relative to TMS. In our studies (*cf.* thianthrene and *trans* dioxide) these shifts were not observed which, if these solvent shifts can be applied to our solutions, means that the α and β protons of thianthrene and the *trans* dioxide both shift to high field as the temperature is raised by the same amount as the solvent! We hasten to note that whatever the origin of this effect, the α and β protons are equally affected in *both the thianthrene and the trans dioxide.* We, therefore, expect no change in $\nu_\alpha - \nu_\beta$ in the *cis* compound either, and our conclusions regarding the existence of inversion in these molecules are still valid.

Summary

In conclusion we can summarize those points which lead us to conclude that thianthrene and its derivatives undergo rapid inversion in solution. (1) There is no apparent reason for a high barrier to inversion. (2) The spectrum of the *trans* dioxide is that of an A_2B_2 system of spins. (3) Only the α protons of the *cis* dioxide exhibit a temperature-dependent resonance energy. (4) This temperature dependence is the same for the two solvents tetrachloroethane and chloroform when a correction for chloroform hydrogen bonding to an aromatic ring is applied. (5) The chemical-shift difference of α and β protons is temperature independent for both thianthrene and the *trans* dioxide. (6) The direction of the α resonance shift indicates the same shielding effect of an adjacent sulfoxide group as for a carbonyl group in N-methylamides.

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Hydration of Ions in Acetonitrile[1]

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Contribution from the School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received November 25, 1966*

Abstract: Equations have been derived which permit the calculation of the hydration constants from the solubility product of the slightly soluble salt and the total ionic solubility in the presence of varying concentrations of water. From the experimentally determined total ionic solubility the hydration constant(s), $K^f{}_{I_{xw}^\pm}$, of the following monovalent cations, Li^+, Na^+, K^+, and Cs^+, and of the monovalent anions, perchlorate, periodate, methanesulfonate, nitrate, 3,5-dinitrobenzoate, salicylate, picrate, and 3,5-dinitrophenolate, were determined in acetonitrile at 25°. For K , Cs , IO_4^-, ClO_4^-, and picrate, $x = 1$. For the other ions x is equal to 1 and to 2. The values of the constants are listed in Table I. The total ionic solubility has been estimated from the electrical conductance of the saturated solutions, making assumptions specified in the paper. The individual hydration constants of the 3,5-dinitrophenolate ion have been determined by the above method and also by an independent spectrophotometric method. The $K^f{}_{I_w^\pm}$ values by both methods were found to be in satisfactory agreement.

Upon addition of water to a solution of an ionized salt in acetonitrile (AN), an interaction between the ions and water with the formation of partially hydrated ions may be expected (eq 1) in which $I_s^\pm$ is a solvated (or

$$I_s^\pm + xH_2O \rightleftharpoons I_{xw}^\pm \tag{1}$$

unsolvated) monovalent cation or anion. In addition hydration of the undissociated salt may also occur; this will be considered in a subsequent paper.

Infrared spectra of water in carbon tetrachloride show the antisymmetric (ν_3) and symmetric (ν_1) -OH stretching bands at 3700 and 3610 cm^{-1}, respectively, which, upon addition of AN,[2] are replaced by ν_3 and ν_1 bands at 3640 and 3545 cm^{-1}, respectively, which are attributed to a hydrogen-bonded complex involving two molecules of AN to one of water. Identical spectra have been observed in 0.045 *M* solutions of water in AN as solvent;[3] apparently, the species designated as H_2O in reaction 1 has the structure $CH_3C{\equiv}N\cdots HOH\cdots N{\equiv}CCH_3$, suggesting that water is monomeric in AN.

In the present paper the equilibrium constant (or constants) of reaction 1 has been determined for several monovalent cations and anions. This was done by measuring conductometrically the ionic solubility of a slightly soluble salt in AN in the presence of known concentrations of water. The mode of calculation of the constant (or constants) is presented in the following section. It was desirable to determine the constant of reaction 1 by an independent method. In previous work[4] it was found that the red 3,5-dinitrophenolate ion (I_s^-) heteroconjugates with water with the formation of a yellow ion I_{mw}^-. The equilibrium constants have been measured spectrophotometrically, m being equal to 1 and 2. From solubility measurements of potassium 3,5-dinitrophenolate, the individual "hydration" constants of the cation and the anion were found. From the independently determined constant for the phenolate ion a check of the reliability of the solubility method was obtained.

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[1] This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-28-63.

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Ionic Hydration Constants Derived from Solubility Data. In the present study, both the monovalent cation and anion of the sparingly soluble salt, MA, are considered to become hydrated in AN solutions containing water. The hydration of the cation and anion involving n and m molecules of water, respectively, may be represented by the following equilibria

$$\mathrm{M_s}^+ + n\mathrm{H_2O} \rightleftharpoons \mathrm{M}_{n\mathrm{w}}^+$$

$$\mathrm{A_s}^- + m\mathrm{H_2O} \rightleftharpoons \mathrm{A}_{m\mathrm{w}}^-$$

with the corresponding formation constants

$$K^{\mathrm{f}}_{\mathrm{M}_{n\mathrm{w}}^+} = \frac{[\mathrm{M}_{n\mathrm{w}}^+]}{[\mathrm{M_s}^+][\mathrm{H_2O}]^n} \qquad f_{\mathrm{M}_{\mathrm{w}n}^+} = f_{\mathrm{M_s}^+} \qquad (2a)$$

$$K^{\mathrm{f}}_{\mathrm{A}_{m\mathrm{w}}^-} = \frac{[\mathrm{A}_{m\mathrm{w}}^-]}{[\mathrm{A_s}^-][\mathrm{H_2O}]^m} \qquad f_{\mathrm{A}_{m\mathrm{w}}^-} = f_{\mathrm{A_s}^-} \qquad (2b)$$

where the subscripts s and w denote AN and water, respectively.

In saturated solutions of MA in AN containing water, the electroneutrality relation is

$$[\mathrm{M_s}^+] + \cdots [\mathrm{M}_{n\mathrm{w}}^+] = [\mathrm{A_s}^-] + \cdots [\mathrm{A}_{m\mathrm{w}}^-] \qquad (3)$$

and the solubility product of MA is given by

$$K_{\mathrm{sp}} = [\mathrm{M_s}^+][\mathrm{A_s}^-]f^2 \qquad f_{\mathrm{M_s}^+} = f_{\mathrm{A_s}^-} = f \qquad (4)$$

Substituting eq 2 and 3 into 4 and solving for $[\mathrm{M_s}^+]$ in the presence of water, eq 5 results. The total ionic solubility, $[\mathrm{M}^+]_\mathrm{t}$, is found by combining eq 1–3 and 5.

$$[\mathrm{M_s}^+] = \frac{1}{f}\sqrt{\frac{K_{\mathrm{sp}}\left\{1 + \sum_1^m K^{\mathrm{f}}_{\mathrm{A}_{m\mathrm{w}}^-}[\mathrm{H_2O}]^m\right\}}{\left\{1 + \sum_1^n K^{\mathrm{f}}_{\mathrm{M}_{n\mathrm{w}}^+}[\mathrm{H_2O}]^n\right\}}} \qquad (5)$$

$$f^2[\mathrm{M}^+]_\mathrm{t}^2 = K_{\mathrm{sp}}\left\{1 + \sum_1^m K^{\mathrm{f}}_{\mathrm{A}_{m\mathrm{w}}^-}[\mathrm{H_2O}]^m\right\} \times \left\{1 + \sum_1^n K^{\mathrm{f}}_{\mathrm{M}_{n\mathrm{w}}^+}[\mathrm{H_2O}]^n\right\} \qquad (6)$$

Upon expansion eq 6 assumes the form

$$f^2[\mathrm{M}^+]_\mathrm{t}^2 = K_{\mathrm{sp}}\{1 + A[\mathrm{H_2O}] + B[\mathrm{H_2O}]^2 + C[\mathrm{H_2O}]^3 + D[\mathrm{H_2O}]^4 + \cdots\} \qquad (7)$$

The coefficients A, B, etc. in eq 7 are related to the individual formation constants of the hydrated ions at various hydration numbers of the cation and anion, *i.e.*, n and m, respectively, as follows.

$$m = 0, n = n\colon \quad A = K^{\mathrm{f}}_{\mathrm{M_w}^+};\ B = K^{\mathrm{f}}_{\mathrm{M_{2w}}^+};\ C = K^{\mathrm{f}}_{\mathrm{M_{3w}}^+} \qquad (8a)$$

$$m = 1, n = 1\colon \quad A = K^{\mathrm{f}}_{\mathrm{M_w}^+} + K^{\mathrm{f}}_{\mathrm{A_w}^-};\ B = K^{\mathrm{f}}_{\mathrm{M_w}^+}K^{\mathrm{f}}_{\mathrm{A_w}^-} \qquad (8b)$$

$$m = 1, n = 2\colon \quad A = K^{\mathrm{f}}_{\mathrm{M_w}^+} + K^{\mathrm{f}}_{\mathrm{A_w}^-};\ B = K^{\mathrm{f}}_{\mathrm{M_w}^+}K^{\mathrm{f}}_{\mathrm{A_w}^-} + K^{\mathrm{f}}_{\mathrm{M_{2w}}^+};\ C = K^{\mathrm{f}}_{\mathrm{A_w}^-}K^{\mathrm{f}}_{\mathrm{M_{2w}}^+} \qquad (8c)$$

$$m = 2, n = 2\colon \quad A = K^{\mathrm{f}}_{\mathrm{M_w}^+} + K^{\mathrm{f}}_{\mathrm{A_w}^-};\ B = K^{\mathrm{f}}_{\mathrm{A_{2w}}^-} + K^{\mathrm{f}}_{\mathrm{M_w}^+}K^{\mathrm{f}}_{\mathrm{M_w}^-} + K^{\mathrm{f}}_{\mathrm{M_{2w}}^+};\ C = K^{\mathrm{f}}_{\mathrm{M_w}^+}K^{\mathrm{f}}_{\mathrm{A_{2w}}^-} + K^{\mathrm{f}}_{\mathrm{M_{2w}}^+}K^{\mathrm{f}}_{\mathrm{A_w}^-};\ D = K_{\mathrm{M_{2w}}^+}K^{\mathrm{f}}_{\mathrm{A_{2w}}^-} \qquad (8d)$$

In the application of eq 7, the following assumptions are made. (a) Water to a concentration of 2 M (usually the concentration of water was less than 2 M) is considered monomeric, and the activity of water is taken to be equal to the equilibrium concentration. (b) Only the anhydrous salt, MA, is present in the solid phase, and the solubility product, K_{sp}, is considered constant over the concentration range of water taken. (c) Independent hydration of the ions is assumed, which implies that the hydration constants of a given ion be independent of the nature of the oppositely charged ion.

In addition, the validity of the limiting Debye–Hückel relation, from which ionic activity coefficients were evaluated, was assumed. The total number of water molecules coordinated to both ions of the salt, $m + n$, corresponds to the degree of the polynomial in eq 7 which describes the experimental solubility data.

In the Experimental Section the hydration of the ions of a series of salts, which have either a cation or an anion in common, has been determined. It was found that all ions form at least a monohydrate ($m = n = 1$).

For salts with only monohydrated ions, a plot of $f^2 \cdot [\mathrm{M}^+]_\mathrm{t}^2$ *vs.* $[\mathrm{H_2O}]$ is linear at low water concentration with intercept K_{sp} and slope AK_{sp}. The coefficient B is found from the above plot at higher water concentrations and $K^{\mathrm{f}}_{\mathrm{M_w}^+}$ and $K^{\mathrm{f}}_{\mathrm{A_w}^-}$ are calculated from the coefficients A and B using eq 8b. The agreement in $K^{\mathrm{f}}_{\mathrm{M_w}^+}$ (or $K^{\mathrm{f}}_{\mathrm{A_w}^-}$) in the series having a common cation (or anion) provided a good check of the reliability of the method. For salts for which $m + n$ is greater than 2, the coefficients A, B, and C were evaluated from the plot of $f^2[\mathrm{M}^+]_\mathrm{t}^2$ *vs.* $[\mathrm{H_2O}]$ using a set of simultaneous equations (eq 7). For such salts the plots, at low water concentrations, also are linear, thus yielding K_{sp} and A, the latter being equal to the sum $K^{\mathrm{f}}_{\mathrm{M_w}^+} + K^{\mathrm{f}}_{\mathrm{A_w}^-}$, as when $n = m = 1$.

When both a mono- and dihydrate anion are formed ($m = 1$ and $m = 2$), $K^{\mathrm{f}}_{\mathrm{M_w}^+}$ is a root of the following cubic equation

$$K^{\mathrm{f}^3}_{\mathrm{M_w}^+} - AK^{\mathrm{f}^2}_{\mathrm{M_w}^+} + BK^{\mathrm{f}}_{\mathrm{M_w}^+} - C = 0 \qquad (9)$$

which is derived by solving the simultaneous equations in (8c) for $K^{\mathrm{f}}_{\mathrm{M_w}^+}$.

For salts with $n = m = 2$, the coefficients A–D can be derived from the $f^2[\mathrm{M}^+]_\mathrm{t}^2$ *vs.* $[\mathrm{H_2O}]$ plot only with difficulty. Therefore, the values of the hydration constants of the cation were determined, first using a salt of the same cation whose anion is monohydrated. Likewise, the hydration constants of the dihydrate anion were found using a salt whose cation is monohydrated. Then the two hydration constants of the cation and the two of the anion are combined, using eq 8d, to calculate the coefficients A–D.

In the present paper, the ionic solubility of a salt, MA, was determined by measuring the conductance of the saturated solution in AN containing from 0.003 M (pure solvent) to 2 M water. A similar technique has been used previously in acetone.[5] This ionic solubility method[5,6] has the advantage over the total solubility method[6] in that the undissociated species, MA, and possibly also its hydrated species need not be considered.

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Experimental Section

Chemicals. Acetonitrile was purified and dispensed as described previously.[7] The following salts have been used previously: potassium and tetrabutylammonium picrate,[8] potassium and tetraethylammonium 3,5-dinitrobenzoate,[9] sodium and tetraethylammonium methanesulfonate,[8] and tetraethylammonium 3,5-dinitrophenolate[4] and salicylate.[10] The following salts were Merck Reagent Grade: potassium nitrate, potassium chloride, sodium chloride, and sodium nitrate. Potassium and sodium periodate and sodium tetraphenylborate were Baker's Reagent Grade product. These salts were used without further purification. Recrystallized potassium perchlorate was obtained from F. Chiang, and tetraethylammonium chloride from F. Thomas,[11] both in this laboratory. Tetraethylammonium perchlorate[12] and nitrate[13] (same procedure as for the tetraisoamylammonium salt) were prepared as described elsewhere. Cesium picrate was prepared by titrating Baker's Analyzed picric acid potentiometrically with cesium hydroxide in aqueous solution to the equivalence point, evaporating to dryness, and recrystallizing from ethanol. The cesium hydroxide was prepared by passing a solution of Fisher Co. cesium sulfate through a column of IRA-400 resin in the hydroxide form.

Potassium and lithium methanesulfonate and potassium 3,5-dinitrophenolate were prepared as described previously for sodium methanesulfonate[8] and potassium 2,4-dinitrophenolate.[4] The latter salt was recrystallized from AN. All salts were dried at 70° *in vacuo* for 10 hr. All measurements were made at 25 ± 0.1°.

Conductivity Measurements of Saturated Solutions. First, a saturated solution of the salt in AN was prepared as described previously.[6] A 5-ml portion of the saturated solution and 40 ± 10 mg of salt were introduced into the conductivity cell, and the conductance was measured. Then water was added from an ultramicroburet, and after each increment the cell and contents were hand shaken until the conductance remained constant to within ±0.3%. The conductivity bridge and cell have been described previously.[6]

Spectrophotometric Measurements. A 10.00-cm cylindrical Pyrex glass-stoppered cell and a Beckman DU spectrophotometer were used.[4] The slit width was set at 0.015 mm for all measurements. All experiments were carried out at 25 ± 0.1°.

Results

Viscosity (Corrections). The following viscosities (in centipoise) of solutions of water in AN were found: 0.45 *M* H_2O, 0.352; 0.91 *M* H_2O, 0.356; 1.92 *M* H_2O, 0.366; and 3.15 *M* H_2O, 0.384. The viscosity of pure solvent is 0.345 cp. All conductivities were corrected for viscosity and Onsager ion atmosphere effects.

Ionic Mobilities. The following ionic mobilities at 25° at infinite dilution have been reported in the literature: Li^+, 59;[14] Na^+, 70;[14] K^+, 86;[14] Rb^+, 97;[15] Cs^+, 102;[15] Cl^-, 89;[14] ClO_4^-, 104;[16] Pi^-, 78;[14] NO_3^-, 104;[14] 3,5-dinitrobenzoate, 96;[8] salicylate, 78,[16] 3,5-dinitrophenolate, 96.[4] The mobility of the methanesulfonate ion was assumed to be the same as that of bisulfate, equal to 90,[7] and that of periodate equal to that of perchlorate.

In Figure 1 are plotted equivalent conductances *vs.* molarity of water of very dilute solutions of tetraethylammonium salts of perchlorate, chloride, nitrate, salicylate, 3,5-dinitrobenzoate, methanesulfonate, tetrabutylammonium picrate, and sodium tetraphenylborate. At the very small concentrations taken all the salts are virtually completely dissociated. It is assumed that the large tetraalkylammonium and tetraphenylborate ions with their symmetrical configuration are not hydrated; hence the change in conductance in Figure 1 can be attributed to the various anions and the sodium ion. From the data in Figure 1, corrections have been made for the effect of water on the equivalent conductance in the calculation of $[M^+]_t$ from the conductance of the saturated solutions of the various salts. These corrections are significant for the chloride and picrate ions, but very small for the other ions. The change in equivalent conductance with concentration of water for potassium and cesium ions have been assumed to be the same as that for the sodium ion.

K_{sp} of Salts in Presence of Water. Plots of $f^2[M^+]_t^2/K_{sp}$ *vs.* $[H_2O]$ on a logarithmic scale presented in Figure 2 are constructed from conductance data of saturated solutions of the following salts: cesium picrate; potassium picrate, perchlorate, periodate, 3,5-dinitrophenolate, nitrate, methanesulfonate, 3,5-dinitrobenzoate, chloride, salicylate; sodium periodate, methanesulfonate, nitrate, chloride; and lithium methanesulfonate. A logarithmic plot permits the plotting of $f^2[M^+]_t^2/K_{sp}$ and $[H_2O]$ values over a wide range.

For the salts, cesium picrate and potassium picrate, perchlorate, and periodate, eq 7 in the quadratic form fits the solubility data presented in Figure 2 to at least 2 *M* water. For these salts *A* and *B* were obtained from the plots in Figure 2. The plots have slopes between 2 and 3 at 2 *M* water for potassium methanesulfonate, 3,5-dinitrobenzoate, chloride, nitrate, salicylate, and sodium periodate. For these salts $n + m = 3$, as eq 7 in the cubic form fits the solubility data. The coefficients *A*, *B*, and *C* for these salts were calculated using simultaneous equations (eq 7) at various concentrations of water and are listed in Table I. Substituting the values of these coefficients into eq 7, $f^2 \cdot [M^+]_t^2$ *vs.* $[H_2O]$ curves were calculated which are also given in Figure 2 (open symbols).

The coefficients *A* and *B* in Table I both differ for potassium and cesium picrates, and it is safely concluded that the ions of both salts are monohydrated. A relatively large number of potassium salts has been studied, the anions being mono- or dihydrated. In all instances $K^f_{K_w^+}$ was found constant within the experimental error and equal to 1.0 ± 0.2. This constant would vary greatly from salt to salt when the potassium ion would be assumed dihydrated ($K^f_{K_w^+} = A$, $K^f_{K_{2w}^+} = B$). The data obtained with periodate show that periodate is monohydrated. Use of this is made in analyzing the data for sodium periodate, the sodium ion forming a mono- and dihydrate.

The hydration constants of lithium ion could not be obtained readily, since a sparingly soluble lithium salt with a monohydrated anion is not available. However, comparison of the curves in Figure 2 of sodium and lithium methanesulfonate indicate that lithium ion is hydrated to a somewhat greater extent than sodium ion, $K^f_{Li_w^+}$ and $K^f_{Li_{2w}^+}$ being of the order of 3 and 5, respectively, as compared to 2 and 3, respectively, for sodium.

The hydration constants of the dihydrated anions (nitrate, methanesulfonate, 3,5-dinitrobenzoate, 3,5-dinitrophenolate,[17] salicylate, and chloride) are found

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[17] Solubility data of potassium 3,5-dinitrophenolate could be ob-

Table I. Hydration of Ions in AN from Solubility Data

Salt[a]	No.[b]	Mode of hydration $n:m$	K_{sp}	Coefficients in eq 7 A	B	C	D	Hydration constants $K^{t}_{M_w^+}$	$K^{t}_{M2w^+}$	$K^{t}_{A_w^-}$	$K^{t}_{A2w^-}$
KPi	2	1:1	2.1×10^{-5}	1.6	0.5			1		0.5	
CsPi	1	1:1	1.9×10^{-5}	0.9	0.2			0.5		0.5	
KIO_4	4	1:1	7.5×10^{-7}	1.84	0.9			1		1	
$KClO_4$	3	1:1	6.1×10^{-5}	1.6	0.6			0.8		0.7	
KCl	9	1:2	8.6×10^{-9}	10	30	20		1		9	20
KNO_3	5	1:2	1.4×10^{-6}	3.0	3.4	1.5		1		2	1
KCH_3SO_3	6	1:2	8.0×10^{-8}	4.5	12	8.0		1		3.6	8
KDNB	7	1:2	6.0×10^{-8}	7.5	12	6.0		1		6	5
KDNP	8	1:2	6.7×10^{-6}	8.2	...[c]	...[c]		1		7[c]	
										8[f]	6[f]
KSal	15	1:2	9.2×10^{-6}	4.5	7.5	3.7		0.8		4	4
$NaIO_4$	10	2:1	1.8×10^{-5}	2.8	4.6	2.2		2	3	0.7	
$NaCH_3SO_3$	12	2:2	1.2×10^{-8}	5.7[d]	19[d]	29[d]	26[d]	...	...	...	...
NaCl	14	2:2	0.9×10^{-8}	11[d]	43[d]	42[d]	65[d]	...	...	...	...
$NaNO_3$	11	2:2	1.1×10^{-6}	3.9[d]	8.2[d]	8.2[d]	3.9[d]	...	...	...	...
$LiCH_3SO_3$	13	2:2	1.0×10^{-8}	...[e]	...[e]	...[e]	...[e]	...	...	...	...

[a] Pi = picrate, Sal = salicylate, DNB = 3,5-dinitrobenzoate, DNP = 3,5-dinitrophenolate. [b] Numbers correspond to the curves in Figure 2. [c] Coefficients B and C cannot be determined, as monohydrate salt precipitates out at 0.2 M water. [d] Calculated values, see text. [e] Coefficients cannot be calculated, as the individual hydration constants could not be determined (see text). [f] Spectrophotometric data.

from their potassium salts. Table I summarizes the values of the hydration constants of the various ions along with the solubility products of the salts used.

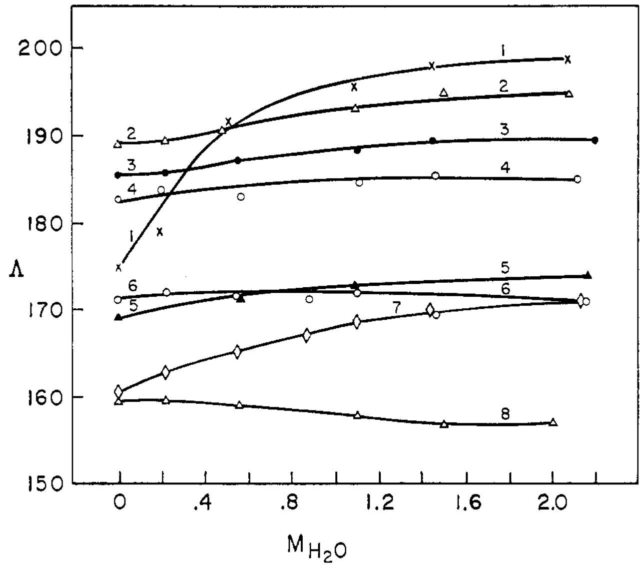

Figure 1. Effect of water on equivalent conductivity of salts in AN: (1) 7.00 × 10^{-5} M tetraethylammonium chloride; (2) 1.08 × 10^{-4} M tetraethylammonium perchlorate; (3) 1.83 × 10 $^{-4}$ M tetraethylammonium nitrate; (4) 7.50 × 10^{-5} M tetraethylammonium 3,5-dinitrobenzoate; (5) 2.35 × 10^{-4} M sodium tetraphenylborate; (6) 2.43 × 10^{-4} M tetraethylammonium methanesulfonate; (7) 5.63 × 10^{-5} M tetrabutylammonium picrate; and (8) 2.30 × 10^{-4} M tetraethylammonium salicylate. Ordinate values displaced 30 units higher in curves.

Table I also lists the values of the coefficients A–D for the salts with $n = m = 2$ (sodium nitrate, methanesulfonate, and chloride) as calculated from the two hydration constants of sodium ion and the two of the anion (Table II) as described in the introductory section. Using these coefficients, the curves in Figure 2 (open symbols) were calculated from eq 7 and compared with the experimental ones. Good agreement is found

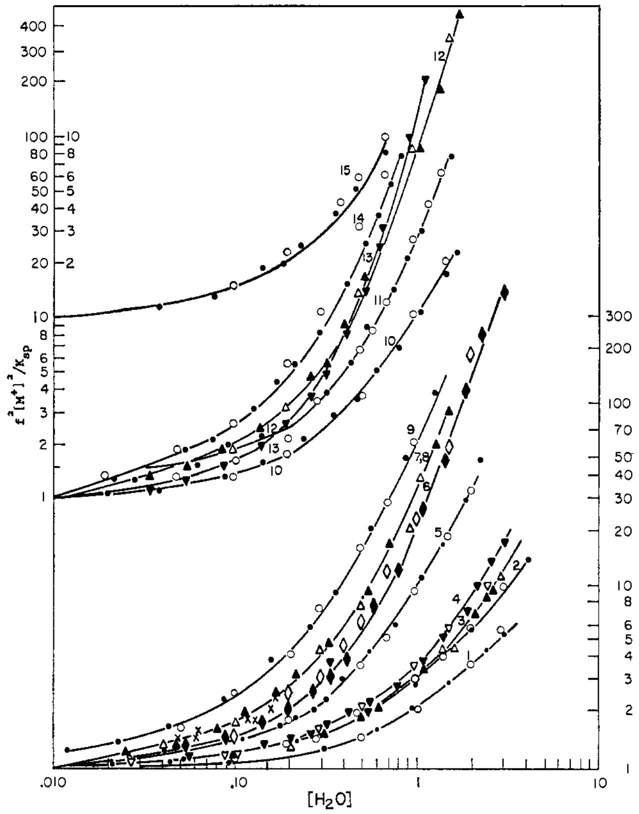

Figure 2. $f^2[M^+]^2/K_{sp}$ vs. $[H_2O]$ plots of salts in AN containing various amounts of water. Curves 1–9, right-hand ordinate; curves 10–14, outer left-hand ordinate; and curves 15, inner left-hand ordinate. Filled-in symbols are experimental points; open symbols are calculated points.

for sodium nitrate and methanesulfonate up to 1.5 M concentration of water. For sodium chloride the agreement is excellent up to 0.2 M water. At higher water concentrations the calculated values become

tained to only 0.2 M water as another solid phase, apparently the monohydrate, separates out. Hence, only the sum of hydration constants of anion and cation can be found, yielding a value of $K^{t}_{A_w^-}$ equal to 7 taking $K^{t}_{K_w^+}$ as 1.0.

higher than the experimental values, the difference becoming 50% at 1 *M* water.

Spectrophotometric Determination of the Hydration Constants of the 3,5-Dinitrophenolate Ion. In a previous paper the spectrophotometric determination of heteroconjugation constants of the 3,5-dinitrophenolate ion with hydrogen bond donors by measuring the absorbance of the 3,5-dinitrophenolate ion was described.[4] Absorbances of 2.41 × 10^{-5} *M* tetraethylammonium 3,5-dinitrophenolate in AN containing up to 0.59 *M* water were measured at 605 mμ. The absorbance indexes of the solvated and dihydrated 3,5-dinitrophenolate were found to be $1.6_8 \times 10^1$ and *ca.* 1.2, respectively, at 605 mμ. The latter was determined in 6 *M* water, in which the dihydrate is the predominant anion species. All absorbances were corrected for those of the mono- and dihydrated anions as described previously,[10] assuming the absorbance index of the monohydrate to be equal to that of the dihydrate. From the spectrophotometrically determined value of $[A^-]$, $K^f{}_{A_w^-}$ and $K^f{}_{A_{2w}^-}$ are calculated from the following relation

$$\frac{C_{A^-} - [A^-]}{[A^-][H_2O]} = K^f{}_{A_w^-}[1 + K^f{}_{A_{2w}^-}[H_2O]/K^f{}_{A_w^-}] \quad (10)$$

which is derived from eq 3 ($[M^+]$ being equal to the concentration of the salt) and the hydration constants $K^f{}_{A_w^-}$ and $K^f{}_{A_{2w}^-}$ (*cf.* eq 2). In eq 10, C_{A^-} represents the analytical salt concentration. The value of $K^f{}_{A_{2w}^-}$ chosen gives the least drift in the value of $K^f{}_{A_w^-}$ in eq 10.

Absorbances corrected for the hydrated anions and the resulting hydration constants are listed in Table II. Average values of 8 and 6 were found for $K^f{}_{A_w^-}$ and $K^f{}_{A_{2w}^-}$, respectively, as compared to a $K^f{}_{A_w^-}$ of 7 derived from solubility data.

Table II. Spectrophotometric Determination of Hydration Constants of 3,5-Dinitrophenolate Ion[a]

$[H_2O]$, *M*	A_{605}	A_{605}[b]	$[A^-]$, *M* × 10^3	$[Et_4N^+]$, C_{A^-}, *M* × 10^3	$(C_{A^-} - [A^-])/[H_2O] \cdot [A^-]$	$K^f{}_{A_w^-}$[c]
0.002	0.405	0.405	2.41	2.41	...	...
0.022	0.355	0.350	2.09	2.41	7.0	...
0.042	0.316	0.307	1.83	2.41	7.6	7.3
0.082	0.258	0.243	1.45	2.41	8.0_6	7.6
0.142	0.205	0.174	1.04	2.40	9.2	8.2_5
0.20	0.170	0.143	0.85	2.40	9.1	7.8
0.30	0.137	0.102	0.61	2.39	9.75	7.8_5
0.44	0.107	0.073	0.43	2.39	10.3	7.6_5
0.59	0.091	0.055	0.33	2.39	10.6	7.2
					Av	7.7

[a] 2.41 × 10^{-3} *M* tetraethylammonium 3,5-dinitrophenolate, 10.0-cm cell, 605 mμ. [b] Corrected for A_w^- and A_{2w}^-. [c] Calculated from eq 10, taking $K_{A_{2w}^-} = 6.1$

Discussion

The hydration constants in AN of the alkali ions ($Cs^+ < K^+ < Na^+ < Li^+$) increase in the order of their hydration energies in water and of their solvation energies in AN.[18] From the values of the alkali ion mobilities and also from potential data,[19] it is evident that the alkali ions are solvated in AN and that their solvation energies decrease in this order. Apparently, the molecules of solvent associated with these cations are easily replaced by water.

Anions which are quite stable and are not or only slightly solvated in AN, like picrate, perchlorate, periodate, react only with one molecule of water and their hydration constants of 0.5 to 0.7 are smaller than that of potassium ion of 1. Among the anions the chloride ion has by far the greatest hydration constants, its $K^f{}_{A_w^-}$ and $K^f{}_{A_{2w}^-}$ being 5 and 20 times, respectively, as large as that of the more stable and less solvated nitrate ion. Undoubtedly, the small size of the chloride ion, as compared to that of the dinitrophenolate, dinitrobenzoate, or salicylate ions, accounts in part for its great affinity for water in AN. It would seem fair to conclude that the assumptions specified in the introductory section are valid at low water concentration at which $K^f{}_{I_w^\pm}$ was found. It is doubtful whether the assumptions made are still valid at water concentrations higher than 1 *M*.

In this connection reference is made to a study of infrared evidence presented by Coetzee[20] that at concentrations above 1 *M* in AN water begins to undergo self-association. For this reason the values of $K^f{}_{I_w^\pm}$ are much more reliable than those of $K^f{}_{I_{2w}^\pm}$. However, the $K^f{}_{I_{2w}^\pm}$ values reported in Table I should be of the correct order of magnitude.

It is difficult to give a simple interpretation of the effect of water on the equivalent conductance of tetraethylammonium salts of various anions (Figure 1). Striking is the large effect on the mobility of the chloride ion. As in water the mobility of the chloride ion in AN is practically equal to that of the potassium ion, indicating that the chloride ion is solvated in anhydrous AN. This conclusion is substantiated by the fact that the mobility of the nitrate ion, which is less solvated than the chloride ion, is 15% greater than that of chloride in AN, but 7% smaller than that of chloride in water. Considering the very large hydration constants of the chloride ion it is tempting to attribute, at least in part, the increase in its mobility by water to a smaller size of the hydrated than of the solvated ion in AN. Undoubtedly, other factors (*e.g.*, deviation from Stokes' law, dielectric constant effect) also must be considered in the interpretation of the effect of water on the mobility of ions in AN.

The results obtained in this paper allow a quantitative interpretation of the effect of water on the pa_H of mixtures of acids and their highly dissociated tetraalkylammonium salts. In mixtures of picric acid and its tetrabutylammonium salt, water up to a concentration of 2.0 *M* has no measurable effect on the pa_H. The acid anion is only very slightly hydrated; the effect of this on the pa_H apparently is compensated by an equally slight hydration of the acid. In a mixture of a carboxylic acid and its tetraethylammonium salt, the change in pa_H can be very large. As an example, in a mixture 3 × 10^{-3} *M* in benzoic acid and 3.1 × 10^{-2} *M* in tetraethylammonium benzoate, the pa_H decreased continuously with the addition of water from 23.6 to 20.6 at a concentration of 1.15 *M* water. Qualitatively the effect of water is easily explained by the very considerable hydration of the benzoate ion, as will be considered from a quantitative viewpoint in a subsequent paper.

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(19) For a review, see I. M. Kolthoff, *J. Polarog. Soc.*, **10**, 22 (1964).
(20) W. Muney and J. F. Coetzee, *J. Phys. Chem.*, **66**, 89 (1962).