410×10^{-76} erg cm.^{8} for NaX. The difference in lattice energy is therefore

$$\Delta U = \Delta C/r^6 + \Delta D/r^8 \simeq 1750 \text{ cal./mole} \quad (9)$$

where $r = 3.08$ Å. This figure is not yet the difference in ΔH^0, for there is also a difference in dispersion energy in the aqueous solution. To estimate this second term, we take the well known Slater–Kirkwood–Buckingham formula[19] for the dispersion energy between two unlike molecules

$$u = -cr^{-6}; c = (3\,hen^{1/2}/4\pi m^{1/2})\alpha_1\alpha_2/(\alpha_1^{1/2} + \alpha_2^{1/2}) \quad (10)$$

where α_1, α_2 are the polarizabilities, e and m are electronic charge and mass, h is Planck's constant and n is the number of outer-shell electrons, taken as 8. We obtain $c \cong 150 \times 10^{-60}$ erg cm.^{6} for H_2O–X^- and $c \simeq 130 \times 10^{-60}$ erg cm.^{6} for H_2O–BH_4^-. Assuming six water molecules in the first hydration sphere at a distance of 3.5 Å. from the ion center, and estimating the contribution of more distant water molecules as about that of two more nearest neighbors, we find

$$\Delta U \simeq 8 \times 20 \times 10^{-60}/(3.5 \times 10^{-8})^6 \text{ erg./ion} \simeq 1250 \text{ cal./mole} \quad (11)$$

The difference between eq. 9 and 11, which should be the difference in ΔH^0 and ΔF^0 of solution between NaX and $NaBH_4$, is thus estimated at about 500 cal., in somewhat fortuitously good agreement with observation. Clearly our calculation contains some rather arbitrary assumptions, particularly in the evaluation of the solution term of eq. 11, so that the above result should be regarded merely as indicating order of magnitude. Additional instability of solid $NaBH_4$ compared to NaX could arise from extra repulsion due to the non-spherical nature of BH_4^-, but from the low temperature (190°K.) of the order–disorder transition[3,16] we believe this cannot be a major effect. A pragmatic test of the above considerations could be made by comparing the solubility products of the other alkali borohydrides in the same way to those of the respective alkali halides, but at present data are not available.

It appears that the difference in dispersion energy discussed above also persists largely in the dihydrate, for the value of ΔF^0 for reaction (1) is very close to that obtained by interpolation on a curve for the sodium halide dihydrates. Hence $NaBH_4 \cdot 2H_2O$ is also more soluble than the hypothetical $NaX \cdot 2H_2O$. We may thus understand the low temperature (35°) of the triple point, dihydrate–anhydrous salt–solutions, for $NaBH_4$ as compared to 0.15° for NaCl, 50.7° for NaBr and 64.3° for NaI,[20] and also why the solid solutions of $NaBH_4 \cdot 2H_2O$ with $NaBr \cdot 2H_2O$ and $NaI \cdot 2H_2O$ show considerable departure from ideality.

We thank Dr. M. D. Banus of Metal Hydrides, Inc., for the samples of the higher alkali borohydrides.

CAMBRIDGE, MASS.

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[19] See, for example, H. Margenau, *Phys. Rev.*, **56**, 1000 (1939).

[20] Gmelin's "Handbuch der Anorganischen Chemie," Vol. 8, Teil 21.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY]

Thermodynamics of Ion Pair Formation in Some Non-aqueous Solvents[1]

BY KURT H. STERN[2] AND ARTHUR E. MARTELL

RECEIVED OCTOBER 1, 1954

Ion conductances have been measured for several quaternary ammonium salts in three alkyl chloride solvents over a range of temperature. The results have been used to calculate thermodynamic functions associated with ion-pair formation and to interpret these in terms of solute–solvent interactions.

It has long been recognized that to account for the mobility of ions and differences in the dissociation constants of ion pairs in different solvents not only the macroscopic physical constants such as viscosity and dielectric constant are of importance, but that the specific constitutional and structural factors of solvents and solutes must also be considered. For instance, in the case of ethylene chloride and ethylidene chloride we have an example of two isomeric solvents with practically the same dielectric constant and similar chemical constitution but with quite different boiling points, viscosities and densities. These solvents offer, therefore, an unusual opportunity to measure the effects of constitutional factors on the properties of solutions. Healey and Martell[3] have measured ion conductances of several salts in ethylidene chloride and Kraus and co-workers[4–8] have obtained corresponding data in ethylene chloride. Some of the structural factors involved in solute–solvent interactions in these two solvents have been discussed previously by Stern, Healey and Martell.[9]

In the present work it was considered of interest to determine whether the thermodynamic functions which can be calculated from the temperature dependence of the ion-pair dissociation constants offer any significant correlation with the forces operative in electrolytic solutions. Almost no work of this kind has been done for neutral electrolytes in non-aqueous solvents. The only exception is a series of measurements by Bien, Fuoss and

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[1] In part from the Ph.D. dissertation of K. H. Stern. Presented before the Division of Physical and Inorganic Chemistry, 124th meeting, American Chemical Society, September, 1953.

[2] Department of Chemistry, University of Arkansas, Fayetteville, Ark.

[3] F. H. Healey and A. E. Martell, THIS JOURNAL, **73**, 3296 (1951).

[4] D. L. Fowler and C. A. Kraus, *ibid.*, **62**, 2237 (1941).

[5] L. F. Gleysteen and C. A. Kraus, *ibid.*, **69**, 451 (1947).

[6] L. M. Tucker and C. A. Kraus, *ibid.*, **69**, 454 (1947).

[7] E. R. Kline and C. A. Kraus, *ibid.*, **69**, 814 (1947).

[8] W. E. Thompson and C. A. Kraus, *ibid.*, **69**, 1016 (1947).

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

Kraus[10] on tetrabutylammonium picrate and nitrate in anisole from −33 to 95°. However, while these authors determined values of K, the dissociation constant of the ion pair, they did not calculate the thermodynamic functions.

In view of the lack of information in this field the conductances at several temperatures of some symmetrical tetraalkylammonium picrates were measured in ethylene chloride, ethylidene chloride and propylene chloride, a solvent of slightly lower dielectric constant but similar in structure to ethylene chloride.

Experimental Part

Apparatus.—The conductance bridge is a modification[11] of the design described by Foy and Martell.[12] A 0-20,000 cycle audio oscillator (General Radio No. 913-G) was used in all measurements. Temperature of the conductance cell was kept constant at the temperatures of the experiment within 0.01°. The conductance cell was designed according to the specifications of Kraus and co-workers[13] and the cell constant was determined by measurement of the conductance of tetraamylammonium picrate in ethylene chloride at 25° taking as standard the measurements of Tucker and Kraus.[6] The value thus determined was 0.0335. As a check the conductance of several other tetraalkyl ammonium picrates were measured in ethylene chloride at 25°. In all cases the values obtained agreed within one per cent. with those found by Tucker and Kraus. It was assumed that the cell constant would not vary significantly over the temperature range.

Solvents.—The purification of all three solvents was carried out as described by Healey and Martell[3] for ethylidene chloride. The specific conductance of all the solvents was less than 10^{-9}. Both ethylene and propylene chloride were quite stable, but ethylidene chloride had to be used within a few hours of distillation. Viscosity data for ethylene chloride and ethylidene chloride were kindly supplied by the Dow Chemical Company. Data for propylene chloride were obtained using an Ostwald viscosimeter and doubly distilled water as the calibrating liquid. Density data for all three solvents were supplied by the Dow Chemical Company. Physical constants used in this work are listed below. The three values given for each property refer to 5.69, 25.00 and 35.00°, respectively. For ethylidene chloride only the values for the lower two temperatures are included. Ethylene chloride: density (g./ml.), 1.269, 1.2455, 1.229; viscosity (cps.), 1.03, 0.735, 0.687; dielectric constant, 11.35, 10.23, 9.65. Ethylidene chloride: density, 1.193, 1.166; viscosity, 0.615, 0.466; dielectric constant, 11.01, 10.00. Propylene chloride: density, 1.174, 1.153, 1.141; viscosity, 1.005, 0.795, 0.700; dielectric constant, 9.20, 8.78, 7.90.

The dielectric constant of ethylene chloride has been measured by Heston, Hennelly and Smyth[14] from 1 to 55° and by Kraus[15] at 25°. At 25° these authors differ, Kraus giving D = 10.23 and Smyth 10.16. When D is plotted against temperature a straight line is obtained if 10.23 is used at 25°. This value was selected. The dielectric constant of ethylidene chloride has been measured[16] at 25°. For other temperatures and for propylene chloride the dielectric constant was measured by a substitution method, using a General Radio bridge (650-A) as null indicator, and a precision condenser (722-D). The dielectric cell consisted of two concentric copper cylinders mounted a fixed distance apart and placed in a double-walled glass cylinder through which the thermostating liquid was pumped from a reservoir maintained at $t \pm 0.1°$.

Salts.—The salts used had been prepared by previous workers. Melting points were in good agreement with values in the literature.

Results

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

TABLE I

CONDUCTANCE DATA

A. Ethylene Chloride

5.69° Tetramethylammonium picrate $C \times 10^4$ (mole/l.)	Λ	5.69° Tetraethylammonium picrate $C \times 10^4$ (mole/l.)	Λ
3.316	19.37	3.412	30.87
2.044	22.70	3.179	31.44
1.179	26.91	2.255	33.67
0.5141	33.43	1.483	36.41
0.3274	36.70	1.382	37.03
		0.8721	39.78

5.69° Tetrapropylammonium picrate		5.69° Tetrabutylammonium picrate	
2.266	31.73	3.212	27.75
1.258	35.13	1.937	30.53
0.8658	37.03	1.379	32.19
.6157	38.58	1.124	33.34
.2797	41.65	0.7878	34.83
.1845	42.73	0.7901	36.77

5.69° Tetraamylammonium picrate		35.00° Tetrabutylammonium picrate	
0.8456	31.00	3.043	37.68
.4266	33.41	2.055	41.11
.3813	33.77	1.349	44.69
.0073	35.09	0.9129	47.77
.1817	35.48		
.0819	36.60		

B. Propylene chloride

Tetrabutylammonium picrate

5.69°		25°		35.00°	
3.525	11.17	4.361	12.19	2.935	14.60
2.200	13.13	3.133	13.75	1.773	17.52
1.837	13.86	2.881	14.16	1.119	20.55
1.321	15.49	1.994	16.14	0.7041	23.91
0.8184	17.86	1.093	16.43	0.4423	27.40
0.7528	18.19	1.211	19.23		
0.4690	20.91	0.8528	21.54		
		0.6175	23.91		

C. Ethylidene Chloride

5.69°

Tetrabutylammonium picrate

3.453	28.73	1.072	40.86
2.456	32.18	0.7036	45.59
2.106	33.52	0.6006	47.21
1.922	34.58		

Discussion

In the range of concentration listed in Table II the Shedlovsky conductance function[17] gives a lin-

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[10] G. S. Bien, R. M. Fuoss, C. A. Kraus, THIS JOURNAL, **56**, 1860 (1934).

[11] K. H. Stern, Ph.D. Dissertation, Clark University, 1953.

[12] W. L. Foy and A. E. Martell, *Rev. Sci. Instruments*, **19**, 628 (1948).

[13] N. L. Cox, C. A. Kraus and R. M. Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

[14] W. M. Heston, E. S. Hennelly and C. P. Smyth, THIS JOURNAL, **72**, 2071 (1950).

[15] C. A. Kraus and R. M. Fuoss, *ibid.*, **55**, 21 (1933).

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

[17] T. Shedlovsky, *J. Franklin Inst.*, 735 (1938).

ear relationship. Thus, large scale plots can be used to determine Λ_0, the equivalent conductance at infinite dilution. From the slope of the plot the value of K, the dissociation constant of ion pairs, was determined. Values of Λ_0 and K are listed in Table II.

TABLE II

VALUES OF Λ_0 AND DISSOCIATION CONSTANTS

A. Ethylene Chloride

Salt	Λ_0 5.69°	Λ_0 25°(a)	Λ_0 35°	$K \times 10^4$ 5.69°	$K \times 10^4$ 25°[a]	$K \times 10^4$ 35°
Me_4NPi	53.0	73.81	..	0.508	0.32	..
Et_4NPi	51.0	69.44	..	2.33	1.59	..
Pr_4NPi	46.2	62.66	..	2.90	1.94	..
Bu_4NPi	42.9	57.40	63.1	3.01	2.26	2.01
Am_4NPi	38.4	54.50	..	3.07	2.38	..

B. Propylene Chloride–Bu_4NPi

t (°C.)	Λ_0	$K \times 10^5$
5.69	36.4	3.22
25.00	51.3	2.67
35.00	52.0	2.30

C. Ethylidene Chloride–Bu_4NPi

t (°C.)	Λ_0	$K \times 10^5$
5.69	73.0	6.42
25.00[b]	96.9	4.54

[a] Reference 5. [b] Reference 2.

The corresponding thermodynamic functions were calculated by standard methods and are listed in Table III. Since in all cases investigated ΔH^0 and ΔS^0 were constant over the temperature range of this study only the average value of these functions is given.

TABLE III

THERMODYNAMIC FUNCTIONS FOR ION-PAIR DISSOCIATION

Salt	ΔF^0 (5.69°) (kcal./mole)	ΔF^0 (25°) (kcal./mole)	ΔF^0 (35°) (kcal./mole)	ΔH^0 (kcal./mole)	ΔS^0, e.u.
A. Ethylene Chloride					
Me_4NPi	5.48	6.15	..	−5.66	−40
Et_4NPi	4.63	5.18	..	3.31	28
Pr_4NPi	4.51	5.05	..	3.39	28
Bu_4NPi	4.49	4.95	5.21	2.35	25
Am_4NPi	4.32	4.93	..	2.30	24
B. Propylene Chloride					
Bu_4NPi	5.73	6.24	6.54	−1.80	−27
C. Ethylidene Chloride					
Bu_4NPi	5.35	5.93	..	−2.96	−30

In connection with the values of Λ_0 and K listed in Table II the following generalizations may be noted.

a. In ethylene chloride at both 5.69 and 25° Λ_0 decreases with increasing ionic size, as would be expected.

b. The ratio $\Lambda_{25}/\Lambda^0_{5.7}$ is virtually constant throughout the series in all three solvents. Its value is 1.35 ± 0.05. Hence the change in ion mobility with temperature can be attributed entirely to the corresponding change in solvent viscosity since $\eta^0_{5.7}/\eta^0_{25} = 1.40$ for both ethylene chloride and propylene chloride. For ethylidene chloride this ratio is 1.48.

c. In ethylene chloride K increases with increasing cation size, as would be expected, at both 5.69 and 25°. From an examination of the data for tetrabutylammonium picrate it is also evident that, at the temperatures studied, the ratio of the dissociation constants in any two of the three solvents is approximately constant. Thus, K is about five times as large in ethylene chloride as in ethylidene chloride, and nine times as large as in propylene chloride. In the latter case the lower dielectric constant of propylene chloride is clearly the major factor. Indeed, measurements of isoamylammonium picrate in dioxane–water mixtures[18] show that when the dielectric constant of the medium is 10, a decrease of 10% in the dielectric constant results in an approximately tenfold reduction in K.

Before proceeding to an examination of the thermodynamic data in Table III it is of interest to list the corresponding functions calculated from the data of Bien, Fuoss and Kraus for tetrabutylammonium picrate and nitrate in anisole.[10]

Salt	K	ΔF^0 (kcal./mole)	ΔH^0 (kcal./mole)	ΔS^0(e.u.)
Bu_4NNO_3	9.2×10^{-11}	+14.1	+10.1	−36
Bu_4NPi	11.5×10^{-10}	12.2	3.83	−28

It thus appears that while ΔS^0 is relatively insensitive to changes in solvent, ΔH^0 for the dissociation of an ion-pair changes with the solvent, even to the extent of changing sign. The constancy of ΔS^0 can be explained in terms of ideas suggested by Gurney.[19] When an ion-pair dissociates, charge separation is increased, resulting in a change of entropy in the dielectric. This entropy change depends only on $d/dT(1/D)$ when the salt is kept constant. For tetrabutylammonium picrate in ethylene chloride, propylene chloride and anisole the value of this quantity is the same, 6×10^{-4}, and ΔS^0 is indeed constant. For the same salt in ethylidene chloride the value is 8×10^{-4}, resulting in a slightly larger value of ΔS^0.

More difficult to understand is the change in the sign of ΔH^0 when going from the alkyl chlorides to anisole. It would be expected that work must always be carried out in separating the constituents of an ion pair against Coulomb forces. However, it is possible to account for the results obtained by including the solvent in a consideration of ion-pair dissociation. To do this it is convenient to write the dissociation of a solvated ion pair as a series of stepwise reactions.

$$(AB)^0\,(Y)_x \rightleftarrows (AB)^0 + xY \qquad (1)$$

$$(AB)^0 \rightleftarrows A^+B^- \qquad (2)$$

$$A^+ + B^- + (s+z)Y \rightleftarrows A^+(Y)_s + B^-(Y)_z \qquad (3)$$

where Y refers to the solvent molecules involved. To explain the fact that the Bjerrum treatment, which involves the assumption that the solvent is a uniform dielectric, accounts satisfactorily for the measured values of K, reaction (2) is postulated to be the step involving the major amount of free energy change. Now, it would be expected that ΔH_2 is always positive since work must always be done to overcome the electrostatic attraction of oppositely charged ions. However, $\Delta H_1 << \Delta H_3$ since ion pair–solvent interaction involves dipole forces which are much weaker than those operating between ions and dipoles. Hence, as an approximation ΔH^0 may be assumed to depend on ΔH_2 and

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[18] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476 (1933).

[19] R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., New York, N. Y., 1953.

ΔH_3 only. Then the following two possibilities may be distinguished

$$\text{(a)}\quad \Delta H^0 > 0 \text{ or } \Delta H_2 + \Delta H_3 > 0$$
$$\text{(b)}\quad \Delta H^0 < 0 \text{ or } \Delta HH_2 + \Delta H_3 < 0$$

Therefore, in (a) $\Delta H_2 > \Delta H_3$ but ΔH_3 may be positive or negative. However, in (b) $\Delta H_2 + \Delta H_3 < 0$ and hence ΔH_3 must be negative. This implies that energy is released by ion solvation.

If these concepts are applied to the results of this study, they are found to be fairly consistent with the facts. The results for the series of tetraalkyl ammonium picrates will be considered first. ΔH^0 is most highly negative for tetramethylammonium picrate. Since ΔH_2 for this salt would be expected to be most highly positive it follows that ΔH_3 is most highly negative. This is reasonable since the smallest ions are the most highly solvated.

Data for tetrabutylammonium picrate in the three solvents studied show that ΔH^0 is most highly negative in ethylene chloride and least so for propylene chloride. Since ΔH_2 is independent of solvent it follows that ΔH_3 becomes increasingly negative in the order propylene chloride < ethylene chloride < ethylidene chloride. This implies that ethylidene chloride is the strongest "solvator" of tetrabutylammonium picrate, and propylene chloride the weakest.

The case of anisole is somewhat different. For tetrabutylammonium picrate in that solvent ΔH^0 is positive. Since ΔH_2 should be the same as for the three alkyl halides it follows that ΔH_3 may be either positive or negative. Now, ΔH^0 for tetrabutylammonium nitrate in anisole is much more highly positive than for tetrabutylammonium picrate. It would be expected that ΔH_2 would be more positive for tetrabutylammonium nitrate since the nitrate ion is smaller than the picrate ion and hence more tightly bound to the cation. However, no relation can be derived on this basis for the relative magnitudes of ΔH_3 for the two salts, and hence no statement can be made as to the relative solvation of the nitrate and picrate ions in anisole. Indeed, it follows from the mathematical considerations involved that the relative ion solvation can be determined by this method only in those cases in which $\Delta H^0 < 0$.

It thus appears that in those solvents having the same value of $\mathrm{d}/\mathrm{d}T(1/D)$ the extent of dissociation for a given salt depends only on the value of ΔH^0. Since for most solvents the temperature coefficient of dielectric constant is negative it follows that the entropy contribution to ΔF^0 is unfavorable to dissociation. Hence the extent of dissociation will be largely determined by ΔH^0. When ΔH^0 is negative it may be concluded that the solvated ions represent a more stable arrangement than the solvated ion pair, *i.e.*, the ion–solvent bond is stronger than the ion pair–solvent bond. When ΔH^0 is positive the reverse is true.

At present we do not have sufficient information to calculate such solute–solvent interactions from the fundamental properties of solute and solvent and to compare these values with experiment. Such a study, using simpler solvents, is now in progress.

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WORCESTER, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KENTUCKY]

Solvents Having High Dielectric Constants. II. Solutions of Alkali Halides in N-Methylacetamide from 30 to 60°[1a,b]

BY LYLE R. DAWSON, PAUL G. SEARS AND RICHARD H. GRAVES

RECEIVED AUGUST 30, 1954

Conductances, densities and viscosities of solutions of lithium chloride and of potassium and sodium chlorides, bromides and iodides in N-methylacetamide have been measured within the temperature range from 30 to 60° for concentrations which ranged from 5×10^{-4} to 1.0 or 2.0 molar. Kohlrausch plots for all of the systems exhibit relatively good agreement with the Onsager limiting equation to concentrations of 0.01 molar or more. Plots of the product of the equivalent conductance and the square root of the relative viscosity of the solution *versus* the square root of the concentration yield straight lines to 0.3 molar or above. The Kohlrausch law of independent ion mobilities is shown to be valid in these solutions.

The first paper of this series[2] described the electrical conductance of potassium chloride in formamide, which has a dielectric constant ranging from 118 to 103 within the temperature interval 3 to 40°.[3] Agreement with the limiting Onsager equation was shown to about 0.01 N where the slope of the Λ *vs.* $\sqrt{C}$ curve became less negative than the theoretical value. This was interpreted as evidence of the practically complete absence of ion association. However, as the concentration increased the plots became nearly linear, apparently as a consequence of an increase in viscosity which tended to counteract the concave-upward pattern observed with strong electrolytes in water.

The study reported herein is the primary phase of an investigation of the application of modern theories of solutions in areas hitherto unexplored in which the solvents have very high dielectric constants.[4] The present paper describes the behavior of several alkali halides in N-methylacetamide.

Experimental

Apparatus.—Conductances were measured at 1000 cycles with a shielded Jones bridge. Numerous additional measurements throughout the investigation at frequencies

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(1) (a) Presented at the 126th Meeting of the American Chemical Society in New York, September, 1954; (b) this work was supported in part by a contract with the Office of Ordnance Research.

(2) L. R. Dawson, T. M. Newell and W. J. McCreary, THIS JOURNAL, **76**, 6024 (1954).

(3) G. R. Leader, *ibid.*, **73**, 856 (1951).

(4) G. R. Leader and J. F. Gormley, *ibid.*, **73**, 5731 (1951).