ADDITION COMPOUNDS OF WATER AND PHENOLS*

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In general, the association constant of ionophores in a mixture of polar and nonpolar solvents increases with decreasing dielectric constant, owing to the increase of electrostatic attraction between ions. In the case of ionogens,¹ however, the dielectric constant is not necessarily the controlling parameter: consider a latent electrolyte such as an acid HX in an aprotic solvent such as acetonitrile (dielectric constant $D = 36.0$). Addition of a basic solvent such as water forms a complex which rearranges to an ion pair $\text{H}_3\text{O}^+\cdot\text{X}^-$, which in turn dissociates into free ions. Reassociation of the latter to re-form ion pairs will occur; the equilibrium

is described by the electrostatic association constant²

$$K_A = K_0 \exp(e^2/aDkT) = K_0 e^b, \quad (1)$$

where K_0 is the excluded volume factor, e is elementary charge, and a is center-to-center distance between ions at contact. But the concentration of free ions is not related to the stoichiometric concentration of acid c by the usual mass action equation because the concentration of ion pairs is, in this case, determined by the equilibria which control the initial formation of a complex $\text{HX}\cdot\text{H}_2\text{O}$ and the rearrangement of the latter to an ion pair. At fixed concentration of acid, concentration of complex and hence of ion pairs increases with increasing base concentration; if the formation constant of the complex is small compared to the association constant of the pairs, the first process now controls the over-all reaction which produces ions from initial acid, and the stoichiometric association constant may then decrease or increase as dielectric constant changes. An example of such systems has recently been described:³ picric acid in acetonitrile, plus base. Addition of water ($D = 78.5$), of ethanol ($D = 24.3$), or of methanol ($D = 32.6$) all sharply *decrease* the conductimetrically observed association constant K_A : in the first case, the dielectric constant of the solvent increases, in the second it decreases, and in the third it remains almost unchanged. The ionogenic reaction and not electrostatic attraction determines the conductivity.

Analysis of the experimental results showed, however, that the sequence

leads to a conductance function $\Lambda(c)$ which utterly failed to reproduce the observed conductance curves. Instead, it was found that the sequence

where X^- is an abbreviation for the complex ion in (4), yields a conductance equation to which the data conform within experimental error over a wide range of the relevant variables (up to six decades in net association constant for picric acid in water-acetonitrile).

The appearance of the coefficient 4 in (4) immediately suggests that one water molecule acts as a base, combining with the proton of picric acid to produce the hydronium ion H_3O^+ , while the other three solvate the picrate ion through hydrogen bonding to the three nitro-groups of the latter. The purpose of this communication is to confirm this hypothesis by presenting data for a series of substituted phenols. It will be shown that reaction (4) can be generalized to

where n is the integer one greater than the number of nitro-groups in the substituted phenol residue Ph (and X^- now means the general solvated anion $(H_2O)_{n-1}Ph^-$).

For highly associated 1-1 ionophores at low concentrations, the conductance function reduces to the simple form

$$c\Lambda^2 = \Lambda_0^2/K_A \quad (8)$$

where c is stoichiometric concentration, Λ is equivalent conductance $= 10^3\sigma/c$ (σ is observed specific conductance, corrected for solvent conductance), Λ_0 is limiting equivalent conductance, and K_A is the association constant. For the phenols in acetonitrile-water mixtures, a plot of $\log \Lambda$ against $\log c$ is linear, with slope equal to minus one half; that is, they follow the functional form $c\Lambda^2 = \text{constant}$ of equation (8). Figure 1 is a plot of the observed values of $\log (\Lambda_0^2/c\Lambda^2)$ against reciprocal dielectric constant for the compounds listed below the figure; if the electrolytes were normal, with association constant given by (2), the plots would be linear. As seen in the figure, they are sharply curved, as if they were dropping from a very high asymptotic value on the right (in anhydrous

FIG. 1.—Dependence of association constant in acetonitrile water mixtures: $\circ$, *o*-nitrophenol; $\bullet$, 2,4,6-tribromophenol; $\ominus$, *p*-nitrophenol; $\oplus$, 2,4-dinitrophenol; $\odot$, 2,6-dinitrophenol; $\bullet$, picric acid (ordinates left). $\square$, *p*-methoxyphenyl; $\triangle$, benzoic acid (ordinates right).

acetonitrile). The dashed line is a plot of the function of equation (1) drawn for $a = 5 \times 10^{-8}$ cm, shifted vertically upward by about five decades to bring it on scale. At the water-rich end, the curves seem to be approaching the slope which would correspond to an ordinary ion pair equilibrium. Qualitatively then, the phenols conduct as if the conductimetric association constant, defined as

$$K_A = \Lambda_0^2/c\Lambda^2, \quad (9)$$

were the product of three terms: an electrostatic factor K_A , a very large factor of the order of 10^5 – 10^{10} (depending on the compound), and a function which is very sensitive to water concentration, especially at low values of the latter.

Picric acid in anhydrous ammonia-free acetonitrile shows negligible absorption in the region of picrate ion absorption; that is, acetonitrile is too weak a base to function as a proton acceptor from picric acid. With the addition of a trace of water, the solution acquires the characteristic yellow color of the picrate ion and conductance increases sharply. Similar changes appear with the other nitrophenols. Both effects show that water acts as a base with respect to nitrophenols in acetonitrile. The simplest mechanism would be that summarized by equations (2) and (3): picric acid hydrogen bonds to water, and then the adduct rearranges to an ion pair which dissociates in the usual way. In other words, the conductimetric K_A is the product of the electrostatic K_A and the constants describing the formation of the ion pair from covalent water and picric acid molecules. As already mentioned, however, a conductance function based on (2) and (3) will not reproduce the observed conductances; it is far too insensitive to water concentration. Increased sensitivity appears if more than one water molecule is involved in generating the electrolyte from its nonelectrolytic precursor. The law of mass action applied to the general equilibria (6) and (7) leads to the relation

$$c f^2 K_A (1 + 1/K_s B^n) \gamma^2 + \gamma - 1 = 0, \quad (10)$$

where γ is the ratio of free ion concentration to stoichiometric concentration c of ionogen, B is concentration of base (here, water), f is ionic activity coefficient, K_A is the electrostatic association constant describing (7), and K_s is defined by

$$K_s = [\text{BH}^+ \cdot \text{X}^-]/[\text{HPh}] B^n. \quad (11)$$

Equation (10) has the form of the usual quadratic for γ , with the association constant K_A multiplied by the factor $(1 + 1/K_s B^n)$. This shows that the conductimetric constant K_A is given by

$$K_A = K_A (1 + 1/K_s B^n) \quad (12)$$

and depends on water concentration, as observed.

In order to test this result against experiment quantitatively, (12) is written in logarithmic form

$$\log K_A = \log K_A + \log (1 + 1/K_s B^n). \quad (13)$$

Neglecting unity compared to $1/K_s B^n$ (as is soon justified by the numerical

values found) and substituting (1), we define a parameter Z by the equation

$$Z = \log K_A - \log K_0 - e^2/aDkT \quad (14)$$

$$= -\log K_s - n \log B. \quad (15)$$

In order to evaluate the last two terms of (14), a was set equal to 5×10^{-8} cm (the value found for picric acid in water³). The values of pK_s , which is defined as the negative of Z at unit activity (assumed equal to concentration) of water, are summarized in Table 1.

TABLE 1. Summary of constants.

Compound	pK_s	pK_a
Phenol	—	10.00
<i>o</i> -Nitrophenol	10.28	7.22
<i>p</i> -Nitrophenol	9.00	7.15
2,4-Dinitrophenol	8.58	4.09
2,6-Dinitrophenol	8.12	3.71
Picric acid	4.60	0.42
<i>p</i> -Methoxyphenol	(9.29)	10.21

Figure 2 shows plots of Z against logarithm of water concentration for the various systems investigated; for completeness, our results for picric acid³ are included as curve 1. Consider first curves 1 (picric acid), 2 (2,4-dinitrophenol), 3 (2,6-dinitrophenol), 4 (*p*-nitrophenol), and 6 (2,4,6-tribromophenol): they are linear and *parallel*. But the ordinate scales are *different*: 4 Z -units per ordinate unit for line 1, 3 for lines 2 and 3, 2 for line 4, and 1 for line 6. According to (15), Z should be linear in $\log [H_2O]$, with slope n , the number of molecules of water needed to produce an ion pair from the ionogen. The results satisfy the requirement of linearity: furthermore, we see that n equals one plus the number of nitro-groups in the phenol, a result which immediately suggests hydration of the nitro-groups. For *p*-nitrophenol, for example, the anion is

and similarly for the others.

The systems described so far are by hypothesis hydrates of phenols in water-acetonitrile mixtures where the molar ratio of water to phenol is 100 or greater. Now consider the nitrophenols in water, where the water (at 55 moles/liter) is in much greater excess. Table 1 gives literature⁴ values of pK_a for some substituted phenols, where⁵

$$pK_a = -\log [H_3O^+] [X^-]/[HPh]. \quad (16)$$

Combining (16) with (11), we obtain

$$pK_a = pK_s - pK_A - n \log B, \quad (17)$$

which at first glance suggests that pK_a is linear in n with slope $\log [H_2O] = 1.744$. The open circles in Figure 3 are for pK_a ; they lie approximately on a straight

FIG. 2.—Test of equation (15). 1, picric acid (ordinates upper left); 2, 2,4-dinitrophenol; 3, 2,6-dinitrophenol (ordinates right); 4, *p*-nitrophenol (ordinates 7–9 left); 5, *o*-nitrophenol; 6, 2,4,6-tribromophenol ($Z + 0.4$); 7, benzoic acid; 8, *p*-methoxyphenol ($Z - 0.5$) (ordinates lower left).

line with the much larger slope 3.2₃. Empirically, Figure 3 shows that

$$pK_a = RT\Delta F_0 - pK_A - k'n \quad (18a)$$

$$= RT\Delta F_0 - pK_A - 1.74 n - k''n \quad (18b)$$

which immediately suggests that pK_s also varies linearly with n . With the clarity of hindsight, we see that such dependence might be expected: we recall that $pK_s = RT \Delta F$, where ΔF is the free energy for the over-all reaction (4), and $\Delta F = \Sigma \Delta F_j$, where the summation is over all the steps involved in (4). One term in ΔF corresponds to the hydrogen bonding of a water molecule to the phenolic $-\text{OH}$, another to the rearrangement of $-\text{OH} \cdots \text{OH}_2$ to $-\text{O}^- \cdots \text{H}_3\text{O}^+$; both of these will depend on the electron density at the O-position which in turn depends on the number and location of substituents in the aromatic ring. Other terms in ΔF correspond to the postulated hydration of the nitro-groups; the energy will depend on the net negative charge on them, and this will decrease as the number of nitro-groups increases, because the single net charge of the anion is spread thinner, the more groups it has to cover. The squares in Figure 3 represent $(pK_a + 1.74 n)$; they are on a line with slope $k' = 1.5_2$. The solid circles in Figure 3 represent pK_s for the nitrophenols in water-acetonitrile mixtures; they approximate linearity, with slope $k' = 2.2_2$. The difference between the slopes for water and the mix-

FIG. 3.—Dependence of constants on number of nitro-groups.

TABLE 2. *Conductance data and derived constants.*

$10^3 \kappa$	$[H_2O]$	$10^6 \sigma$	$\log K_A$	Z
2,4-Dinitrophenol				
3.789	0.00	0.047	(10.64)	—
3.722	1.27	0.338	8.90	8.09
3.689	1.77	0.462	8.61	7.82
3.615	2.86	0.855	8.05	7.28
3.437	5.49	2.517	7.00	6.30
2,6-Dinitrophenol				
2.519	0.00	0.061	(10.24)	—
2.482	0.91	0.241	9.04	8.21
2.456	1.47	0.448	8.48	7.68
2.431	2.03	0.708	8.12	7.33
2.384	3.11	1.169	7.59	6.83
2.270	5.63	2.608	6.80	6.11
<i>p</i>-Nitrophenol				
2.741	0.00	0.022	(11.15)	—
2.715	0.56	0.065	10.16	9.33
2.703	0.81	0.081	9.96	9.14
2.680	1.31	0.130	9.34	8.53
2.656	1.80	0.179	9.25	8.46
2.610	2.75	0.254	8.92	8.15
2.501	5.00	0.393	8.44	7.73
<i>o</i>-Nitrophenol				
4.605	0.00	0.0016	(13.79)	—
4.592	0.34	0.0139	11.78	10.95
4.564	0.59	0.0213	11.39	10.56
4.519	1.16	0.0315	11.04	10.23
4.476	1.73	0.0381	10.87	10.07
4.291	2.82	0.0475	10.62	9.85
4.189	5.38	0.0728	10.17	9.47
2,4,6-Tribromophenol				
3.377	0.00	0.031	(10.96)	—
3.368	0.34	0.053	10.47	9.64
3.348	0.58	0.067	10.27	9.44
3.315	1.15	0.090	10.00	9.19
3.284	1.71	0.113	9.78	8.98
3.222	2.80	0.144	9.54	8.77
3.075	5.35	0.219	9.08	8.38
<i>p</i>-Methoxyphenol				
6.128	0.00	0.052	(11.73)	—
6.111	0.34	0.081	10.36	9.53
6.074	0.59	0.095	10.22	9.39
6.014	1.17	0.111	10.08	9.27
5.956	1.73	0.126	9.95	9.15
5.842	2.79	0.142	9.81	9.04
5.573	5.40	0.167	9.57	8.87
Benzoic Acid				
4.649	0.00	0.015	(11.73)	—
4.637	0.34	0.043	10.80	9.97
4.608	0.59	0.062	10.48	9.65
4.563	1.16	0.092	10.12	9.31
4.519	1.73	0.121	9.86	9.06
4.434	2.82	0.170	9.53	8.76
4.230	5.38	0.391	8.72	8.02

tures can be rationalized by the argument that hydration of solute in water and in acetonitrile containing water are energetically different processes; in the former, the water molecules must be abstracted from the water structure, while in the latter, they are already free-swimming single molecules. (The maximum water concentration of 5 *N* in Table 2 corresponds to a ratio of about 1:4 for $\text{H}_2\text{O}:\text{CH}_3\text{CN}$.)

Three compounds included in Table 2 require further comment. Line 5 of Figure 2, for *o*-nitrophenol, has unit slope unlike line 4 for *p*-nitrophenol, which has the expected slope of 2. Now *o*-nitrophenol is one of the classical examples of compounds which form internal hydrogen bonds. If it is assumed that this bond is so stable that solvation of the nitro-group cannot occur until *after* the reaction between water and the $-\text{OH}\cdot\text{OH}_2-$ to form $-\text{O}^-\cdot\text{H}_3\text{O}^+$, it can be shown that

$$K_A (\text{ortho}) = K_A/K_1 [\text{H}_2\text{O}], \quad (19)$$

where K_1 describes the formation of H_3O^+ . To (19) corresponds the observed unit slope of a Z -log $[\text{H}_2\text{O}]$ plot. Benzoic acid, represented by curve 7, is a carboxylic acid and should require only one water molecule to form H_3O^+ , if the carboxylate ion is unsolvated. As seen in Figure 2, benzoic acid gives a curve which approaches unit slope only at low water concentrations. Carboxylic acids are known to dimerize in solution; inclusion of the dimerization equilibrium in the over-all reaction scheme calls for curvature of the Z -log $[\text{H}_2\text{O}]$ plot, as observed. Finally, *p*-methoxyphenol gives a linear curve, but the slope is about 0.70. The *ad hoc* hypothesis of a complex anion containing one *p*-methoxyphenol molecule, one water molecule, and two phenolate ions would call for a slope of 2/3; this is admittedly sheer speculation, not to be taken seriously unless other similar examples of such clusters can be found.

Experimental.—Acetonitrile⁶ was dried with calcium hydride, followed by phosphorus pentoxide to remove ammonia. Its conductance was about 0.04×10^{-6} . The phenols (Eastman) were recrystallized several times and dried under vacuum. Conductance measurements were made using a cell with constant 0.03763, parallel to 100,000 ohms, at 25.00°. Procedure was as follows: acetonitrile was pumped into the cell by dry nitrogen pressure. The cell was placed in the thermostat and after 30 min the solvent conductance was measured. Then a sample of phenol was weighed in from a micro-weighing bottle. The cell was swirled to dissolve the phenol, keeping the body of the cell under the thermostat oil, so that the temperature of the solution remained at 25°. Resistance was measured; the corresponding conductance was due to combination of a minute amount of the phenol with the traces of water, ammonia, and possible other basic impurities in the acetonitrile, and to any other electrolytic impurities present. This conductance was subtracted from the subsequent conductances as the solvent correction. Then a portion of water was added from a micropipette. After mixing, resistance was again measured. At 5-min intervals, successive portions of water were added, and resistance was measured for each. This procedure minimized errors due to slow drift of conductance with time which was observed for some³ of the solutions. For water concentrations less than about 0.3 *N* (about 0.5 wt %), conductances were erratic, probably due to trace impurities still in the solvent; only data for water concentrations higher than 0.3 *N* were considered.

The systems all are solutions of very weak electrolytes, and at concentrations so low that the $\log \Lambda - \log c$ plots are linear with slope equal to -0.5 ; for such systems, the concen-

tration dependence of equivalent conductance Λ is given by the simple equation $c\Lambda^2 = \Lambda_0^2/K_A$. For the limiting conductance Λ_0 , we used 160, the value found for picric acid in acetonitrile, multiplied by the ratio of the viscosity of pure acetonitrile to the viscosity of the water-acetonitrile mixture. This is, of course, an approximation, in that it assumes that Walden's rule is valid, and that all of the anions have the same mobility as the picrate ion; since the bulk of the anion is the aromatic ring, differences in mobility among the substituted rings should be relatively small. Also, we shall be primarily interested in *slopes* of log-log plots; corrections to Λ_0 can only displace such curves vertically. The results are summarized in Table 2, where c is concentration of phenol, $[H_2O]$ is concentration of water (both in equiv./liter), σ is specific conductance corrected for solvent conductance, K_A is association constant, and Z is the variable defined in the discussion. Also included in the table are results for benzoic acid. Duplicate runs were made for several compounds; agreement was within 5%.

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⁵ Usually pK_a is defined as $-\log [H_3O^+][Ph^-]/[HPh]$, a definition which ignores possible interaction with water beyond the one molecule needed to form H_3O^+ , and conventionally the water concentration is absorbed in K_a (or else water activity is set equal to unity). This definition involves no ambiguity when applied to aqueous solutions where the water concentration is *constant*. In our case, however, the water concentration is one of the experimental variables. Our definition (16) reduces to the conventional one in water, because $[X^-]$, the concentration of hydrated ion, equals the stoichiometrically calculated concentration $[Ph^-]$ of the (in our opinion, nonexistent) bare nitro-phenolate ion.

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