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The Influence of Solvation on the Acid-Base Properties of Organic Compounds in Various Media

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The influence of non-specific (electrostatic) and specific (with formation of a hydrogen bond) solvation of ions in water on the strength of different organic acids is considered by comparing their deprotonation constants (pK_d) in water, nitromethane (a solvent which serves as a model for electrostatic solvation), and in the gas phase. The decisive role of the electrostatic solvation of ions in the variation of pK_d and in the weakening of the influence of substituents on the pK_d for ammonium, anilinium, and pyridinium cations, benzoic acids, and phenols on passing from the gas phase to water and also in the differentiation of the basicities of primary, secondary, and tertiary amines in water is demonstrated. The pK_d for organic OH-, $\dot{O}$H-, NH-, $\dot{N}$H-, $\dot{P}$H-, and CH-acids in water, dimethyl sulphoxide, and nitromethane are compared, which permits the determination of the relation between the localisation of the charge in organic ions and dipolar species, on the one hand, and their solvation via hydrogen bonding and dispersion interaction in solution, on the other. The relation between the capacity of bridge groups to transmit electrons and the medium is considered.
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I. INTRODUCTION

The considerable influence of solvation on the rate and direction of chemical reactions in solutions is generally known[1-5]. One of the reactions most convenient for the quantitative study and interpretation of the influence of solvation effects is the reversible acid–base interaction which consists of a very simple reversible system, whose equilibrium constant can be measured for a wide range of compounds in many different media:

$$HA \rightleftharpoons A^- + H^+, \quad K_d\ (\Delta G_d^\circ) \qquad (1)$$

$$BH^+ \rightleftharpoons B + H^+, \quad K_d\ (\Delta G_d^\circ) \qquad (2)$$

The standard free energy of the deprotonation reactions (1) and (2) in a solvent S ($\Delta G_d^{S\circ}$) is determined by the "internal" and "external" components of the free energy[1,4]:

$$\Delta G_d^{S\circ} = \Delta G_{d,\,int}^{S\circ} + \Delta G_{d,\,ext}^{S\circ} = \Delta G_d^{g\circ} + \Sigma \Delta G_s^{S\circ}. \qquad (3)$$

The internal component depends only on the structure of the acid and the conjugate base and is determined by the free energy of the process in the gas phase (g): $\Delta G^{S}_{d,int} = \Delta G^{g}_{d}$.

The external component is determined by the influence of the medium on the deprotonation process, i.e. by the free energy of solvation (ΔG^{S}_{s}) of all the species; for example, for reaction (1) we have

$$\Delta G^{S}_{d,ext} = \Sigma \Delta G^{S}_{s} = \Delta G^{S}_{s}(H^{+}) + \Delta G^{S}_{s}(A^{-}) - \Delta G^{S}_{s}(HA). \quad (3)$$

It follows from Eqn.(3) that, in order to elucidate the solvation effects in the solvent S, it is necessary to know the acid–base properties not only in this solvent but also in the gas phase. In the course of many decades chemists investigating protolytic equilibria in solutions (mainly in water) were unable to do this. However, during the last ten years the position changed radically: with the aid of methods developed recently, it has been possible to measure the acidities in the gas phase of a large number of organic compounds[6], for example, substituted aliphatic[7] and aromatic carboxylic acids[8], alcohols[9], phenols[10], and aliphatic and aromatic ammonium cations[11–15].

It is noteworthy that the characteristics of water—high dielectric constant ε, high capacity for the formation of hydrogen bonds (HB), and a highly developed structure—lead to very complex solvation interactions in an aqueous medium[16]. Since any type of solvation can influence the deprotonation constant pK_d and the transmission of the effects of substituents, an unambiguous interpretation of the results for the aqueous medium is difficult[1] even when data are available for the gas phase: thus the same experimental data for substituted $\overset{+}{N}H$-acids have been explained[17–20] by the effect of specific solvation (with formation of the $\overset{+}{N}H\ldots OH_2$ hydrogen bond), while in other studies[11,12] they have been accounted for by the non-specific (electrostatic) solvation of ammonium cations. The subdivision of the solvation effects under consideration into reactions (1) and (2) involves considerable fundamental difficulties[19]: for example, both effects are intensified with increase of the charge on the $\overset{+}{N}H$ group of the substituted ammonium cations; furthermore, the hydrogen bond with the ions (at any rate $\overset{+}{N}H\ldots OH_2$) is largely electrostatic[11,19,21] and is determined by the charge of the ions.

Despite the above difficulties[3], problems of this kind can be solved. One of the possible ways involves the consideration of the influence of solvation on the pK_d in a medium which serves as a model of only the electrostatic solvation of the ions A^- and BH^+, i.e. in a solvent with a fairly high dielectric constant and a greatly weakened capacity for the formation of hydrogen bonds with different hydrogen donors and acceptors. A comparative study of data for the gas phase, the model solvent, and water would make it possible to elucidate the influence of electrostatic solvation and solvation via hydrogen bonding on the acid–base properties in an aqueous medium. There is no doubt that the model solvent must be sought among aprotic polar solvents (APS) incapable of forming the $A^-\ldots HS$ bond. During the last 10 years, the acid–base properties of a large number of organic compounds have been determined quantitatively in a series of APS (see, for example, Refs.22–29), which permits an approach to the solution of the problem under consideration.

II. COMPARISON OF THE ABILITIES OF APROTIC POLAR SOLVENTS TO FORM HYDROGEN BONDS

Examination of numerous literature data shows that the model solvent which satisfies the conditions specified above most satisfactorily is nitromethane. Since its dielectric constant ($\varepsilon = 38.6$) is fairly high, the free energies of the electrostatic solvation $\Delta G_S(I^{\pm})_{el}$ of the ions $I^{\pm}$ in water ($\varepsilon = 80.1$) and nitromethane, calculated from the Born equation[1,30,31]

$$\Delta G_S(I^{\pm})_{el} = -\frac{e^2}{2r}\left(1 - \frac{1}{\varepsilon}\right) \quad (4)$$

(here e is the charge and r the radius of the ion), are similar and differ only by ~1%.

Table 1. The dielectric constants ε and indices of the capacity of the solvents S for electron-donating solvation.

Solvent	ε[35,36]	DN[36,37]	$\delta^{23}Na^{+}$[38]	$10^{3}\Delta g$[39]	$\Delta\nu_{PhOH\ldots S}$[40]	$\Delta\nu_{MeOD\ldots S}$[41]	$10^{3}(\Delta\nu/\nu)_{HOH\ldots S}$[42,43]	$K_{MeOH\ldots S}$[44]	$-\Delta H_{PhOH\ldots S}$[45]	$\lg W^{S}_{H^{+}}$
Dimethyl sulphoxide (DMSO)	48.9	29.8	0.9	43	362	192	—	7.6	6.5	−3.3[46]
Dimethylformamide (DMF)	36.7	26.6	5.8	42	291	166	—	4.24	6.1	−2.7[46]
Diethyl ether	4.3	19.2	—	—	280	130	40.0	1.16	5.0	—
Methanol	32.7	19.0	4.4	39	218	—	—	—	—	1.9[46]
Water (W)	80.1	18.0	0.0	46	156	—	74.6	—	—	0.0
Acetone	20.7	17.0	—	33	224	123	35.1	1.60	4.7	7[32]
Propylene carbonate	69.0	15.1	—	26	—	—	—	—	—	—
Sulpholane	42.0	14.8	—	—	157	—	—	—	4.9	10.3*
Acetonitrile	37.5	14.1	7.8	31	160	103	31.8	1.22	4.3	8.1[46]
Nitrobenzene	34.8	4.4	7.6	—	67	53	20.5	—	2.0*	—
Nitromethane (NM)	38.6	2.7	15.4	3	65	59	21.1	0.20	1.9*	15[47]
Benzene	2.3	0.1	—	0**	48	52	18.6	0.80	1.5	—
Carbon tetrachloride	2.2	(0)	—	—	0	31	11.9	0	0	—
Cyclohexane	2.0	(0)	—	—	(0)	25	—	(0)	(0)	—
Gas phase (g)	1.0	—	—	—	—	0	0	—	—	

* From data in Ref.48; **toluene.

Notation: DN is the Gutmann donor number, $-\Delta H$ the heat of formation of the complexes $SbCl_5\ldots S$ in $C_2H_4Cl_2$ (kcal mol^{-1}), $\delta^{23}Na^{+}$ the shift of the $^{23}Na^{+}$ peak in the NMR spectrum of the $NaBPh_4$ solution in S (p.p.m), Δg the change in the parameter of the EPR spectrum of the copper complex in S, $\Delta\nu_{PhOH\ldots S}$ the shift of the vibration frequency of the OH group of phenol following the PhOH...S interaction in CCl_4 (cm^{-1}), $\Delta\nu_{MeOD\ldots S}$ the shift of the vibration frequency of the OD group in MeOD on passing from the gas phase to the solvent S (cm^{-1}), $(\Delta\nu/\nu)_{HOH\ldots S}$ the ratio of the vibration frequency shift of the OH group of water on passing from the gas phase to the solvent S to the frequency in the gas phase, $K_{MeOH\ldots S}$ the formation constant of the complex MeOH...S in CCl_4, $-\Delta H_{PhOH\ldots S}$ the enthalpy of formation of the complex PhOH...S in CCl_4 (kcal mol^{-1}), and $\lg W^{S}_{H^{+}}$ the coefficient of proton solvation (transition from water to the polar solvent S).

Nitromethane[32] belongs to the class of APS containing hydrogen atoms linked only to carbon atoms and exhibiting a very weak capacity for the specific solvation of anions via hydrogen bonds[2,16,33,34]. On the other hand, the molecules of the majority of APS contain electronegative O, N, and S atoms and are capable of relatively intense specific solvation of acid and cationic centres[16]. However, numerous experimental data (Table 1) have shown that nitromethane is in fact less capable, compared with all other APS, of specific electron-donating solvation of electrophilic and cationic centres, particularly solvation involving the formation of the $XH\ldots O_2N$Me bond.

Inspection of the data in Table 1 and also the values of *DN*, $\Delta\nu_{PhOH...S}$, $\Delta\nu_{MeOD...S}$, and other indices of the electron-donating capacity[48-53] for a wider range of solvents shows that, among the known (~15) APS, nitromethane exhibits the weakest capacity for specific electron-donating solvation, particularly with formation of hydrogen bonds with uncharged acids. In conformity with this conclusion, measurements of the dissociation constants of the salts BH^+Cl^- (BH^+ = quinuclidinium or tributylammonium)[37] have shown that nitromethane solvates ammonium cations much more weakly than, for example, propylene carbonate, dimethylformamide (DMF), and dimethyl sulphoxide (DMSO).

It also follows from the data in Table 1 that nitromethane resembles more closely alkanes and CCl_4, which are incapable of forming hydrogen bonds with hydrogen donors, than water†, DMF, or DMSO, i.e., compared with these solvents, the capacity of nitromethane to behave as a hydrogen acceptor in the formation of hydrogen bonds is very low. This has also been confirmed by studies of the dependence of ν for the OH groups of water[43] and phenol[54] and the NH group of pyrrole[42,55,56] in solutions on the dielectric constant of the solvent, where the point of nitromethane fits satisfactorily on the linear plot of $\Delta\nu/\nu$ against $(\varepsilon-1)/(2\varepsilon+1)$ for the gas phase, alkanes, and chloroalkanes, while the points for solvents forming the hydrogen bonds XH...S with water, phenol, and pyrrole, namely water, DMSO, acetonitrile, ketones, ethers, and amines, deviate from this relation. The weak# capacity of nitromethane for the formation of the XH...,O_2NMe bond is apparently due to the distribution of the partial negative charge in the nitro group between the two oxygen atoms, which sharply weakens its tendency towards interaction with hydrogen donors[32,57-59] compared with other APS.

Thus the capacity of nitromethane for specific donor and acceptor solvation and particularly for the formation of hydrogen bonds with the ions A^- and BH^+ is very low and constitutes an insignificant fraction of the corresponding property of water. Consequently nitromethane can be regarded as a model solvent suitable for the elucidation of the influence of hydrogen bonding on the pK_d of various acids in water.

The availability of data for a large series of neutral and cationic organic acids in nitromethane, in which the proton is attached to oxygen, nitrogen, phosphorus, and carbon atoms (see Tables 3, 4, and 6)§ also permits an approach to the problem of the relation between the structure and solvation of these compounds.

Table 2. The standard free energies of deprotonation (ΔG_d, kcal mol^{-1}) of organic acids in various media[a].

Medium	$\overset{+}{N}H_4$	$MeN\overset{+}{H}_3$	$Me_2\overset{+}{N}H_2$	$Me_3\overset{+}{N}H$	$Ph\overset{+}{N}H_3$	$C_5H_5\overset{+}{N}H$	$Me_3\overset{+}{P}H$	*N*-Methyl-2-hydroxypyridinium	MeCOOH	PhCOOH	PhOH	Fluorene
Gas phase[b]	193[11]	203[11]	210[11]	214[11]	200[11]	210[11]	215[18]	209[64]	342[6]	332[6]	343[6]	346[6]
Nitromethane[c]	24.2[27]	27.1[27]	28.0[27]	26.9[65]	15.9[27]	19.8[66]	25[d,67]	14.1[66,68]	31.5[28]	30.1[28]	38.5[29]	48[e]
Acetonitrile	22.4[69]	25.0[69]	25.6[69]	24.0[69]	14.4[70]	16.8[70]	—	—	30.5[70]	28.3[71]	37[72]	—
DMF	12.9[73]	—	—	11[f,73]	6.0[74]	7[9]	—	—	18.5[74]	16.8[74]	25[72]	—
DMSO	14.3[70]	15[f,70]	14[f,70]	11[f,26]	5.0[26]	4.6[70]	7.0[75]	—	17[26]	15[26]	23[26]	31[26]
Water[27,76,77]	12.6	14.5	14.7	13.4	6.3	7.1	11.8[75]	0.4[64]	6.5	5.7	13.6	28.7[26]

[a] The values of ΔG_d in the solutions were calculated from the literature values of $pK_d^{25°}$ by the equation $\Delta G_d(\text{kcal mol}^{-1}) = 1.365pK_d^{25°}$.

[b] The values for $\overset{+}{N}H$-acids have been adjusted to $\Delta G_d^g(Me\overset{+}{N}H_3) = 203$ kcal mol^{-1}.[64]

[c] Quoted in accordance with the scale of Bauer and Foucqult[47] (see Korolev and Kashkovskaya[28]).

[d] $Et_3\overset{+}{P}H$; the values of pK_d for $Me_3\overset{+}{P}H$ and $Et_3\overset{+}{P}H$ in water and DMSO are virtually equal[75].

[e] Estimated from the $pK_d^{NM}-pK_d^W$ correlation for CH-acids (Table 6, series 5).

[f] Calculated from data for ethylamines (the difference between the basicities of the corresponding ethyl- and methyl-amines in water, $MeNO_2$,[27] and MeCN [69] agree to within 0.2 of a pK unit and have the following values: ~0 between $EtNH_2$ and $MeNH_2$ and between Et_2NH and Me_2NH; ~1.0 pK unit between Et_3N and Me_3N).

† In contrast to other solvents, the tendency of water to form hydrogen bonds is much greater (by a factor of 1.5 to 2)[17,53] than that[48] of isolated water molecules; in order to characterise water as a medium, the values of *DN* and $\Delta\nu_{PhOH...S}$, describing the properties of water molecules in dilute solutions in chloroalkanes, must be increased by a factor of 1.5–2. For example, for an aqueous medium *DN* ≅ 33.[48]

Contradictory views on this problem are still being expressed in the review literature (see, for example, Bell[34] and Yanovskaya[60]).

§ In the case of other APS data are available for a much more restricted range of compounds (4–6 series, see Tables 3 and 4) compared with nitromethane. The solvation-induced weakening of the sensitivity of the pK_d of three series of organic acids to the influence of substituents on passing from the gas phase to DMSO and water was examined in a recent study by J.E.Bartmess, J.A.Scott, and R.T.McIver, J.Amer. Chem.Soc., 101, 6056 (1979).

III. CONTRIBUTION OF ELECTROSTATIC SOLVATION TO THE CHANGES IN THE RELATIVE STRENGTHS OF $\overset{+}{N}H$- AND OH-ACIDS ON PASSING FROM THE GAS PHASE TO APROTIC POLAR SOLVENTS AND WATER

It is known that the changes in the deprotonation constants [pK_d; Eqns.(1) and (2)] on passing from one medium to another are determined mainly by the solvation of the charged species[2,11,61,62]. More than 80% of the solvation energy of ions in polar solvents is determined by the non-specific electrostatic solvation[16], which depends on the dielectric constant ε; the specific solvation, which is to a large extent determined by the formation of hydrogen bonds[35], makes a smaller contribution. On passing from the gas phase ($\varepsilon = 1$) to polar solvents ($\varepsilon \geq 30$), the change in acid strength should therefore depend mainly on the electrostatic solvation. In other words, the values of pK_d should vary markedly on passing from the gas phase to water, nitromethane, and other APS and should vary comparatively little on passing from one polar solvent to another.

Table 3. Transmission of the electronic effects of substituents in $\overset{+}{N}H$-acids in different media.

No. of series	Acid[a] X–M–$\overset{+}{N}H$	Bridge group	ρ^g	ρ^{NM}	ρ^W	α^{NM}	$R^{NM,g}$	$R^{W,g}$	$R^{W,NM}$
1	X (X′) (X″) $\overset{+}{N}H$	—	6.5[b9]	4.1[b,c27]	3.2[b79–81]	0.73	1.6	2.0	1.3
2	$XC_5H_4\overset{+}{N}H$	C_5H_4	13.8[d]	7.6[e88]	6.0[e82]	0.80	1.8	2.3[12]	1.3
3	$XC_6H_4\overset{+}{N}H_3$	C_6H_4	7.5[d]	4.2[e65]	2.9[e83]	0.72	1.8	2.6[13]	1.45

[a] X = substituent and M = bridge group; [b] the value of ρ^* is quoted; [c] the value of ρ^* in MeCN is 4.2;[24] [d] calculated from the values of $R^{W,g}$ and ρ^W; [e] the value of ρ in MeCN and MeOH is 4.1 [65] and that in DMSO is 3.8.[65]

Notation: $\alpha^{NM} = (\rho^g - \rho^{NM})/(\rho^g - \rho^W)$; $R^{NM,g} = \rho^g/\rho^{NM}$; $R^{W,g} = \rho^g/\rho^W$; $R^{W,NM} = \rho^{NM}/\rho^W$.

Table 4. Transmission of the electronic effects of substituents in OH-acids in different media.

No. of series	Acid[a] X-M-OH	Bridge group	ρ^g	ρ^{NM}	ρ^W	α^{NM}	$R^{NM,g}$	$R^{W,g}$	$R^{W,NM}$
4	XOH	—	7.0[b9]	4.6[c98]	2.7[b9]	0.6	1.5	2.6	1.7
5	XC_6H_4OH	C_6H_4	15.0[d]	4.5[e29]	2.2[83]	0.82	3.3	6.8[10]	2.0
6	XCOOH	CO	5.5[b9]	3.6[b,f28]	1.8[b99]	0.51	1.5	3.0	2.0
7	XC_6H_4COOH	C_6H_4CO	10.6[1e]	2.55[g65]	1.00	0.84	4.2	10.6	2.55

[a] X = substituent and M = bridge group; [b] the value of ρ^* is quoted; [c] the value of ρ^{*DMSO} is quoted instead of ρ^{*NM}, which is permissible, since the values of $\rho(\rho^*)$ for OH-acids in $MeNO_2$, DMSO, and DMF are similar (see Ref.33 and footnotes *e*, *f*, and *g*); [d] calculated from the values of $R^{W,g}$ and ρ^W; [e] $\rho^{MeCN} = 4.5$, $\rho^{DMF} = 4.5$, and $\rho^{DMSO} = 4.3$ [72]; [f] the values of ρ^* for MeCN, DMF, and DMSO are 3.5 [24]; [g] $\rho^{MeCN} = 2.4$ [100] and 2.6,[9] $\rho^{DMF} = 2.35$,[9,100] and $\rho^{DMSO} = 2.5$ [100] and 2.6.[9] For the significance of the notation, see Table 3.

This conclusion is fully confirmed by the experimental data in Table 2 and Fig.1: the change in ΔG_d for OH-, $\overset{+}{O}H$-, $\overset{+}{N}H$-, $\overset{+}{P}H$-, and CH-acids on passing from water to nitromethane and other APS (10–25 kcal mol^{-1}) amounts to a very small fraction (5–8%) of the decrease of ΔG_d in the transition gas phase → polar solvent (170–320 kcal mol^{-1}).¶ The solvation energy of the proton $\Delta G_s^S(H^+)$, which amounts to -260.5 kcal mol^{-1} for water[11] and ~-240 kcal mol^{-1} for nitromethane (calculated from $\lg {}^W\gamma_{H^+}^{NN}$; Table 1) plays a decisive role in the enormous increase of acidity in solutions. The energy of solvation of organic ions $\Delta G_s^S(I^\pm)$ (50–80 kcal mol^{-1}; [15,25] see Table 5) likewise plays an important role; the solvation of uncharged species is several times weaker[2,15].

Table 5. The solvation energies of organic ions determined by the charge [$-\Delta G_s^S(I^\pm)_{el+hb}$, kcal mole^{-1}*].

Ion $I^\pm$	Water	Nitromethane	Dimethyl sulphoxide
$\overset{+}{N}H_4$	80	71	86
$Me\overset{+}{N}H_3$	72 (8)	64 (7)	77 (9)
$Me_2\overset{+}{N}H_2$	65 (7)	58 (6)	69 (8)
$Me_3\overset{+}{N}H$	60 (5)	53 (5)	63 (6)
$C_5H_5\overset{+}{N}H$	58	50	60
$Ph\overset{+}{N}H_3$	67	56	70
$Me_3\overset{+}{P}H$	52	44	51
$MeCOO^-$	83	74	70
$PhCOO^-$	76	67	64
PhO^-	78	69	66

* The solvation energies were calculated from the equations[11,38] $\Delta G_s^S(BH^+)_{el+hb} = \Delta G_d^g - \Delta G_d^S + \Delta G_s^S(H^+)$ and $\Delta G_s^S(A^-)_{el+hb} = -\Delta G_d^g + \Delta G_d^S - \Delta G_s^S(H^+) + \Delta G_s^S(HA)_{hb}$. The values of ΔG_d^g and ΔG_d^S are listed in Table 2; $\Delta G_s^W(H^+) = -260.5$ kcal mole^{-1},[11] $\Delta G_s^{NM}(H^+) = -240$ kcal mole^{-1} (see above), and $\Delta G_s^{DMSO}(H^+) = -265$ kcal mol^{-1} (calculated from $\lg {}^W\gamma_{H^+}^{DMSO}$,[46] Table 1). Using Kolthoff's data[33] and assuming that the $\Delta G_s^S(HA)_{hb}$ for $PhNO_2$ and $MeNO_2$ are close to zero (see above), we have $\Delta G_s^W(HA)_{hb} \cong -5$ kcal mol^{-1} and $\Delta G_s^{DMSO}(HA)_{hb} \cong -7$ kcal mol^{-1}. The accuracy of the absolute values of $\Delta G_s^S(I^\pm)_{el+hb}$ is to within several kcal mol^{-1}, while the relative values are correct to within 1 kcal mol^{-1}. The effect of each methyl group in the ammonium cations is indicated in brackets.

When the pK_d are compared in a single medium, the proton solvation factor cancels out and the differences in the solvation of the ions BH^+ and A^- become of primary importance. Bearing in mind the foregoing, it is logical to assume that the change (weakening) of the influence of substituents on pK_d in the gas phase → water transition is caused mainly by the non-specific electrostatic solvation of ions. However, the literature data on this problem are contradictory. Thus the weakening (compared with the gas phase) of the influence of substituents on the basicity of amines and pyridines ($\overset{+}{N}H$-acids) and the differences in basicity between different classes of amines in water have been explained[17–20], in conformity with the most widely held view, by the specific hydration of ammonium cations via the hydrogen bonds $\overset{+}{N}H\ldots OH_2$,

¶ These figures correspond to the increase of K_d in solutions by a factor of 10^{125}–10^{230}. Fig.1 also shows that the effect of solvation on pK_d is much greater than that of the structure[1,63].

while other workers[11,12] explain it by the non-specific electrostatic hydration of cations due to the high dielectric constant. For neutral acids HA, the weakening of the influence of substituents on the pK_d in water can also be caused by both types of solvation of the anions A^- indicated above[78], but in many investigations only the formation of the $A^-...HOH$ hydrogen bond has been discussed[7,10,62].

Table 6. Parameters of the relations between the pK_d for acids in nitromethane[27-29,65-68,107-112] and water[22,73,77,113]: $pK_d^{NM} = R^{W,NM}\, pK_d^W + b$.

No.	Series	$R^{W,NM}$	b	r	s	n	pK_d^W for $pK_d^{NM} = 16$
			Neutral acids				
1	$XCOOH$[107]	2.04±0.11	11.23	0.994	0.42	6	2.3
2	XC_6H_4COOH[107]	2.61±0.11	8.44	0.993	0.20	9	2.9
3	XC_6H_4OH[107]	1.94±0.09	6.24	0.997	0.24	5	5.0
4	X_2NH[a]	1.1[b]	7.4[b]	—	—	2	8.1[b]
5	X_3CH[c]	1.2[b]	4.8[b]	—	—	2	7.8[b]
			Cationic acids				
6	$X_3\overset{+}{P}OH$[d]	2.3	10.9	—	—	2	2.2
7	$X_3\overset{+}{A}sOH$[112]	1.96	8.31	0.980	0.37	5	3.9
8	$X_2C{=}\overset{+}{O}H$[e]	1.85±0.06	6.39	0.996	0.39	9	5.2
9	$XC_5H_4\overset{+}{N}OH$[107]	1.64±0.18	7.61	0.982	0.45	5	5.1
10	$X(NH_2)_2C_3N_3H^+$[f]	1.39±0.05	5.67	0.995	0.14	9	7.4
11	XC_5H_4NH[107]	1.22±0.03	5.77	0.996	0.25	13	8.4
12	$X_3\overset{+}{P}H$[107]	1.22±0.12	4.76	0.991	0.53	4	9.2
13	$X_3\overset{+}{N}H$[g]	1.35±0.04	3.85	0.995	0.30	13	9.0
14	$X_2\overset{+}{N}H_2$[g]	1.30±0.03	3.56	0.997	0.27	12	9.6
15	$X\overset{+}{N}H_3$[g]	1.26±0.01	3.50	0.999	0.26	27	9.9

[a] Polynitroarylamines[107]; [b] approximate data; [c] 9-substituted fluorenes[107]; [d] Et_3PO,[110,113], $PhCH=CHP(O)Alk_2$;[111,113] the parameters of line 6 are close to those of the relation calculated[107] on the basis of the correlation between $pK_d^W(6)$ and $pK_d^{NM}(6)$ with $\Sigma\sigma^P$; [e] pyridones, $(H_2N)_2CO$, DMF, $MeCONH_2$, phenalenone[107]; [f] 6-substituted 2,4-diamino-*sym*-triazines[109]; [g] aliphatic and aromatic amines[27,65].

The results of the study of the relative roles of the above solvation factors with the aid of nitromethane as a model solvent[65] are presented in Tables 3 and 4. Before discussing the data in these two Tables, we shall consider the relations between the constants of equilibria (1) and (2) and ion solvation. It has been shown[11,33] that the change in the influence of substituents X on the pK_d for reactions (1) and (2) on passing from the gas phase to a polar solvent S is determined to a first approximation by the change in the free energy of solvation of the ions A^- and BH^+, which is due to the presence of the charge† and includes both the contribution ΔG_s^S.

† This quantity represents the solvation energy of ions A^-, and BH^+, from which the neutral component, assumed equal to the solvation energy of the neutral species HA or B, has been subtracted[11,33]. It has been called[11,33] the "electrostatic" [11] or "electrical" [33] component, having in view solvation caused by the charge of the ion, i.e. solvation due to the purely electrostatic interaction and the formation of a hydrogen bond; we believe that this component is best referred to as the "solvation energy determined by the charge" and that it should be designated by $\Delta G_s^S(I^\pm)_{el+hb} = \Delta G_s^S(I^\pm)_{el} + \Delta G_s^S(I^\pm)_{hb}$.

$(I^\pm)_{el}$ due to electrostatic solvation and the contribution $\Delta G_s^S(I^\pm)_{hb}$ due to the formation of the hydrogen bonds $A^-...HS$ and $BH^+...S$:

$$1.36(\delta p K_d^g - \delta p K_d^S) = \delta \Delta G_d^S (I^\pm)_{el} + \delta \Delta G_d^S (I^\pm)_{hb},$$

where the operator δ [4,17,18] denotes a change in the substituent, for example, $\delta pK_d(BH^+) = pK_d(XBH^+) - pK_d(BH^+)$. In order to elucidate the contribution of each of these components, the changes in δpK_d on passing from the gas phase to nitromethane (incapable of forming a hydrogen bond) and from the gas phase to water (forming strong hydrogen bonds) are considered in Tables 3 and 4:

$$\alpha^{NM} = (\delta p K_d^g - \delta p K_d^{NM})/(\delta p K_d^g - \delta p K_d^W).$$

Bearing in mind the limited number of known values of δpK_d for the same X in different media (for example, for aliphatic amines in the gas phase and in solutions), the quantities δpK_d can be conveniently expressed in terms of the values of ρ in the Hammett and Taft equations ($\delta pK_d^S = -\rho^S \sigma_X$):

$$\alpha^{NM} = (\rho^g - \rho^{NM})/(\rho^g - \rho^W).$$

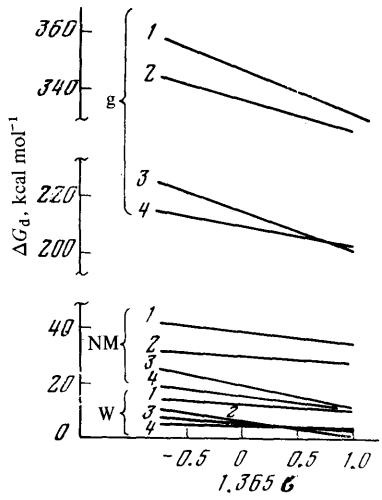


Figure 1. Schematic representation of the Hammett relations between the ΔG_d for the acids XC_6H_4OH (line *1*), XC_6H_4COOH (line *2*), $XC_5H_4\overset{+}{N}H$ (line *3*), and $XC_6H_4\overset{+}{N}H_3$ (line *4*) in the gas phase (g), nitromethane (NM), and water (W) and the σ constants of the substituents (according to the data in Tables 2, 3, and 4).

The data for ammonium cations of different structure in the gas phase, nitromethane, and water are compared in Table 3. For series 1–3, the values of ρ in nitromethane are much closer to those in water than in the gas phase; the values of α^{NM} show that the decrease of ρ on passing from the gas phase to nitromethane is 73–80% of the corresponding change in ρ on passing from the gas phase to water. Consequently the specific solvation of ammonium cations with formation of the $\overset{+}{N}H...OH_2$ hydrogen bond is responsible for only a small proportion (1/5–1/4) of the weakening of the influence of substituents in the gas phase → water transition and a major proportion of this effect is caused by the purely electrostatic hydration of the ammonium cations.

An interesting feature of amines is that, when $pK_d - \Sigma\sigma^*$ plots based on the variables of the Taft equation are constructed, the points for primary, secondary, and tertiary amines in the gas phase fit on a single straight line to a first approximation[9] #, while the points for the amines in water give rise to different straight lines[79,80]; the values of pK_d increase in the sequence $X_3\overset{+}{N}H < X_2\overset{+}{N}H_2 < X\overset{+}{N}H_3 < \overset{+}{N}H_4$, which is usually explained[9,79-81] by the formation of hydrogen bonds with different numbers of hydrogen atoms in the ammonium cations. According to the results already examined, the change in the degree of hydration of substituted ammonium cations must be determined not by hydrogen bonding but by electrostatic solvation and the relations between pK_d and $\Sigma\sigma^*$ for water and nitromethane should be similar. This conclusion has been confirmed by the data of Korolev et al.[27]: the distances between the $pK_d - \Sigma\sigma^*$ straight lines for $X_3\overset{+}{N}H$, $X_2\overset{+}{N}H_2$, and $X\overset{+}{N}H_3$ are similar for both solvents. Comparison of the basicities of the amines in the two solvents leads to the same results (see Section IV).

Consequently, a major proportion of the differences between the $pK_d - \Sigma\sigma^*$ straight lines for the conjugate acids of primary, secondary, and tertiary amines is caused by the electrostatic solvation of the ammonium cations in water and not by the number of $\overset{+}{N}H\ldots OH_2$ hydrogen bonds formed; it has been shown[11] that the increase in the degree of electrostatic solvation in the sequence $X_3\overset{+}{N}H < X_2\overset{+}{N}H_2 < X\overset{+}{N}H_3 < \overset{+}{N}H_4$ can be explained by the decrease of the effective radius of the cations, which is determined by the size of the cations and the degree of asymmetry of their charges.

These results show that the weakening of the influence of substituents on the pK_d and the differentiation of the basicities of the series of X_3N, X_2NH, and XNH_2 amines on passing from the gas phase to water are determined mainly by the change in the degree of non-specific electrostatic hydration of the ammonium cations. This conclusion is unexpected, because in most studies (specially devoted to this subject) it has been claimed up to the present time (see, for example, Refs.17–20, 81, and 96) that the above characteristics of the behaviour of amines in water are caused by the formation of the $\overset{+}{N}H\ldots OH_2$ hydrogen bonds§. However, the data presented above agree with those of Aue et al.[11], who concluded that the additional (compared with the metal cations or $X_4\overset{+}{N}$) interaction of the $\overset{+}{N}H_4$ ion with water is small and amounts to ~2 kcal mol^{-1} per hydrogen atom, while the decrease of the hydration energy in the successive transitions from $\overset{+}{N}H_4$ to $Me_4\overset{+}{N}$ is ~6–8 kcal mol^{-1} per hydrogen atom.

The data presented below (Table 5) confirm these conclusions. Indeed, the differences between the solvation energies of the $\overset{+}{N}H_4$, $Me\overset{+}{N}H_3$, $Me_2\overset{+}{N}H_2$, and $Me_3\overset{+}{N}H$ ions in solvents differing very greatly in their capacity for the formation of $\overset{+}{N}H\ldots S$ hydrogen bonds vary in the range 1–2 kcal mol^{-1} and, as might have been expected, they increase only slightly as the $\overset{+}{N}H\ldots S$ hydrogen bonds are strengthened in the sequence nitromethane, water, DMSO.

Inspection of the data in Table 4 for neutral OH-acids shows that their values of α^{NM} are in the range 0.5–0.8, i.e. that a considerable proportion of the weakening of the influence of substituents on the pK_d of the acids HA on passing from the gas phase to water is caused by the electrostatic solvation of the ions A^- in the aqueous medium. For benzoic acids and phenols, this proportion is 80%. Consequently, contrary to the widely held view[10,62], the $XC_6H_4COO^-\ldots HOH$ and $XC_6H_4O^-\ldots HOH$ hydrogen bonds are responsible for only 1/5 of the decrease of ρ in the gas phase → water transition¶.

We may note that McMagon and Kebarle[10] infer the degree of solvation of anions in water and APS from the factor by which ρ^g is greater than ρ^W and ρ^{APS}. However ρ^S is none other than ρ^g decreased as a result of the solvation of the ions; therefore in elucidating the solvation effects, one must consider not the factor by which ρ^W and ρ^{APS} have been reduced compared with ρ^g but the actual amount of the reduction. For example, for the XC_6H_4COOH series ($\rho^g = 10.6$, $\rho^{NM} = 2.55$, and $\rho^W = 1.00$), one must compare the differences $\rho^g - \rho^W = 10.6 - 1.00 = 9.6$ and $\rho^g - \rho^{NM} = 10.6 - 2.55 = 8.00$, which are fairly close, and not the ratios $\rho^g/\rho^W = 10.6/1 = 10.6$ and $\rho^g/\rho^{NM} = 10.6/2.55 = 4.2$, which differ considerably.

The possibility of a marked change in the degree of electrostatic solvation of the anions in APS follows from the results of studies[102-104] where the solvation of the halide, XO^-, $XC_6H_4O^-$, and $XC_6H_4COO^-$ ions was considered in DMSO, which is incapable of behaving as a hydrogen donor on formation of a hydrogen bond.

The significant role of the electrostatic solvation of the ions A^- and BH^+ in the decrease δpK_d on passing from the gas phase to water is due to the fact that ~80% of the entire solvation energy of ions in polar solvents (particularly in water) is determined by their electrostatic solvation[16]. The substituents X, which intensify (or weaken) the localisation of the charge in the organic ion, increase (or diminish) both the degree of electrostatic solvation[31] and the degree of ion solvation via hydrogen bonding[19]. Both these effects decrease δpK_d, but the much greater energy of the electrostatic solvation of ions explains its considerable role in the weakening of the influence of the substituent X on the pK_d in water. The

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It has been observed[15] that the points of alkyl substituents on this approximate straight line, common to alkyl and polar (electronegative) substituents, form linear groups with an increased slope, which has also been observed for other series for both the gas phase[9,84] and for solutions[35,85-88]. It has now been established that the effects of alkyl substituents are of a different type compared with the inductive influence of polar substituents[1] and that the effects of all groups cannot be described by a single Taft equation[21,35,89-94], i.e. in plotting pK_d against $\Sigma\sigma^*$ polar substituents should be used[21,35,93,94]. Bearing in mind that the points for amines with polar substituents in the gas phase do not exhibit a tendency towards the formation of individual straight lines, we think it most reasonable to consider the $\Delta G_d^g - \Sigma\sigma^*$ correlation for ammonium cations as an approximately single straight line[9] distorted by the specific effects of hydrocarbon substituents (for example, the effect of the polarisability of alkyl substituents[9,14,85,95]). Despite these distortions, the values of ρ^* obtained in this way[9] for amines (6.5) and alcohols (7.0) in the gas phase are apparently correct, since an approximate estimate of the transmission of only the inductive effect in the gas phase leads to similar values of ρ^* for these series (increased by ~15–20%; calculated from the data of Taft et al.[85]).

§ The view has been expressed[15,97] that the role of solvation in the changes of the relative basicities of amines in water is small.

¶ It has been shown recently[101] that the interaction of substituted pyridinium ions and phenoxides with a single water molecule in the gas phase (with formation of the $XC_5H_4\overset{+}{N}H\ldots OH_2$ and $XC_6H_4O^-\ldots HOH$ hydrogen bonds) leads to a much smaller (by a factor of ~5) weakening of the influence of substituents than the solvation of these ions in aqueous solution.

cause of the change in the degree of electrostatic solvation becomes clear[31,105] from an examination of the Born equation [Eqn.(4)]: the introduction of a substituent capable of delocalising the charge (for example, of an electron acceptor into the anion A^-) increases the effective ionic radius and leads to a corresponding decrease of the degree of electrostatic solvation of the ion. This effect is always directed towards the compensation of the influence of the substituent on pK_d.[105]

IV. THE INFLUENCE OF SOLVATION VIA HYDROGEN BONDING ON THE RELATIVE STRENGTHS OF ORGANIC ACIDS IN APROTIC POLAR SOLVENTS AND WATER

Examination of the data of the previous section shows that the change in the strength of acids and of their sensitivity to the influence of substituents on passing from the gas phase to polar solvents is determined mainly by the non-specific electrostatic solvation of ions. However, on passing from one polar solvent to another, the degree of electrostatic solvation of ions changes very little[16,106] and the difference in the specific solvation of ions, which is to a large extent caused by the formation of hydrogen bonds, may become of primary importance. In order to elucidate the role of hydrogen bonds, it was of interest to compare different types of acids in polar solvents with markedly different capacities for the formation of hydrogen bonds, for example, in water, DMSO, and nitromethane:

HB	A^-...HS	BH^+...S
Water	s.	s.
Dimethyl sulphoxide	v.w.	v.s.
Nitromethane	v.w.	v.w.

Notation: s., v.w., and v.s. denote strong, very weak, and very strong hydrogen bonds.

The experimental data obtained in the last ten years for DMSO and nitromethane (Tables 6 and 7) permit such a comparison[107]. We may note that if the specific solvation of the ions A^- and BH^+ [Eqns.(1) and (2)] were absent from all the solvents or were the same, then the points for all types of acids on the plot of pK_d^S against $pK_d^{S_1}$ should fall on a single straight line to a first approximation. The results of a comparison of the pK_d for 15 series of neutral and cationic oxygen, nitrogen, phosphorus, and carbon acids in these solvents, presented in Figs.2–4 and Tables 6–8, show that each structural series gives rise to an individual straight line displaced relative to the other series and having a slope different from unity. Consequently, each class of acids in the given solvent has a characteristic solvation energy, different from those of the other classes and depending on the substituents, the differences in the positions of the straight lines for different types of acids being fairly large (up to 10 pK units; see Fig.3).

Examination of the data in Fig.2 and Table 6 for the neutral acids HA (series 1–5) shows that the acids can be arranged in the following sequence in terms of the displacement relative to the pK_d^W axis (for example, for $pK_d^{NM} = 16$):

$$pK_d^W : XCOOH \ll XC_6H_4COOH < XC_6H_4OH < X_2NH \simeq X_3CH.$$

For $pK_d^{DMSO} = 10$, the acids HA give rise to a similar sequence of the plots of pK_d^{DMSO} against pK_d^W (Fig.3 and Table 7):

$$pK_d^W : XCOOH \ll XC_6H_4COOH < XC_6H_4OH < X_2NH < X_3CH.$$

This behaviour is explained by the fact that, in contrast to nitromethane and DMSO, water is a fairly powerful hydrogen donor in the formation of the A^-... HOH hydrogen bonds. This leads to additional stabilisation in water of anions with a localised charge and to a decrease of the pK_d of their conjugate acids in water. Thus the lowest values of pK_d in water are those of carboxylic acids in the conjugate bases of which (carboxylates) the charge is localised on the carboxylate group; on passing to phenoxides, where the degree of delocalisation of the charge is greater[10,29], and A^-...HOH hydrogen bond is weakened, and the pK_d for phenols are higher. The A^-...HOH hydrogen bond is weaker still for NH-acids (polynitroarylamines) and CH-acids (9-substituted fluorenes), where the charge on the anions is even more localised owing to the smaller electronegativity of the nitrogen and carbon atoms and the "electron withdrawing" influence of the nitrogroups.

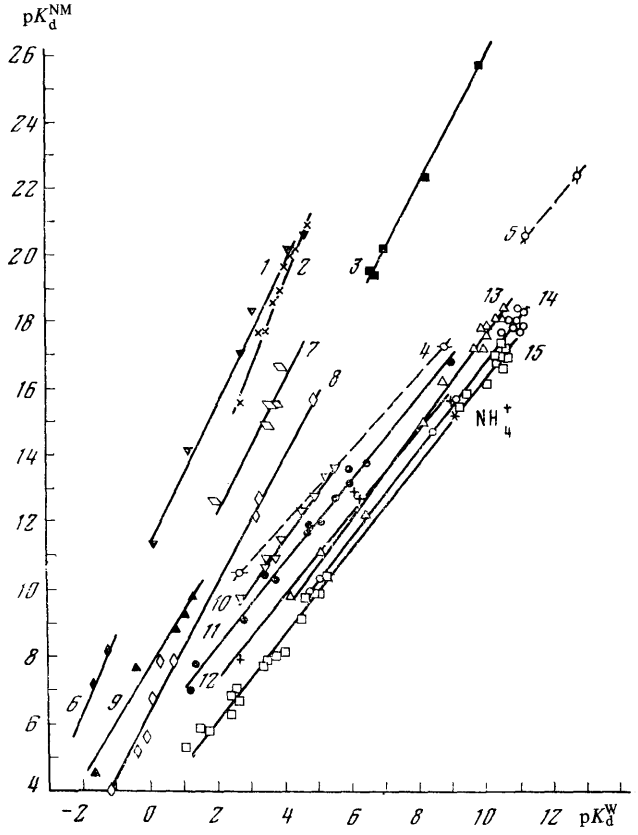


Figure 2. Relations between pK_d in nitromethane and water[65,107,109,112]: *1*)–*15*) see Table 6.

The intensification of ion solvation with formation of hydrogen bonds is known to weaken the influence of substituents of the pK_d,[3,61] which should lead to an increase of the slope R of the plots of pK_d^{NM} and pK_d^{DMSO} against pK_d^W. The data in Tables 6 and 7 show that the values of $R^{W,NM}$ and $R^{W,DMSO}$ to

a first approximation obey this rule for all the series (except XCOOH)#:

$$R^{W,NM}: XC_6H_4COOH\ (2.6) > XC_6H_4OH\ (1.95) > X_2NH\ (\sim 1.1) \sim X_3CH\ (\sim 1.2);$$
$$R^{W,DMSO}: XC_6H_4COOH\ (2.45) > XC_6H_4OH\ (2.15) > X_2NH\ (1.55) \geqslant X_3CH\ (1.45).$$

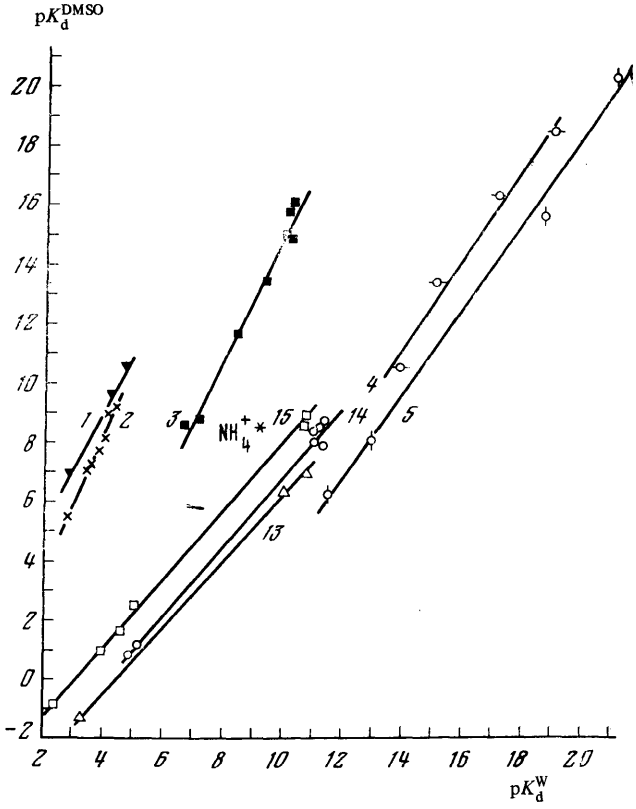


Figure 3. Relations between pK_d in dimethyl sulphoxide and water[65,107]: *1*)–*5*) and *13*)–*15*) see Table 7.

Taking into account the very weak ability of nitromethane and DMSO to function as hydrogen donors in the formation of hydrogen bonds, one may expect that the points for all neutral acids on the plot of pK_d in these solvents (Fig.4) should lie on a single straight line with a slope close to unity. Examination of Fig.4 shows that this prediction holds only for oxygen acids: the XCOOH, XC_6H_4COOH, and XC_6H_4OH series give rise to closely spaced straight lines with a slope of approximately unity. As regards NH- and CH-acids, their pK_d in DMSO are greatly reduced compared with OH-acids. The NH- and CH-acids investigated, forming anions with a highly delocalised charge, are apparently additionally stabilised in DMSO as a result of a disperson interaction[3], which is determined by the increased polarisability of DMSO compared with nitromethane[2]. This hypothesis is consistent with available data showing that the dispersion stabilisation of the carbanions in DMSO can lead to a decrease of the pK_d for CH-acids in DMSO by several pK units[61]. This factor must operate also in the correlation between pK_d in DMSO and water (Fig.3), where, together with the factor associated with the formation of the $A^-...HOH$ hydrogen bond, it leads to a decrease of pK_d for NH- and CH-acids in DMSO by up to 12 pK units compared with OH-acids.

Table 7. Parameters of the relations[107] between the pK_d for acids in DMSO [22,26,70,72,73,100] and water[22,73,77]: $pK_d^{DMSO} = R^{W,\,DMSO} pK_d^W + b$.

No.	Series	$R^{W,DMSO}$	$-b$	r	s	n	pK_d^W for $pK_d^{DMSO} = 10$
			Neutral acids				
1	XCOOH	1.94±0.07	−3.32	0.999	0.09	3	3.4
2	XC_6H_4COOH	2.43±0.13	−0.61	0.993	0.17	7	3.9
3	XC_6H_4OH	2.14±0.10	4.14	0.993	0.39	8	6.6
4	X_2NH *	1.55±0.15	8.17	0.990	0.60	4	11.7
5	X_3CH *	1.46±0.09	8.52	0.997	0.67	4	12.7
			Cationic acids				
13	$X_3\overset{+}{N}H$ *	1.14±0.04	3.03	0.999	0.21	3	11.4
14	$X_2\overset{+}{N}H_2$ *	1.19±0.04	2.94	0.997	0.30	7	10.9
15	$X\overset{+}{N}H_3$ *	1.18±0.02	1.67	0.999	0.14	6	9.9

* See footnote *a*, *b*, and *g* to Table 6.

Table 8. Parameters of the relations[107] between the pK_d for acids in nitromethane[28,29,65,107] and DMSO [22,26,70,72,73,100,107]: $pK_d^{NM} = R^{DMSO,\,NM} pK_d^{DMSO} + b$.

No.	Series	$R^{DMSO,NM}$	b	r	s	n	pK_d^{DMSO} for $pK_d^{NM} = 16$
			Neutral acids				
1	XCOOH	0.99±0.16	8.30	0.987	0.43	3	7.8
2	XC_6H_4COOH	1.13±0.06	7.23	0.994	0.18	7	7.8
3	XC_6H_4OH	0.94±0.05	9.54	0.997	0.26	4	6.9
4	X_2NH *	0.8**	13.6**	—	—	2	3.0**
5	X_3CH *	1.0**	13.0**	—	—	2	3.3**
			Cationic acids				
13	$X_3\overset{+}{N}H$ *	1.08±0.05	8.47	0.994	0.38	7	7.0
14	$X_2\overset{+}{N}H_2$ *	1.08±0.01	6.73	1.000	0.11	7	8.6
15	$X\overset{+}{N}H_3$ *	1.12±0.01	4.81	1.000	0.13	6	10.0

*See footnotes *a*, *c*, and *g* to Table 6.

**Approximate data.

Proceeding now to the consideration of cationic acids BH^+, we may note that, according to the results of the previous Section, the $\overset{+}{N}H...OH_2$ hydrogen bonds should not play a major role in increasing the values of pK_d^W in the sequence $X_3\overset{+}{N}H < X_2\overset{+}{N}H_2 < X\overset{+}{N}H_3 < \overset{+}{N}H_4$. Examination of the relation between pK_d^{NM} and pK_d^W for $\overset{+}{N}H$-acids (Fig.2, series 13–15) confirms this conclusion, since primary, secondary, and tertiary amines form comparatively closely spaced straight lines (the distances between them are 0.3–0.5 of a pK unit, while the distance between the $pK_d^W - \Sigma\sigma^*$ straight lines is 1.1–2.5

The cause of the lower slope for the XCOOH series compared with XC_6H_4COOH was examined in Section V.

pK units). For DMSO, which is a much weaker hydrogen acceptor in the formation of a hydrogen bond than water, the influence of the number of $\overset{+}{N}H...OSMe_2$ hydrogen bonds is more appreciable: when pK_d^{NM} is plotted against pK_d^{DMSO} and pK_d^{DMSO} is plotted against pK_d^{W}, the straight lines of amines are displaced along the pK_d^{DMSO} axis in such a way that the values of pK_d^{DMSO} decrease in the sequence $\overset{+}{N}H_4 > X\overset{+}{N}H_3 > X_2\overset{+}{N}H_2 > X_3\overset{+}{N}H$ (Figs. 3 and 4).

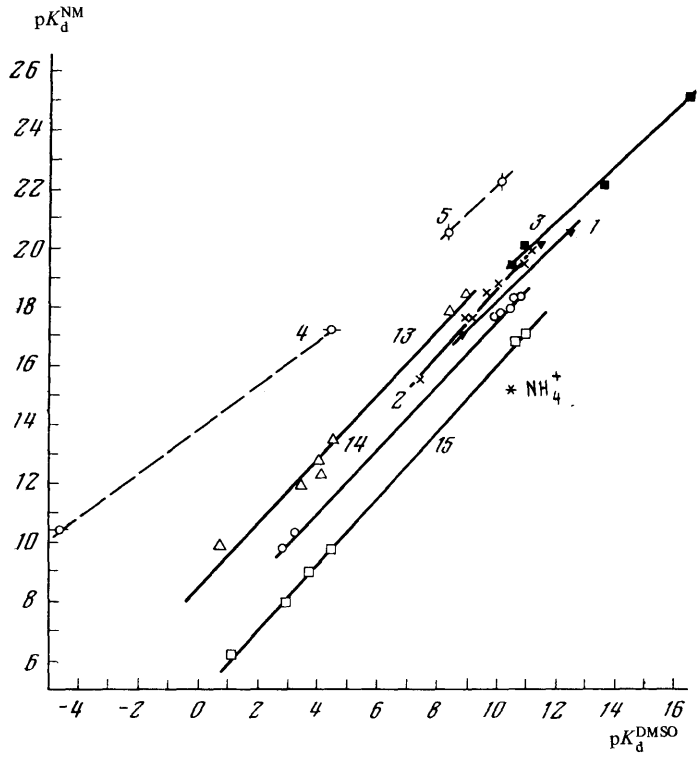


Figure 4. Relations between pKd in nitromethane and dimethyl sulphoxide[65,107]: *1*)–*5*) and *13*)–*15*) see Table 8.

In contrast to OH-acids, where a significant increase in sensitivity to the influence of substituents is observed on passing from water, forming $A^-...HOH$ hydrogen bonds, to APS incapable of such solvation [$R^{W,S} = 2.0–2.6$ for S = nitromethane, DMSO, acetonitrile, or DMF (Table 4)[72,100]], for $\overset{+}{N}H$-acids the difference between water and nitromethane, which differ very markedly as regards their capacity for the formation of the $\overset{+}{N}H...S$ hydrogen bond, is small [$R^{W,NM} = 1.3–1.4$ (Table 3)]. Furthermore, the decrease of $R^{W,S}$ for $\overset{+}{N}H$-acids in the sequence acetonitrile (1.3-calculated from Korolev's data[65]) ≅ nitromethane (1.3) > DMSO(1.17) > water (1.0) agrees satisfactorily with the slight increase of the dielectric constants of the solvents in this sequence (Table 1). The data obtained confirm the conclusion that the $\overset{+}{N}H...OH_2$ hydrogen bonds play a very insignificant role in the decrease δpK_d for $\overset{+}{N}H$-acids in an aqueous medium. The increased energy of the hydrogen bonds formed by the anions of OH-acids ($XO^-...HOH$, $XCOO^-...HOH$) compared with the energy of the $\overset{+}{N}H...OH_2$ bond can apparently be explained by the considerable localisation of the negative charge on one or two electronegative oxygen atoms in these anions, while in $\overset{+}{N}H$-acids the positive charge is either distributed between the four hydrogen atoms in $\overset{+}{N}H_4$ or is delocalised by virtue of the substituent in $X_n\overset{+}{N}H_{4-n}$ (for example, the charge on the $\overset{+}{N}H$ group in $Me_3\overset{+}{N}H$ is only 0.3).[114]

The fact that the relative values of pK_d for pyridinium cations in water are lower by 0.6–1.0 of a pK unit than for tertiary ammonium cations (Fig. 2, series 11 and 13) is probably due to the difference between the capacities for the formation of hydrogen bonds: the $\rangle N...HOH$ bond is more favourable than $X_3N...HOH$. This conclusion is consistent with the results of a study[115] of the formation of complexes of pyridines and tertiary amines with *p*-fluorophenol. The basicity of 2,4-diamino-*sym*-triazines in water (Fig. 2, series 10; the proton adds to the ring nitrogen atom[109]) is lower by a further 0.4–0.7 of a pK unit, which can apparently be explained by the increased stabilisation of the bases in water via the formation of an N...HOH bond with several nitrogen atoms of the heterocycle and the amino-groups; the energy of these hydrogen bonds should diminish greatly after protonation. The results obtained show that, within the limits of the same type of acids, the positions of the straight lines for acids of different structure can be determined by the differences between the solvation of species without a formal charge.

Examination of the relations between pK_d^{NM} and pK_d^{W} for the cationic acids BH^+ of different types (Fig. 2, series 6–13) shows that they are displaced along the pK_d^{W} axis, forming the series

$$pK_d^W: X_3\overset{+}{P}OH < X_3\overset{+}{A}sOH < X_2C{=}\overset{+}{O}H \simeq XC_5H_4\overset{+}{N}OH < X_3\overset{+}{N}H \simeq X_3\overset{+}{P}H.$$

It is noteworthy that, in contrast to $\overset{+}{N}H$- and $\overset{+}{P}H$-acids, the conjugated bases of the $\overset{+}{O}H$-acids ($E{=}O - E^+{-}O^-$, where $E = \rangle P$, $\rangle As$, $\rangle N$, or $\rangle C$) carry a considerable partial negative charge localised on the electronegative oxygen atom, which cannot be stabilised by the formation of hydrogen bonds, with nitromethane, while in water they are very effectively solvated with formation of the $E^+{-}O^-...HOH$ bond. As a result of this, $\overset{+}{O}H$-acids exhibit an additional acidity in water compared with $\overset{+}{N}H$- and $\overset{+}{P}H$-acids. The increase of the acidity in water of the $\overset{+}{O}H$-acids in the series $\overset{+}{N}OH \cong \overset{+}{C}OH < \overset{+}{A}sOH < \overset{+}{P}OH$ can evidently be explained by the increased tendency towards the formation of $E^+{-}O^-...HOH$ hydrogen bonds in the series of bases $\overset{+}{N}{-}O^- \cong C{=}O < As{=}O < P{=}O$. This series is consistent with the relative increase of the strength of the hydrogen bonds between the above bases and *p*-fluorophenol; for example, for $pK_d^W \cong 0$, the enthalpies of formation of complexes with *p*-fluorophenol are $\overset{+}{N}{-}O^-$ (6.7 kcal mol^{-1}) ≦ C=O (7.0–7.1 kcal mol^{-1}) < P=O (8.7 kcal $mole^{-1}$).[116]

The slope of the plots of pK_d^{NM} against pK_d^{W} for the cationic acids BH^+ increases, as is to be expected, with increase in the degree of hydration of the conjugated bases via the formation of B...HOH hydrogen bonds (Table 6):

$$R^{W,NM}: X_3\overset{+}{P}H\,(1.2) \simeq X_3\overset{+}{N}H\,(1.2–1.3) < XC_5H_4\overset{+}{N}OH\,(1.65) \leqslant$$

$$\leqslant X_2C{=}\overset{+}{O}H\,(1.85) < X_3\overset{+}{A}sOH\,(1.95) < X_3\overset{+}{P}OH\,(2.4).$$

Thus, comparison of the strengths of the organic acids HA and BH^+ of different structure in water, DMSO, and nitromethane shows that the $A^-...HOH$ and B...HOH hydrogen bonds have an appreciable influence on their pK_d, increasing their acidity and weakening their sensitivity to the effects of substituents with increasing strength of the hydrogen bond,

which is associated with the increased localisation of the negative charge in the conjugate bases A^- and B; the influence exerted by the $BH^+...OH_2$ hydrogen bond is much smaller. The enhanced acidity of CH- and NH-acids in DMSO is consistent with additional dispersion stabilisation of the anions with a delocalised charge in this solvent.

V. THE INFLUENCE OF THE MEDIUM ON THE TRANSMISSION OF ELECTRONIC EFFECTS VIA BRIDGE GROUPS

Tables 3 and 4 present the values of $R^{W,g}$ characterising the weakening of the transmission of the electronic effects of substituents to the reaction centre on passing from the gas phase to water and also the values of $R^{NM,g}$ and $R^{W,\tilde{N}M}$. These data[65] show that the $R^{W,g}$ increase with increasing size of the bridge group M in series 1,2, and 3,4 and 5, and 6 and 7 (Tables 3 and 4). The values of R in the neutral acids HA increase to a particularly marked extent: the introduction of the phenylene bridge group entails an increase of $R^{W,g}$ by a factor of 2.6–3.5 ($R^{NM,g}$ increases by a factor of 2–3). If carboxylic acids are regarded as OH acids with a CO bridge group, then, despite the different reaction centres, the values of $R^{W,g}$ increase monotonically in the series X–M–OH, where M = –, CO, C_6H_4, or C_6H_4CO (Table 4). The increase of $\delta pK_d^g/\delta pK_d^W$ with increase of n has also been observed for the compounds $CF_3(CH_2)_n\overset{+}{N}H_3$ ($n = 1,2,3$).[14]

The above data show that the effect under discussion is probably general. It can be accounted for qualitatively[14] on the basis of the Kirkwood–Westheimer theory[21], which takes into account the effective dielectric constant of the medium between the substituent and the charged reaction centre: the greater the distance between the polar substituent and the charged centre, the greater proportion of its interaction with the charge takes place via the solvent and the effective dielectric constant of the space transmitting the influence of the substituent will approach the dielectric constant of the solvent. The greater increase of $R^{W,g}$ than that of $R^{NM,g}$ in the series 4 and 5 and 6 and 7 in Table 4 as well as the comparatively small but appreciable increase (by a factor of ~1.2) of the values of $R^{W,\tilde{N}M}$ in the same series can be understood from the standpoint of this theory.

The data presented have a direct bearing on the question of the dependence of the transmission coefficient π' (characterising the ability of the bridge group M to transmit electrons[117]) on the medium. According to the initial postulate, π' is determined by the structure of the bridge M and should be independent of the medium[118–120]. Many experimental data are consistent with this hypothesis[117,121], but there are some which conflict with it[35,122]. The results presented above§ show that in the general case the ability of the group M to transmit electrons cannot be independent of the medium in which its determined; it should remain unchanged only in media with comparatively similar dielectric constants.

§ The values of ρ_I for series 1,4, and 6 can be calculated from the relation $\rho_I = 6.23\,\rho^*$ (which follows from $\sigma^* = 6.23\,\sigma_I$),[117] taking into account the fact that the ρ_I for series 5 and 7 (Koppel' and Karel'son[9]) (and probably also series 3) are close to the values of ρ in Tables 3 and 4, which makes it possible to find the transmission coefficient π' characterising the transmission of the inductive effect via the phenylene group; for example, $\pi'(C_6H_4) = \rho_I(7)/\rho_I(6) \cong \rho(7)/6.23\rho^*(6)$. Hence it follows that the ratio of the values of π' in two series is equal to the ratio of the values of R for the two series in the same media.

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The data presented in this review show that comparison of the pK_d of substituted organic acids in the gas phase and in water with the pK_d in aprotic polar solvents (particularly in nitromethane) can yield important information about the characteristics of the solvation of these compounds. Thus the results demonstrate the decisive role of the non-specific electrostatic hydration of the ions A^- and BH^+ in weakening the effect of the substituents on the pK_d for the ammonium, anilinium, and pyridinium cations, benzoic acids, and phenols on passing from the gas phase to water and in the differentiation of the basicities of primary, secondary, and tertiary amines in water. The influence of hydrogen bonds on the acid–base properties of organic compounds of various types in water has been elucidated; it has been found that, for identical protonation constants, the tendency of charged and dipolar species A^- and B towards the formation of the hydrogen bonds $A^-...HOH$ and $B...HOH$ increases with the localisation of the charge: $X_3C^- \leqslant X_2N^- < XC_6H_4O^- < XC_6H_4COO^-$ and $X_3P \cong X_3N < XC_5H_4\overset{+}{N}O^- \cong X_2C=O < X_3As=O < X_3P=O$. The role of the dispersion solvation of anions with a delocalised charge (X_3C^-, X_2N^-) in solvents such as DMSO has been demonstrated. An appreciable increase of the ratio ρ^g/ρ^W with increase of the size of the bridge group has been observed for different $\overset{+}{N}H$- and OH-acids, which is qualitatively consistent with the Kirkwood–Westheimer theory and indicates the dependence of the ability of the bridge group to transmit electrons on the medium.

There is no doubt that the study of acid–base properties in the gas phase and in non-aqueous solvents, which is developing at a high rate, will make it possible to elucidate in the future new characteristics of the solvation of organic molecules, which are very important for the explanation and prediction of reactions which are not only of theoretical interest but also play an important role in industry.

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