SOLVENT EFFECTS ON THE THERMODYNAMIC FUNCTIONS OF PROTON DISSOCIATION OF PHENOLS AND ANILINES

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For a systematic series of phenols and aniline, the thermodynamic functions of proton dissociation have been determined in a 50 weight per cent water-methanol solvent system, using an e.m.f.-spectrophotometric technique.

For phenols, the change in free energy on transferring from water to the mixed solvent system has been found to arise from a change in entropy — and therefore to a change in solvation — assuming entropy effects are primarily due to solvation of anions.

For aniline, solvent effects are minor, possibly because of no anion solvation in either water or mixed solvent systems.

INTRODUCTION

It is customary to define acids and bases in terms of some structural concept; but since proton transfer reactions are almost always studied in liquid solvents, then the solvent itself can be expected to play some role in the overall process[1-2]. The extent to which such acid-base reactions do occur, however, depends on such solvent features as is dielectric constant, its acidic or basic character, and its ability to solvate ions and molecules of the acid or base.

The dielectric constant, ϵ, of a solvent expresses its effect on the electrostatic force between ions. The work of separating SH_2^+ and X^- ions will vary inversely with the dielectric constant of the solvent. Thus the reaction:

$$SH + HX \rightleftharpoons SH_2^+ + X^-$$
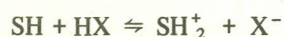
would be expected to occur to a greater extent in water ($\epsilon = 78$ at $25°$) than in methanol ($\epsilon = 33$ at $25°$).

Interactions in which protons are transferred from acid to solvent, or from solvent to base, call into play the basic or acidic nature of the solvent itself.

The prime question, however, is: Why is one acid stronger or weaker than another? Or what conjugate base, and the solvent determine acid strength? A simple and convenient classification is to divide the effects into two, internal and environmental[3-4]. Internal effects are those intrinsic to the molecules and ions of the acid or base, e.g., inductive and resonance effects. Environmental effects are those which result from interaction of the molecules and ions of the acid and base with the solvent.

The strength of an acid is related to the standard Gibbs free energy:

$$\Delta G° = -RT \ln Ka$$

and by determining changes in Ka over a range of temperature, the Van't Hoff equation:

$$d \ln K/dT = \Delta H / RT^2$$

allows calculation of ΔH.

Using, then, the equation:

$$\Delta G = \Delta H - T\Delta S$$

the magnitude of ΔS can be evaluated.

Thus, it becomes possible to discuss such effects as substituent or solvent upon ΔG in terms of ΔH and/or ΔS, where ΔS is usually considered[3-4] to be due solely to environmental effects, i.e. solvation.

EXPERIMENTAL

The e.m.f.-spectrophotometric technique[5-7] was used to determine the acidity constants for five related phenols and aniline over a limited temeperature range. The thermodynamic pKa values obtained and the special experimental conditions for each compound are given in Table 1. The buffers used were taken from Table 1 of Reference[8].

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Table 1. Thermodynamic pKa values of phenols and aniline studied.

Compound	Wave length (nm)	molality	Buffer table 1 of ref.[8]	Thermodynamic pKa values at various temperatures								
				5°	10°	15°	20°	25°	30°	35°	40°	45°
O-NO$_2$ phenol	420	1x10^{-3}	Phosphate	8.184	8.128	8.076	8.028	7.980	7.936	7.894	7.854	7.822
p-NO$_2$ phenol	400	1x10^{-3}	Phosphate	8.009	7,921	7,860	7,804	7.717	7.669	7.631	7.585	7.529
2,6 di-Cl phenol	300	1x10^{-4}	Phosphate	8.168	8.130	8.093	8.058	8.027	8.003	7.982	7.960	
2,4,6 tri-Cl phenol	314	1x10^{-4}	Phosphate	7.514	7.483	7.461	7.442	7.425	7.411	7.400	7.388	
2,6 di-Cl 4-acetyl phenol	334	2.5x10^{-4}	Acetate	6.106	6.085	6.067	6.051	6.037	6.028	6.019	6.013	
Aniline	285	5x10$^{-?}$	Acetate	4.938	4.859	4.776	4.689	4.598	4.504	4.408	4.308	4.204

Table 2. Solvent effect on ΔG_{25}, ΔH_{25}, and ΔS_{25}.

Compound	ΔG_{25} KJ mol^{-1}			ΔH_{25} KJ mol^{-1}			ΔS_{25} Jdeg mol^{-1}		
	H$_2$O	mixed	$\delta\Delta G$	H$_2$O	mixed	$\delta\Delta H$	H$_2$O	mixed	$\delta\Delta S$
O-Nitrophenol	41.3	45.5	+4.2	19.0	16.0	−3.04	− 74.5	−100.4	−26.0
p-Nitrophenol	40.8	44.1	+3.3	19.5	19.4	−0.01	− 71.5	− 83.0	−11.5
2,6-Dichlorophenol	38.9	45.8	+6.9	10.5	9.6	−0.90	− 95.0	−121.5	−26.5
2,4,6-Trichlorophenol	37.0	42.4	+5.4	6.5	5.0	−1.50	−102.2	−125.5	−23.3
2,6-Dichloro-4-Acetyl phenol	26.4	34.5	+8.1	3.7	4.0	0.30	− 76.1	−102.0	−25.9
Aniline	26.2	26.2	0	31.2	32.3	1.00	16.6	20.4	3.8

Errors in pKa are estimated at ±0.02 units or better, depending on the pH of the buffer compared to the experimental pKa of the compound under study.

Table 2 shows the effect of solvent on ΔG, ΔH and ΔS. The Clarke and Glew equation[9] was used to evaluate the results for ΔH and ΔS. The values quoted for water as solvent were previously measured in this laboratory using the same e.m.f.-spectrophotometric technique.

DISCUSSION

The free energy of transfer of an uncharged species or of a neutral electrolyte from one solvent to another is a concept with rigorous thermodynamic definition. However, thermodynamics offers no assistance in separating the free energy into the individual contributions of the ions making up the electrolyte.

The change in proton activity as solvent composition is altered, can, however, be attributed to the effect of the properties of the solvent on the free energy of the ions; that is, to ion-solvent interactions. The transfer free energy includes contributions of both electrostatic charging effects and solvation, i.e:

$$\Delta G°t = \Delta G°t \text{ (elec)} + \Delta G°t \text{ (solv)}$$

but neither component can be easily estimated.

From our results for phenols, though, it seems clear that an acid-base reaction of the type:

$$HA + SH \leftrightharpoons SH_2^+ + A^-$$
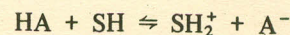
is markedly influenced by solvation, if solvation of the two species HA and A$^-$ is different in different solvents; for

influences of this type are revealed by comparing the strengths of the acids as solvent is changed.

Grunwald[10] and Parker[11] have made interesting contributions to an understanding of the role of anion solvation, although hydrogen bonding, which exists in both solvent systems of this present study, complicates a quantitative interpretation of their ideas.

In mixed solvents it has to be recognised that different types of solvent molecules may interact individually and to different extents with acidic and basic species present in the solvent medium. It has been commonly assumed that ions in a binary solvent are predominantly surrounded by molecules of the more polar constituent, that is, by water rather than by methanol. However, in this present study, if solvation is a major contributor to the thermodynamic parameter, ΔG — arising through ΔS — then it would appear that in water-methanol the phenolate ion is appreciably solvated by the methanol.

The apparent enhancement of the stability of cations upon transfer from water to water-methanol systems has been attributed[12-13] to changes in the structure of the primary solvation shell in which the increased electron density on the oxygen of the solvating species plays a major role. This increase results from the inductive effect of the methyl group and may well be exerted both on the oxygen of the methanol molecule and that of water molecules bonded to methanol. On the other hand, anions become less stable because anion solvation is also influenced by a reduction in charge on the hydrogen atoms of the solvent OH groups, bringing about decreased coulombic interaction with the anionic charge.

The complexity of the ion-solvent interactions is well illustrated by the conflicting evidence concerning the relative basicities of water and methanol. The investigation of transfer free energies brings one to the conclusion that anions are in a higher free energy state in water-methanol mixtures than in water alone; whereas cations, including protons, are in a lower free energy state.

The dissociation of anilinium ions is an isolectric process:

$$BH^+ + SH \leftrightharpoons B + SH_2^+$$
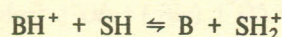
and therefore changes in solvation effects should be minimal. Solvatin in water is not very significant so it is not to be expected — nor was it found — that mixed solvents significantly affect the solvation process.

Consequently, changes in ΔS may be considered to arise mainly from solvation effects, and when considering our experimental values for phenols it is significant that the increase in ΔG values arise primarily from an increase in ΔS values, with ΔG values remaining substantially constant. Further, it would appear that the significant feature of solvation relates to the anion and that, quantitatively, the $\delta \Delta S$ values in Table 2 are somewhat similar, suggesting solvation is of the same order of magnitude for this series of phenols.

REFERENCES

1. E.J. King, *Acid-base Equilibria*, (London: Pergamon Press, 1965).
2. I.F. Coetzee and C.D. Ritchie, *Solute-solvent Interactions*, (New York, Dekker, 1969).

3. L.G. Hepler, J. Am. Chem. Soc., **3089**, 85 (1963).
4. K.J. Laidler, Trans. Faraday Soc., **1725**, 55 (1959).
5. R.A. Robinson, and A.I. Biggs, J.Chem.Soc., **338**, (1961).
6. P.D. Bolton, F.M. Hall and .H. Reece, Spectrochim Acta, 1149, 1825, **22** (1966).
7. P.D. Bolton and F.M. Hall, Aust.J.Chem., 1797, **20** (1967).
8. R.G. Bates, M. Paabo and R.A. Robinson, J. Am. Chem. Soc., **87**,415 (1965).
9. E.C.W. Clarke, and D.N. Glew, Trans. Faraday Soc., **62**, 539 (1966).
10. H. Grunwald and E. Price, J.Am.Chem.Soc., **86**, 4517 (1964).
11. A.J. Parker, Quart.Revs. (London), **16**,163 (1962).
12. H.P. Bennetoo, D. Feakins, and D.J. Turner, J.Chem. Soc., 1211 (1966).
13. R.P.T. Tomkins, *Thermodynamics of Ion Solvation in Methanol-Water Systems* (Thesis, Birkbeck College, University of London, 1966).