

To account for the orders observed, Brown, Bartholomay and Taylor[3] have advanced the theory of B- or back strain. The theory involves the assumption that the bond angles in the free amine are somewhat greater than the normal tetrahedral value. In order to demonstrate basicity a fourth group must be introduced into the vacant position on the nitrogen atom, thereby forcing the molecule into a tetrahedral configuration. The methyl, or other alkyl groups in tertiary amines, are thus crowded toward each other setting up a strain which reduces the stability of the addition compound. Hence, even a proton as a reference acid can cause B-strain.

Others[4-6] have attributed the tertiary amine weakness, as found in water, to solvation effects. The argument here is that the solvation or hydration energy of the ammonium ion decreases with in-

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[1] (a) Taken in part from a dissertation submitted by D. C. Vogelsong to the graduate school of Northwestern University in partial fulfillment of the requirements for the Ph.D. degree, August, 1956; (b) predoctoral fellow, E. I. du Pont de Nemours and Co., 1955–1956.

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