Proton-Transfer Equilibria between Nitrophenols and Alkylamines in N-Methylformamide

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The equilibrium constants, K_e, of the proton-transfer reactions between o-, m-, and p-nitrophenols (ONP, MNP, and PNP, respectively), and monomethylamine and di- and triethylamines (MMA, DEA, and TEA, respectively) in N-methylformamide (NMF) were measured spectrophotometrically by using amine-amine hydrochloride buffers at different temperatures and 0.1–0.2 M ionic strength. Together with the previously measured pK_a of *p*-nitrophenol, these values allowed the determination of the acidity constants of alkylamines and the other nitrophenols in this solvent. The reported values are compared with literature data in other media including the gas phase. The reaction enthalpies and entropies are also reported and discussed for some of these systems.

Introduction

Solvent effects on protolytic processes are a topic of increasing interest from thermodynamic and kinetic points of view.¹⁻⁴ Information acquired in the last decade on protolytic equilibria in the gas phase reveals the enormous contributions of a condensed medium on these processes in solution.^{5,6} For a long time, a variety of acid-base interactions have been recognized in solution, ranging from hydrogen-bond formation to the complete transfer of a proton leading to formation of the conjugated acid and base as independent units.⁷⁻⁹ Specifically, the solvents with poor solvating ability promote the formation of hydrogen-bonded complexes, ion pairs, and homo- or heteroconjugated species while the solvents with a high solvating ability favor the formation of separated (free) protolysis products. On the other hand, these highly polar solvents usually exhibit themselves important acidic or/ and basic properties and their protolysis often interferes with the other protolytic processes. Classification of solvents with regard to a simple measure of their "solvating ability" reveals interesting correlations but is not sufficient to understand the detailed balance of the rather large enthalpic and entropic contributions to the different solute-solvent interactions lumped together in the term "solvation". Detailed study of particular classes of compounds remains necessary to obtain better insight into the different factors that determine local proton affinities in a solution of proton-exchanging molecules.

The study of proton-transfer reactions in N-methylformamide (NMF) has recently indicated¹⁰ its amphiprotic

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behavior characterized by an autoprotolysis constant K_{s} = 1.8×10^{-11} M² at 298 K. As NMF is a polar solvent with a high dielectric constant and solvating ability, the protolytic process

$$AH + B \rightleftharpoons A^- + BH^+ \tag{1}$$

is expected to yield only separated acid and base species, at least at low concentrations.

We have studied equilibrium 1 in NMF, where AH was o-, m-, or p-nitrophenol (ONP, MNP, PNP) and B was monomethylamine (MMA), diethylamine (DEA), or triethylamine (TEA).

The spectrophotometric titration of PNP solutions in NMF (with $c_{PNP}^0 = 2.5 \times 10^{-5}$ M) with different amines led to a characteristic family of absorption spectra with two maxima at $\lambda_1 = 410$ nm and $\lambda_2 = 320$ nm, corresponding to phenoxide ion (PNP-) and PNP, respectively, and an isosbestic point at $\lambda_i = 352$ nm. Under the assumption that $[A^-] = [BH^+]$, the equilibrium constant

$$K_{\rm e} = [{\rm A}^{-}][{\rm B}{\rm H}^{+}]/([{\rm A}{\rm H}][{\rm B}])$$
 (2)

was calculated from the measured phenoxide absorbance and known initial concentrations. These calculations led to continuously increasing values of $K_{\rm e}$ which later proved to be smaller than the true value, indicating the existence of some other protolytic processes, competing with the main one.

Among the possible competing processes, the phenol autoassociation is unlikely in this concentration range (10^{-5}) M) and the autoassociation of amine does not seem to be important as long as TEA, which cannot associate, has a behavior similar to MMA and DEA. The assumption that A⁻ and BH⁺ form an ion pair (also unlikely in this solvent and at these low concentrations) was also incompatible with the data. The only explanation which subsequently proved to be valid was that the solvent participates itself in the overall protolytic process. As the calculation of the equilibrium constants taking into account the solvent protolysis is more difficult and the equilibrium itself is more sensitive to the existence of acidic or basic impurities, the use of buffer solutions containing the base B and its

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conjugate acid BH⁺ (as BH⁺Cl⁻) within the range 10^{-3} – 10^{-1} M is a simpler and more reliable approach. Since the pK_a of alkylammonium ions BH⁺ is close to p[SH₂⁺] of neutral NMF (as will be shown subsequently), the buffer ratio¹¹

$$[BH^{+}]/[B] = (c^{0}_{BH^{+}} - [SH_{2}^{+}] + [S^{-}])/(c^{0}_{B} + [SH_{2}^{+}] - [S^{-}])$$
(3)

can be taken with a good approximation as the ratio of the initial concentrations, i.e., $c^0_{\rm BH^+}/c^0_{\rm B}$. The change of this ratio as a result of reaction 1 can also be neglected because the initial phenol concentration was at least 2 orders of magnitude smaller than those of the buffer components.

Experimental Section

Solvent. NMF (Fluka purum) was purified by a method already described.¹⁰

Nitrophenols. PNP, ONP, and MNP (Merck) were recrystallized twice from toluene, ethanol, and hot water, respectively, dried in vacuo at 298 K, and stored over P_2O_5 (mp 386.5–387, 317.8, and 369.8 K, respectively).

Amines. MMA (Fluka purum) was used without further purification. DEA (Austranal R.G.) and TEA (Carlo Erba R.G.) were treated with NaOH pellets and then with metallic sodium, refluxed 2 h over metallic sodium under dried argon, and finally distilled, the middle fraction being taken (bp 328.7 and 362.2 K, respectively). DEA and TEA were kept in dark-colored vessels under dried argon at low temperature.

Amine Hydrochlorides. The amine hydrochlorides were obtained by bubbling dried HCl into a solution of amine in anhydrous ethyl ether. The salts were repeatedly washed with anhydrous ethyl ether, filtered, and dried in a desiccator with P_2O_5 .

Buffers B-BH⁺. The buffers are very stable. When all the chemicals were properly purified, the spectrophotometric measurements gave, within experimental error, the same results after 1 week (if the solution is kept at low temperature, i.e., under 277 K). Moreover, the presence of small amounts of water does not seem to shift equilibrium 1. When water was added up to 0.1 M to a buffer solution in NMF containing water less than 0.004% (~2 $\times 10^{-3}$ M), no change could be observed in the spectra of PNP and PNP⁻. The solvent was however purified as previously reported in order to avoid extensive hydrolysis. The buffer solutions also show reversible behavior when heated to 330 K and cooled again to 298 K.

Apparatus. Electronic absorption spectra were obtained on a Pye Unicam SP 8000 spectrophotometer using thermostated stoppered cells.

Results

The equilibrium constants, K_{e} , were calculated according to

$$K_{\rm e} = (A_{\rm A}^{\lambda} - c^0{}_{\rm BH^+} / \epsilon_{\rm A}^{\lambda} - l) / c^0{}_{\rm B}(c^0{}_{\rm AH} - A_{\rm A^-}^{\lambda} - \epsilon_{\rm A}^{\lambda} - l)$$
(4)

where $A_{\rm A}^{\Lambda-}$ is the absorbance of phenoxide at its absorption maximum, $\epsilon_{\rm A}^{\Lambda-}$ is the corresponding molar absorptivity (M⁻¹ cm⁻¹), l is the optical length (cm), and $c_{\rm BH^+}^0$, $c_{\rm B}^0$, and $c_{\rm AH}^0$ are the initial concentrations of the specified species (M). Both amines and their hydrochlorides present no absorption in the range where NMF is transparent ($\lambda > 275$ nm) and therefore only the spectra of AH and A⁻ were recorded.



Figure 1. Effect of temperature on K, for the system PNP-TEA-TEAH⁺CI⁻ in NMF; $c^{0}_{PNP} = 3.46 \times 10^{-5}$ M; $c^{0}_{TEA} = 5.02 \times 10^{-2}$ M; $c^{0}_{TEAH^{+}CI^{-}} = 5.00 \times 10^{-2}$ M; I = 0.2 M.

TABLE I:	Equilibrium Constants of the Sys	tems
PNP-MMA,	, -DEA, -TEA in NMF at Differen	t
Ionic Streng	gths	

$10^5 \times$	$10^2 \times$	10 ² ×								
c°_{PNP} ,	с° _в ,	c°_{BH} ,	A^{410}/l ,							
Μ	М	М	cm⁻¹	<i>I</i> , M	K^{298}					
PNP-TEA-TEAH ⁺ Cl ⁻										
4.58	0.502	0.500	0.520	0.014	0.88					
5.83	0.502	0.500	0.650	0.015	0.85					
3.44	5.02	5.02	0.395	0.075	0.90					
4.77	0.502	0.500	0.560	0.155	0.94					
3.38	5.02	5.00	0.420	0.200	1.05					
3.38	5.02	5.00	0.425	0.200	1.08					
PNP-DEA-DEAH*Cl ⁻										
5.26	0.492	5.02	0.726	0.073	13.56					
4.82	0.492	5.02	0.710	0.162	15.85					
5.11	0.495	5.05	0.747	0.118	15.56					
5.29	0.486	4.96	0.742	0.118	14.05					
5.21	0.197	5.02	0.487	0.200	16.02					
5.31	0.340	4.96	0.647	0.200	14.75					
5.05	0.489	4.99	0.737	0.200	15.50					
PNP-MMA-MMAH ⁺ Cl ⁻										
5.65	0.213	5.00	0.653	0.065	21.50					
5.65	0.213	5.00	0.653	0.065	21.50					
4.43	0.042	0.50	0.682	0.083	22.52					
4.47	3.40	2.82	1.050	0.118	26.40					
5.39	0.213	5.00	0.705	0.129	27.58					
4.62	2.13	5.00	1.020	0.135	24.15					
5.25	0.213	5.00	0.658	0.192	25.25					

The ionic strength was changed or adjusted to a desired value by adding NaNO₃ ($10^{-3}-1.5 \times 10^{-1}$ M). In these cases a solution of NaNO₃ of the same concentration in NMF was used as reference, because NO₃⁻ has an absorption band with $\lambda_{max} = 306$ nm and a molar absorptivity 6.68 M⁻¹ cm⁻¹. The equilibrium constants were measured within 292 and 328 K at different ionic strength between 0.1 and 0.2 M.

System PNP-B-BH⁺. Several spectra at different buffer ratios [TEAH⁺]/[TEA] between 0.5 and 5 constant total ([PNP] + [PNP⁻]) concentrations around 5×10^{-5} M⁻¹ were taken at different temperatures and evaluated according to eq 4 with $\epsilon_{\rm A}^{10} = 2.42 \times 10^4$ M⁻¹ cm⁻¹ as determined previously.¹⁰ When the ionic strength increases from 0.1 to 0.2 M, there seems to be no change of $K_{\rm e}$ outside the experimental errors. The average value obtained for $K_{\rm e}^{\rm PNP/TEA}$ is 1.0 ± 0.1 at 298 K. The plot log $K_{\rm e}$ against 1/T is illustrated in Figure 1, where $\Delta H_{\rm e}$ and $\Delta S_{\rm e}^{\circ}$ are also given.

Similar spectra were obtained for the buffers DEA-DEAH⁺ yielding $K_e^{PNP/DEA} = 15.3 \pm 0.7$ at 298 K, and for the buffers MMA-MMAH⁺ obtaining $K_e^{PNP/MMA} = 26.4 \pm 1.0$ at 298 K. Although there is no trend in the variation of K_e with the ionic strength within the range 0.1–0.2 M, and reproducible values were obtained with different samples of solvent and reagents purified independently,

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TABLE II: Equilibrium and Thermodynamic Data for the Proton Transfer between Nitrophenols and Alkylamines in NMF, H₂O, and Gas Phase at 298 K

		NMF			H₂O			
system	<i>K</i> _e (298 K)	−ΔH _e , kJ mol ⁻¹	$-\Delta S_{e}, J$ mol ⁻¹ K ⁻¹	К _е . (298 К) ^b	$-\Delta H_{e}^{\circ}, d$ kJ mol ⁻¹	$-\Delta S_{e}^{\circ}, {}^{e} J$ mol ⁻¹ K ⁻¹	gas phase, $10^{68}K_e^f$	
PNP-MMA	26.4 ± 1.0^{a}	61.8 ^a	181 ^a	3162	35.275	51.40	1.6×10^{-8}	
PNP-DEA	15.3 ± 0.7^{a}	21.7^{a}	50.1^{a}	7244	33.377	38.14	9.8	
PNP-TEA	1.0 ± 0.1^{a}	15.8^{a}	52.9^{a}	3715	23.303	9.89	3.5×10^{5}	
ONP-MMA	126^{b}	84.2^{c}	242^{c}	2630	35.463	53.56		
ONP-DEA	72.4^{b}	43.9^{c}	112^{c}	6025	33,565	40.31		
ONP-TEA	4.8 ± 0.7^{a}	38.0^{a}	113^{a}	3090	23,491	12.05		
MNP-MMA	0.45^{b}			186	35.254	74.88		
MNP-DEA	0.28^{a}			426	33,356	61.62		
MNP-TEA	0.016^{a}			219	23.282	33.34		

^a Our data, direct measurements, at 0.2 ionic strength. Standard error on ΔH_e and ΔS_e values is below 10%. ^b Calculated from pK_a values, Table IV, pK_e = pK_a^{AH} - pK_a^{BH+}. ^c Calculated from the differences between $\Delta H_e^{\text{ONP/TEA}}$ and $\Delta H_e^{\text{PNP/TEA}}$, $\Delta H_e^{\text{PNP/DEA}}$, $\Delta H_e^{\text{PNP/DEA}}$, $\Delta H_e^{\text{PNP/MAA}}$: $\Delta H_e^{\text{ONP/TEA}}$, $\Delta H_e^{\text{ONP/TEA}}$, $\Delta H_e^{\text{PNP/TEA}}$, $\Delta H_e^{\text{PNP/MAA}}$: $\Delta H_e^{\text{ONP/TEA}}$, $\Delta H_e^{\text{ONP/TEA}}$, $\Delta H_e^{\text{ONP/TEA}}$, $\Delta H_e^{\text{PNP/TEA}}$, $\Delta H_e^{\text{ONP/TEA}}$, $\Delta S_e^{\text{ONP/DEA}}$, $\Delta S_e^{\text{ONP/MAA}}$ were calculated from corresponding ΔG_e and ΔH_e values. ^d Calculated from ionization enthalpies of nitrophenols ΔH_{AH} (L. P. Gernandez and L. G. Hepler, J. Am. Chem. Soc., 81, 1783 (1959)) and ammonium ions ΔH_{BH} (F. M. Jones III and E. M. Arnett "Progress in Physical Organic Chemistry", Vol. II, A. Streitwieser and R. S. Taft, Eds., Wiley, New York, 1974); $\Delta H_e = \Delta H_{AH} - \Delta H_{BH}^{+}$. ^e Calculated from Kebarle's data quoted by; M. Arnett, L. E. Small, D. Oancea, and D. Johnston, Eds., J. Am. Chem. Soc., 98, 7346 (1976) (PNP \rightarrow PNP⁻ + H⁺; ΔG^o_{PNP}); D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid*, 94, 4726 (1972) (B + H⁺ \rightarrow BH⁺; ΔG^o_B); $\Delta G_e^o = \Delta G^o_B + \Delta G^o_{PNP}$.

there is an evident decrease of K_e at lower ionic strengths (expected for an ionogenic reaction) as can be seen in Table I.

System ONP-TEA-TEAH⁺. The spectra of o-nitrophenol (ONP) in NMF and in the presence of excess amine or excess HCl show absorption maxima corresponding to ONP^- ($\lambda_{max} = 428 \text{ nm}$) and ONP ($\lambda_{max} = 345 \text{ nm}$), respectively. There is a significant overlap of the two absorption bands. The molar absorptivity of ONP⁻ at each wavelength was obtained from nine independent measurements shifting the equilibrium by addition of MMA or TEA, giving $\epsilon_{0NP^-}^{428} = (5.63 \pm 0.08) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{0NP^-}^{345} = (1.32 \pm 0.22) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. From the recorded spectra of ONP solutions in the presence of HCl or the molar absorptivities of ONP at 345 and 428 nm were evaluated as $\epsilon_{ONP}^{345} = 3.26 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{ONP}^{428} = 1.71 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$. Equilibrium constants were calculated from the absorbance measurements at 428 nm where ONP has a smaller absorption. The measured absorbances at 428 nm were corrected for the absorption of ONP by using an iterative procedure. These corrections are small and self-consistency is attained after two iterations. The data obtained at various buffer ratios give the value $K_{e}^{ONP/TEA}$ = 4.8 ± 0.7 , $\Delta H_{e} = -38.0 \text{ kJ mol}^{-1}$, $\Delta S_{e}^{\circ} = -113 \text{ J mol}^{-1} \text{ K}^{-1}$ for the TEA/TEAH⁺ system.

Systems $\dot{M}NP$ -TEA-TEAH⁺ and MNP-DEA-DEAH⁺. MNP⁻ has a well-separated absorption maximum at 415 nm and MNP an absorption maximum at 338 nm, overlapping a comparable absorption of MNP⁻. From the absorbance measurements in the presence of excess amine the molar absorptivity of MNP⁻ at 415 nm was estimated at $(1.43 \pm 0.12) \times 10^3 \,\mathrm{M^{-1} \, cm^{-1}}$. The equilibrium constant K_e was also calculated from the absorbance measurements at 415 nm, where only MNP⁻ exhibits a measurable absorption. One obtains $K_e = 0.28$ for DEA-DEAH⁺ buffers and $K_e = 0.016$ for TEA-TEAH⁺ buffers at 298 K and 0.2 M ionic strength.

Discussion

The equilibrium constants K_e of the process 1 either measured directly or obtained from known pK values of phenols and alkylammonium ions are given in Table II together with the corresponding thermodynamic data, and comparison data for the same equilibria in water and the gas phase. The acidity constants (pK_s) of alkylammonium



Figure 2. Effect of ionic strength on K_{\bullet} for the system PNP-TEA-TEAH⁺ in NMF at 298 K.

ions in NMF, given in Table IV, were calculated from measured K_e and the primary value K_a of PNP reported in the previous paper: ¹⁰

$$K_{\rm e} = K_{\rm a}^{\rm AH} / K_{\rm a}^{\rm BH^+} \tag{5}$$

With $K_{a}^{BH^{+}}$ thus obtained it is possible to calculate K_{a}^{AH} of ONP and MNP.

Before we discuss K_{e} values, some comments about the range of validity of these thermodynamic quantities are necessary. The figures given in the second column of Table II are actually concentration quotients and are related to the thermodynamic K_e^0 (at infinite dilution of the species in equilibrium) through the corresponding activity coefficients accounting for solute-solute interactions. The data presented in Table I indicate a lowering of K_{e} at lower ionic strength, particularly when the experimental errors are minimized by carrying out the experiments from the same stock solutions. It was not possible to lower the ionic strength below 0.015 M without weakening the buffer capacity. Within the ionic strength range 0.015-0.2 M, log $K_{\rm e}$ increases monotonically with $I^{1/2}$ for the system PNP-TEA-TEAH⁺Cl⁻ as shown in Figure 2. The ionic strength was varied or adjusted to a desired value by using different initial concentrations of BH⁺Cl⁻ or adding NaNO₃. It is worth noting that the slope of the linear part at lower ionic strengths (0.15) approaches the theoretical value predicted by the Debye-Hückel limiting law for uni-univalent electrolytes at 298 K in NMF:

$$\log f_{\pm} = -0.14I^{1/2} \tag{6}$$

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me- dium	$\begin{array}{ll} \text{me-} & \epsilon = 1 \text{ (gas phase)} \end{array}$			$\epsilon = 78 (H_2O)$				$\epsilon = 185 (\text{NMF})$				
base	$\Delta G^{0}_{\mathrm{measd}}$	ΔG^{o}_{el}	$\Delta G^{\circ}_{\rm res}$	$\Delta G^{0}_{\rm sym}$	$\Delta G_{\rm measd}^{\rm H_2O}$	${\scriptstyle \Delta G^{\mathbf{H_2O}}_{\mathbf{1d}}}$	$\Delta H_{id}^{H_2O}$	$\Delta S^{H_2O}_{id}$	$\Delta G_{\rm meascl}^{\rm NMF}$	$\Delta G^{\rm NMF}_{\rm id}$	ΔH_{id}^{NMF}	$\Delta S^{\rm NMF}_{~\rm id}$
MMA DEA TEA	434.6 384.2 358.3	466.4 406.9 386.3	-31.8 -22.7 -28.0	-9.1 -5.7 0.0	-19.9 -22.0 -20.4	-25.9 -17.5 -23.1	-36.8 -26.4 -29.9	- 36.6 - 29.9 - 22.9	$-7.86 \\ -6.77 \\ 0.0$	-29.3 -20.5 -30.0	-38.7 -28.1 -36.1	-31.7 -25.6 -20.4

^a The following molar volumes and dipole moments have been used: PNP, $V_{\rm m} = 118.7 \,{\rm cm}^3$, $\mu = 4.84 \,{\rm D}$; PNP⁻, $V_{\rm m} = 125.4 \,{\rm cm}^3$, $\mu = 2.8 \,{\rm D}$; MMA, $V_{\rm m} = 44.8 \,{\rm cm}^3$, $\mu = 1.3 \,{\rm D}$; MMAH⁺, $V_{\rm m} = 54.6 \,{\rm cm}^3$, $\mu = 0.6 \,{\rm D}$; DEA, $V_{\rm m} = 109.8 \,{\rm cm}^3$, $\mu = 0.9 \,{\rm D}$; DEAH⁺, $V_{\rm m} = 118.5 \,{\rm cm}^3$, $\mu = 0$; TEA, $V_{\rm m} = 155.4 \,{\rm cm}^3$, $\mu = 0.6 \,{\rm D}$; TEAH⁺, $V_{\rm m} = 162.4 \,{\rm cm}^3$, $\mu = 0$. ^b ΔG values in kJ mol⁻¹; ΔS values in J mol⁻¹ K⁻¹.

Although the data are not sufficiently accurate and, moreover, are measured outside the concentration range where the limiting law allows a reliable extrapolation to infinite dilution, they clearly point out the significant influence of electrostatic solute-solute interactions in the range where the buffer method is applicable. This influence does not seem to be so large, however, as to invalidate the conclusions from the comparison of the behavior of a series of related compounds in NMF with that in water where the true thermodynamic quantities are available. Moreover, the equilibrium data in NMF obtained in this study will be required for a kinetic study using the temperature-jump method where the use of solutions with ionic strength of about 0.1-0.2 M is necessary to ensure a fast Joule heating.

An analysis of Table II reveals several features of proton-transfer equilibria (eq 1) in NMF as compared to gas phase and aqueous solution:

(a) In the gas phase the free enthalpy difference between the neutral reactants and the ionic products is dominated by the electrostatic energy of the field associated with their electric charge. This energy is inversely proportional to the radius of the volume over which the charge is distributed. Ab initio calculations for methylammonium¹¹ using STO-4.31G basis sets show that the positive excess charge is distributed almost evenly over all the hydrogen atoms of the molecule. The NH_3^+ group carries 51% and the CH_3^+ group 48% of the excess charge, indicating that the repulsive Coulombic forces push the excess charge as much as possible to the surface of the molecule. The electrostatic energy of a uniform charge distribution on a spherical surface is located entirely outside the surface. Only the modulations of the charge density on the surface create nonzero fields inside as well as outside the enclosed volume. The electrostatic work required to establish the surface charges and their dipolar modulations, corresponding to the changes in charge distribution inside the molecules during the proton-transfer reaction is, under vacuum, given by

$$\Delta G^{0}_{el} = \frac{1}{2\epsilon_0} \left(\frac{N_{A}^{4}}{3(4\pi)^2} \right)^{1/3} \Sigma \frac{\nu_i q_i^{2}}{\nu_i^{1/3}} + \frac{N_{A}^{2}}{6\epsilon_0} \Sigma \frac{\nu_i \mu_i^{2}}{\nu_i} \quad (7)$$

 v_i/N_A is the volume (assumed to be spherical) of a molecule of species i. This volume will be approximately given by $v_i = 0.74V_i$, where V_i is the molar volume of the species in the condensed state, corrected by the packing factor for close-packed spheres. q_i and μ_i are the charge and dipole moment of species i, and v_i is its signed stoichiometric coefficient. The results of a calculation for proton transfer from *p*-nitrophenol to the three amines under vacuum is given in Table III. For this calculation the dipole moment of methylammonium (0.6 D) was estimated from the theoretically predicted charge distribution.¹¹ For diethylammonium, with a structure similar to *n*-pentane, and for triethylammonium, which is similar to 3-ethylpentane, the dipole moments were assumed to be negligible. The molar volumes of the ammonium ions were assumed to be the same as those of the isoelectronic alkanes with the same symmetry, rather than using arbitrary corrections to the volumes of the parent compounds. The molar volume and the dipole moment used for the *p*-nitrophenolate anion were those of *p*-nitrofluorobenzene. The dipole moment may be slightly overestimated since the delocalized electron provides the ion with a large polarizability, so that the centers of gravity of positive and negative charge may nearly coincide. The present value, however, contributes only +6.5 kJ mol⁻¹ to each of the calculated electrostatic energies. All molar volumes were taken from the density of the liquid state, extrapolated to the boiling temperature at atmospheric pressure.

Subtracting these calculated electrostatic energies from the total free enthalpy changes measured in the gas phase gives the residual contributions ΔG_{res} , which are still for a considerable part of electrostatic origin. The absolute values of ΔG_{res} for the three reactions should not be given too much importance for our present discussion. They shift in parallel, depending on the acidity of the protonating acid which is, in this approximation, corrected only for the influence of its ionic size and its change in dipole moment. These values would have been overestimated by about 30% if the dipolar term, dominated by the contributions of PNP and PNP⁻, had been neglected. The difference between the squares of the dipole moments of an acid and its conjugate base is thus not an unimportant factor in determining its relative acidity in the gas phase or in a nonpolar medium. The small remaining differences between the three alkylammonium ions must not be given significance, considering the approximate nature of the calculation. The positive deviation for DEAH⁺ as compared to the two other ions may be a remaining electrostatic energy, which could have been underestimated by representing the linear chain structure of this ion by a spherical model. Some of the nonelectrostatic parts included in ΔG_{res} have an entropic origin. The reduction of orientational phase space when the symmetry of the base in changed by protonation is reflected in ΔS_{sym} . Other contributions result from changes in the principal moments of inertia when the bond angles between the nitrogen ligands are reduced, from changes in the zero-point energy of the molecular vibrations, etc.

(b) In solution, the electrostatic work is strongly reduced by polarization of the solvent. Even an inert polarizable solvent, behaving as an ideal dielectric, now participates in the reaction. At constant T and P, the work done to polarize the solvent represents a free enthalpy change. The predicted reaction free enthalpy in an ideal dielectric medium is now

$$\Delta G_{\rm id}^{\rm sol} = \frac{1}{\epsilon} \Delta G^0_{\rm charge} + \frac{3}{2\epsilon + 1} \Delta G^0_{\rm dip} + \Delta G^0_{\rm res} \qquad (8)$$

where ΔG^{0}_{charge} and ΔG^{0}_{dip} represent the original charge

and dipole terms and ΔG^0_{res} represents the residual part in the gas phase. There is an accompanying entropy change in the dielectric, related to its polarization and given by

$$\Delta S_{\rm el}^{\rm sol} = \frac{\partial \ln (\epsilon - 1)}{\partial T} \left(\frac{\epsilon - 1}{\epsilon^2} \Delta G^0_{\rm charge} + \frac{6(\epsilon - 1)}{(2\epsilon + 1)^2} \Delta G^0_{\rm dip} \right) \tag{9}$$

as well as a volume change due to electrostriction

$$\Delta V_{\rm el}^{\rm sol} = -\kappa_T \frac{\epsilon + 2}{3} \left(\frac{\epsilon - 1}{\epsilon^2} \Delta G^0_{\rm charge} + \frac{6(\epsilon - 1)}{(2\epsilon + 1)^2} \Delta G^0_{\rm dip} \right)$$
(10)

where κ_T is the isothermal compressibility of the dielectric. With these equations the changes in internal energy $\Delta U = \Delta G + T\Delta S - P\Delta V$ and $\Delta H = \Delta G + T\Delta S$ may be obtained. The values $\Delta X_{\rm id}^{\rm sol}$ in Table III, where X are the thermodynamic parameters G, H, or S, refer to ideal dielectric media with the dielectric properties of H₂O or NMF¹⁴ ($\epsilon = 78$ and 185, respectively; $\partial \ln (\epsilon - 1)/\partial T = 4.7 \times 10^{-3}$ and 9.2 × 10⁻³ K⁻¹, respectively), and suppose that the residual terms $\Delta G^0_{\rm res}$ are medium independent. They serve as reference values to which the measured values in the real solvents can be compared.

The comparison between Tables II and III shows that the dielectric approximation reasonably predicts the effect of a polar solvent on an ionogenic process. In general, the predicted free enthalpy changes are too large, especially in the case of NMF, and the predicted entropy changes are too small. The values for NMF in Table II, however, refer to measurements at finite ionic strength, whereas those for H₂O are thermodynamic values obtained from the pK difference. Since ionic species are stabilized by the space charge of the counterions, the amount of proton transfer in NMF at zero ionic strength is expected to be even smaller than indicated in Table II. This is demonstrated in Figure 2. The suppression of proton transfer from phenols to amines in NMF as compared to H₂O is in contrast to the autoprotolysis of NMF, which is much more favorable in pure NMF than in aqueous solution.

(c) The most important difference between the ideal dielectric medium and the polar solvents compared here is their ability to form hydrogen bonds to the proton that is transferred, to other donors or acceptors on the parent neutral molecules and the ions formed, and between themselves. The differential free enthalpy of changes in these bonds becomes a part of the free enthalpy change of the proton-transfer reaction. The observed reduction in the equilibrium constants in NMF indicates that the H bonds formed between the solvent and the ions are weaker than those between the solvent and the neutral acid and base. If there is any similar reduction in water, it must be much less significant; the difference might even be in the opposite direction. H₂O has more H-bond donors than NMF. It tends to stabilize molecules that are good acceptors. NMF has only a single and rather weak donor. In aqueous medium, NMF is a much weaker acid than H_2O .

The more differentiated behavior of p- and o-nitrophenol in NMF as compared to H₂O supports the hypothesis that the main cause for the reduced acidity difference of the phenol-ammonium pair in NMF is the inability of the solvent to form H bonds to acceptor sites with a highly delocalized electron density, in this case, the phenolate ion. In NMF o-nitrophenol is the stronger acid, although usually one observes that the ability to form a hydrogen bond to a neighboring atom stabilizes the ortho phenols and appreciably lowers their acidity, especially in nonpolar solvents. In H₂O the difference is small, but ONP is still slightly weaker than PNP. The contrasting behavior in NMF can be explained if the *o*-phenolate ion, with its more localized acceptor region, is stabilized by more or stronger H bonds, at the expense, of course, of an increased entropy loss. Some part of the larger entropy decrease in the case of ONP as compared to PNP could be due to the participation of an additional solvent molecule, making an H bond to the proton transferred to the cation, whereas no such solvent molecule was engaged in an H bond to the ONP molecule. But this would imply that the neighboring nitro group is at least as good an acceptor as the carbonyl group of NMF.

(d) The order of the amine basicities in NMF is different from that in H_2O . In both solvents it is different from the gas phase. The partial reversal in water has been long recognized and attributed to differences in specific solvation of the amines and the ammonium ions.^{12,13} As our calculation has shown, the gas-phase basicities are strongly dependent on the ionic volume. The remaining free enthalpy differences of nonelectrostatic origin are small. It is not surprising, then, that a solvent able to reduce the electrostatic part to a negligible amount determines the final relative free enthalpies of the amine-ammonium pair by factors related to its own structure. As already observed with the different phenols, the differentiation between the three bases is more pronounced in NMF than in H_2O . The difference in solvation and H bonding between methylammonium and methylamine involves the participation of at least two additional solvent molecules, as compared to the two other bases. This seems to imply that (i) either methylamine does not form H bonds to the solvent whereas all three hydrogens on the nitrogen of methylammonium are involved in such bonds or (ii) the additional H-bond interactions in methylammonium involve the methyl hydrogens, which are carrying their share of the charge. The first hypothesis is not very probable, in view of the strong H-bond acceptor properties of NMF. The second hypothesis would reveal a quite unexpected property of sufficiently electron-deficient methyl hydrogens in this medium. A CNDO/2 optimization¹¹ shows CH-bond lengthening one-third as large as that of the NH bonds, when six H₂O molecules are arranged around the methylammonium ion, their oxygens pointing toward the hydrogens of the ion. If the carbonyl group of NMF is a better H-bond acceptor than H_2O , the interactions with the methyl hydrogens could become strong enough to force the solvent molecules into a state of much lower entropy. It is not clear how much of the entropy difference for methylammonium in water has the same origin, because the effect of hydrophobic forces must be added.

In diethylammonium and triethylammonium the charge is distributed over many more hydrogen atoms, lowering their ability to become hydrogen-bond donors. In contrast to water, there is probably no requirement to encage the alkyl residues of the amines in a "solvophobic" structure in NMF. The solvent dipoles can orient themselves freely around these methyl groups. In DEA and TEA they retain their rotational degrees of freedom, with an orientational Boltzmann distribution as required by the electric field of the ion. Around the methylammonium ion their rotational thermal energy is presumably converted into the (lower) zero-point energy of vibrational motions, while the

TABLE IV: Acidity Constants pK_a of Nitrophenols and Alkylamines in NMF and Other Media at 298 K

solvent								
H ₂ O	FA	NMF	NMA	DMF	Me ₂ SO	MeOH	gas phase	
7.15^{a} 7.23^{b}	8.52 ^e	5.16^{f} 4.48^{f}	8.8 ^g	12.34^{h}	10.4, ^h 9.9 ⁱ	11.15^{h}	230 ^j	•
8.38 ^c		6.93 ^f		15.43^{h}				
10.65^{d}		6.58^{f}	12.2^{g}				154^{k}	
11.01^{d}		6.34^{f}	9.3 ^g				162^{k}	
10.72^{d}	9.99 ^e	5.17^{f}			9.0^{h}	10.9^{h}	167^{k}	
14.0	16.8	10.7	10.5	~18	33.1	18		
78.5	111.3	185.5	178.9	36.7	48.9	32.6	1	
1	14	24	10	8.3		0.16		
264	237	227	218	183	188	232		
100	39.8	31.8			19.3	41.3		
	$\begin{array}{r} H_2O\\ \hline 7.15^a\\ 7.23^b\\ 8.38^c\\ 10.65^d\\ 11.01^d\\ 10.72^d\\ 14.0\\ 78.5\\ 1\\ 264\\ 100\\ \end{array}$	$\begin{array}{c ccc} H_2O & FA \\ \hline 7.15^a & 8.52^e \\ 7.23^b \\ 8.38^c \\ 10.65^d \\ 11.01^d \\ 10.72^d & 9.99^e \\ 14.0 & 16.8 \\ 78.5 & 111.3 \\ 1 & 14 \\ 264 & 237 \\ 100 & 39.8 \\ \end{array}$	$\begin{tabular}{ c c c c c c c } \hline H_2O & FA & NMF \\ \hline \hline 7.15^a & 8.52^e & 5.16^f \\ \hline 7.23^b & 4.48^f \\ \hline 8.38^c & 6.93^f \\ \hline 10.65^d & 6.58^f \\ \hline 11.01^d & 6.34^f \\ \hline 10.72^d & 9.99^e & 5.17^f \\ \hline 14.0 & 16.8 & 10.7 \\ \hline 78.5 & 111.3 & 185.5 \\ \hline 1 & 14 & 24 \\ \hline 264 & 237 & 227 \\ \hline 100 & 39.8 & 31.8 \\ \hline \end{tabular}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	H2OFANMFNMADMF7.15a 8.52^e 5.16^f 8.8^g 12.34^h 7.23b 4.48^f 8.38^c 6.93^f 15.43^h 10.65^d 6.58^f 12.2^g 11.01^d 6.34^f 9.3^g 10.72^d 9.99^e 5.17^f 14.0 16.8 10.7 78.5 111.3 185.5 78.5 111.3 185.5 78.5 111.3 185.5 100 39.8 31.8	H ₂ O FA NMF NMA DMF Me ₂ SO 7.15 ^a 8.52 ^e 5.16 ^f 8.8 ^g 12.34 ^h 10.4, ^h 9.9 ⁱ 7.23 ^b 4.48 ^f 10.65 ^d 6.93 ^f 15.43 ^h 10.4, ^h 9.9 ⁱ 10.65 ^d 6.58 ^f 12.2 ^g 9.99 ^e 5.17 ^f 9.0 ^h 14.0 16.8 10.7 10.5 ~18 33.1 78.5 111.3 185.5 178.9 36.7 48.9 1 14 24 10 8.3 264 237 227 218 183 188 100 39.8 31.8 19.3 19.3	Solvent H_2O FA NMF NMA DMF Me ₂ SO MeOH 7.15 ^a 8.52 ^e 5.16 ^f 8.8 ^g 12.34 ^h 10.4, ^h 9.9 ⁱ 11.15 ^h 7.23 ^b 4.48 ^f 10.4, ^h 9.9 ⁱ 11.15 ^h 8.38 ^c 6.93 ^f 15.43 ^h 10.4, ^h 9.9 ⁱ 11.15 ^h 10.65 ^d 6.58 ^f 12.2 ^g 11.01 ^d 6.34 ^f 9.3 ^g 10.72 ^d 9.99 ^e 5.17 ^f 9.0 ^h 10.9 ^h 14.0 16.8 10.7 10.5 ~18 33.1 18 78.5 111.3 185.5 178.9 36.7 48.9 32.6 1 14 24 10 8.3 0.16 264 237 227 218 183 188 232 100 39.8 31.8 19.3 41.3	solvent H_2O FANMFNMADMFMe2SOMeOHgas phase7.15a 8.52^e 5.16^f 8.8^g 12.34^h $10.4, h$ 9.9^i 11.15^h 230^j 7.23b 4.48^f 15.43^h $10.4, h$ 9.9^i 11.15^h 230^j 8.38^c 6.93^f 15.43^h 10.65^d 6.58^f 12.2^g 154^h 10.65^d 6.34^f 9.3^g 162^h 162^h 10.72^d 9.99^e 5.17^f 9.0^h 10.9^h 167^h 14.0 16.8 10.7 10.5 ~ 18 33.1 18 78.5 111.3 185.5 178.9 36.7 48.9 32.6 1 14 24 10 8.3 0.16 264 237 227 218 183 188 232 100 39.8 31.8 19.3 41.3 41.3 31.8 30.8

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orientation is pointing toward the methyl hydrogens. This provides for the decrease in enthalpy and entropy.

In aqueous solution, the entropy change expresses the difference in ordering between the hydrophobic structure and the "polarization" structure. There is a gradual entropy decrease predicted for the ideal dielectric.

The explanation presented here to account for the observed behavior of NMF as a solvent for acid-base equilibria is necessarily a very preliminary one. The conclusions are still qualitative rather than quantitative, but they allow predictions about the solvation of certain ions in NMF that could be studied with more specific methods, e.g., optical or NMR spectroscopy. When the dielectric permittivity of a solvent is sufficient to reduce the electrostatic work of an ionogenic process to an amount that is small compared to individual intermolecular interactions, the properties that are most important in determining its characteristics are the affinities, numbers, directivities, and mutual coupling and cooperativity of its H-bond donor and acceptor sites. The variety of combinations of these categories obviously cannot be characterized under the single heading of "basicity". The available data for the comparative acidities of nitrophenols and alkylammoniums in some other solvents are listed in Table IV, together with our data in NMF, converted to pK_a values by using the dissociation constant of PNP in pure NMF that we determined earlier.¹⁰ Consistent with the reduction of the logarithm of the ionic product pK_s of NMF as compared to that of H_2O , the pK_a values for the ammonium acids are 4-5 units below those in H_2O . The pK_a of the phenols are only 2–3 units below those in H_2O . We have ascribed this to a lack of NMF to donate H bonds to the phenolate ions.

The lowering of pK_s of NMF by 4 units as compared to that of H₂O, whereas in aqueous solution NMF is barely able to transfer its proton to H₂O, indicates that the solvated proton in NMF is a much more stable, well-defined structure than the solvated proton in H₂O. In NMF there is almost no interference or competition from other H-bond donors to lone-electron pairs on the two carbonyl groups holding the proton, because there is a large excess of lone-electron pairs over H-bond donors. In formamide, the ratio between lone-electron pairs and H-bond donors is the same as in water. In the crystalline state, formamide forms centrosymmetric hydrogen-bonded dimers, interconnected to form a layered network. Each oxygen makes two H bonds, one with the dimeric partner, one to form the network. A low-energy solvation structure, using two oxygens exclusively for one proton, is probably not possible in formamide because of the strong competition for the lone-electron pairs on the carbonyl oxygens. This could explain the very large difference between the pK's of formamide and NMF. One must also consider in this comparison that these values were obtained with different experimental methods, and not always with carefully purified materials. In N-methylacetamide the acidity difference between PNP and DEA is not very different from that in NMF, but, relative to solvent autoprotolysis, the reported values are apparently much too high, or the latter too low. Completely puzzling, even with the hypothesis of strong solvent interactions with the methyl protons, is the reported value for the pK_a of methylammonium in this solvent.

There have been several efforts to find easily measurable correlations that would characterize different solvents on a relative scale. Dimroth's solvent polarity parameter E_T (obtained by comparing the frequency shift of an electronic excitation of a solute dye molecule in different solvents) or Gutmann's solvent acceptor number¹⁵ are examples of such parameters. Their values for the different solvents listed have been included in Table IV. As our measurements and discussion show, single empirical parameters of this kind are too crude to account for some major quantitative differences due to specific solute-solvent interactions. The difficulties commonly arising in comparing pK_a values in different solvents are inevitably connected with the interference of very many factors such as solvent autoprotolysis, relative proton and defect proton solvation, donor/acceptor ratio, interaction reinforcement by dispersion forces, localization and directivity of electron density of acceptors, etc. The comparative examination of solvent effects on proton-transfer reactions (eq 1) is more suitable to evaluate these influences than protolytic reactions involving proton transfer to or from the solvent.

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Since pK_{\bullet} differences are essentially free enthalpy differences, they do not always reveal the true nature of the stabilizing or destabilizing factors. Temperature dependencies are of considerable interest for the comparative study of ionogenic processes in different solvents.

Registry No. o-Nitrophenol, 88-75-5; m-nitrophenol, 554-84-7; p-nitrophenol, 100-02-7; monomethylamine, 74-89-5; diethylamine, 109-89-7; triethylamine, 121-44-8; N-methylformamide, 123-39-7.

Electronic States in Solution and Charge Transfer

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The Fermi level of electrons in solution is not the negative of the vacuum scale redox potential. One needs to know the ground states of the donor and acceptor ions in solution and the distribution of their higher energy states. Gaussian distribution of electronic states in solution is not consistent with experimental results, whereas Maxwell-Boltzmann distribution of such states exhibits conformity with it. Activation of ions in solution before electron exchange occurs by means of collisional energy transfer. It is possible because of the presence of continuum of vibration-rotation states in the ion-solvent complex. Auger transitions in the electrochemical system are unlikely. Shifting of an applied potential shifts the bulk energy levels (measured with respect to an electron at infinity) in both metal and solution in opposite directions.

Introduction

Electrode kinetics now borders a quantal phase, not only in considerations given to the actual electron transfer step but particularly in those aspects which pertain to electronic energy states in the solid and those in the solution. To account for the charge transfer at the interface it is essential to know the electronic energy states of ions in solution and also in solid phase and their corresponding distribution.

During the past 20 years, a number of new concepts in this area have entered the literature, particularly in those aspects which pertain to electronic states in solution; a number of ambiguities have arisen.

In the present paper, an attempt is made to state, and partly to resolve, these matters.

Fermi Level in Solution

The normally defined value of the Fermi level of an electron in metal with respect to an assumed zero value of the energy of the electron in vacuo¹ is this particles' electrochemical potential, $\bar{\mu}_e^{m}$. It therefore seems reasonable to assume that, if it is a good concept to refer to the Fermi level of an electron in the solution² (as is often done $^{3-5}$), this quantity must be the electrochemical potential of the electron in the solution, $\bar{\mu}_{e}^{s}$.

One knows that⁶⁻⁸

$$nFV_{\text{redox}}(\text{vacuum scale}) = nF^{\text{m}}\Delta^{\text{s}}\phi - \mu_{\text{e}}^{\text{m}}$$
$$= nF\phi^{\text{m}} - nF\phi^{\text{s}} - \mu_{\text{e}}^{\text{m}}$$

or

$$\mu_{\rm e}^{\rm m} - nF\phi^{\rm m} = -nFV_{\rm redox}(\text{vacuum scale}) - nF\phi^{\rm s}$$

or

$$\bar{\mu}_{e}^{m} = -nFV_{redox}(vacuum \ scale) - nF\phi^{s}$$
(1)

Since at equilibrium

$$\bar{\mu}_{e}^{m} = \bar{\mu}_{e}^{s} \tag{2}$$

one can write

$$\bar{\mu}_{e}^{s} = -nFV_{redox}(vacuum \ scale) - nF\phi^{s}$$
(3)

where n is the number of electron transferred and F is the Faraday.

 V_{redox} (vacuum scale) is well-known (= V_{NHS} + 4.5 V), but the inner potential of the redox solution ϕ^{s} is in general not known. Further, even in aqueous solutions it will vary with the electrolyte because each ion will be adsorbed in a different way at the solution-air interface. Hence, the so-called Fermi level of electrons in solution $\bar{\mu}_e^s$ is not determinable by equating it to the potential of a redox system on the vacuum scale.

The latter quantity is the work done in transferring, in a thought experiment, the electron from a vacuum to the ion of the higher valence state in solution to form the same ion of the lower valency in solution. It concerns the overall electron transfer work and not the transfer to a specific energy state. For this kind of reason alone, it is difficult to identify the Fermi energy of an electron in solution with $-nFV_{redox}$ (vacuum scale).

What is needed in electrode kinetics calculation of the electronic state in solution is the ground state of the relevant acceptor ion in a cathodic reaction (correspondingly to the donor for the anodic reaction). Such calculations

⁽¹⁾ This concept raises difficultites because of the artificial nature of the reference state. Thus, it is implied that the electron in vacuum is stationary, or else a considerable translational entropy could develop.

⁽²⁾ In fact, there are no free electrons in aqueous solution. Taking a reference state in a thought experiment as one which is not attainable may be acceptable but making the principle of finding the equilibrium state of electron in solution depend on a nonexistent state appears ne gatory and even dubious.

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