# Effect of solvent composition on the acidity of phenols in dimethyl sulfoxide – water mixtures

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ABSTRACT: The effect of solvent composition on the acidity of substituted phenols in DMSO- $H_2O$  systems was examined. It is shown that in DMSO- $H_2O$  mixtures with up to 35 mol% DMSO there is a linear relationship between the  $pK_a$  values of monosubstituted phenols in the binary solvent mixtures of different compositions and the corresponding  $pK_a$  values in water. This leads to an equation relating the slope and intercept terms,  $pK_a(DMSO-H_2O) = \text{slope}[pK_a(H_2O)] + \text{intercept}$ . The basis of this relationship in the Kirkwood-Westheimer equation is examined. The significance of a possible 'supersolvent' is discussed. The applicability of the relationships derived herein to other rate-equilibria relationships and solvent mixtures is considered. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: phenols; acidity; solvent composition; supersolvent

## **INTRODUCTION**

Although the properties of binary solvent mixtures have been studied for many years, their continued relevance cannot be overstated. <sup>1-3</sup> This sub-discipline of physical organic chemistry is constantly evolving and being applied not only in traditional studies, such as the solvent effect on enzyme activity,<sup>4</sup> but also in emerging fields such as supercritical fluids.<sup>5</sup> One of our ongoing interests has been the study of the effect of solvent composition on the nucleophilic reactivity of substituted phenoxide anions with various substrates in binary mixtures of dimethyl sulfoxide (DMSO) and water,6-8 a solvent system which has been intensely studied. Unfortunately, comprehensive sets of  $pK_a$  values for organic acids in aqueous binary solvent are not always available. The need for more comprehensive sets of  $pK_a$  values for organic acids in various solvent mixtures prompted our exploration of the factors governing the extent to which the  $pK_a$  values of typical organic acids vary in aqueous binary solvent mixtures.

The focus here was on exploring correlations that would permit the prediction of  $pK_a$  values of substituted phenols in DMSO-H<sub>2</sub>O mixtures and extend currently available data.<sup>7,9,10</sup> We use the empirical models of

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Poh<sup>11,12</sup> and Halle *et al.*,<sup>13</sup> who related empirical linear free energy relationships to the Kirkwood–Westheimer equation. <sup>14</sup> A general expression is obtained which predicts the p $K_a$  value of a phenol in DMSO–H<sub>2</sub>O mixtures in the water-rich region ( $\leq$ 35.5% DMSO) given its p $K_a$  value in water.

#### **EXPERIMENTAL**

The p $K_{\rm a}$  values of the phenols in 59.3 mol% DMSO were determined as described previously.<sup>7,9</sup> The results, together with previously determined values in 48.6, 35.5, 19.5 and 9.7 mol% DMSO, are collated in Table 1.<sup>9,10</sup>

#### **RESULTS AND DISCUSSION**

#### pK<sub>a</sub> relationships

In the 1970s, Poh<sup>11,12</sup> proposed two different methods for predicting  $pK_a$  values of organic acids in various solvent systems. In his first method Poh used the sphere-incontact model developed by Born<sup>15</sup> to derive the equation:

$$pK_0(sol)_A = [(pK_0(sol)_B - pK_0(H_2O)_B] + pK_0(H_2O)_A$$
(1)

which applies to two unsubstituted carboxylic acids

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**Table 1.**  $pK_a$  values of phenols in DMSO-H<sub>2</sub>O mixtures<sup>7,9</sup>

Phenol		$H_2O$	9.7% DMSO	19.5% DMSO	35.5% DMSO	48.6% DMSO	59.3% DMSO <sup>a</sup>
2-CN	Experimental	7.22	7.54	7.97	8.88	9.53	9.71
	Calculated		7.48	7.83	8.37		
	Difference		-0.06	-0.14	-0.51		
3,4,5-Cl <sub>3</sub>	Experimental	7.68	7.85	8.01	8.77	9.43	9.96
	Calculated		8.00	8.41	9.05		
	Difference		0.15	0.40	0.28		
4-CN	Experimental	7.80	8.17	8.45	9.31	10.22	10.44
	Calculated		8.14	8.56	9.23		
	Difference		-0.03	0.11	-0.08		
3,5-Cl <sub>2</sub>	Experimental	8.03	8.27	8.53	9.38	10.08	10.59
	Calculated		8.40	8.85	9.57		
	Difference		0.13	0.32	0.19		
2,4-Cl <sub>2</sub>	Experimental	7.65	8.01	8.31	9.08	10.17	10.67
	Calculated		7.97	8.38	9.01		
	Difference		-0.04	0.07	-0.07		
3,4-Cl <sub>2</sub>	Experimental	8.51	8.78	9.10	10.08	10.67	11.41
	Calculated		8.94	9.46	10.27		
	Difference		0.16	0.36	0.19		
2-Br	Experimental	8.45	8.96	9.64	10.57	11.37	11.68
	Calculated	0	8.88	9.38	10.19	11.07	11.00
	Difference		-0.08	-0.26	-0.38		
Phenol	Experimental	9.88	10.62	11.21	12.44	13.59	13.95
	Calculated	7.00	10.49	11.18	12.30	10.09	10.50
	Difference		-0.13	-0.03	-0.14		
3-CH <sub>3</sub> O	Experimental	9.65	10.35	11.05	12.24	13.11	13.68
	Calculated	,	10.23	10.90	11.96	10.11	10.00
	Difference		-0.12	-0.15	-0.28		
4-C1	Experimental	9.35	9.85	10.18	11.52	12.45	12.91
	Calculated	7.55	9.89	10.52	11.52	12.15	12.71
	Difference		-0.04	0.34	0.00		
4-CH <sub>3</sub> O	Experimental	10.27	10.70	11.47	12.90	13.97	14.53
	Calculated	10.27	10.93	11.67	12.88	13.71	11100
	Difference		0.23	0.20	-0.02		

<sup>&</sup>lt;sup>a</sup> This work.

(denoted A and B) in two different solvents, one of which is typically H<sub>2</sub>O.

The requirement of this model is that all carboxylic acids experience the same relative change in  $pK_a$  upon transfer from a given solvent to a second solvent. Learly, this is not the case for phenols in DMSO- $H_2O$  mixtures: the change in  $pK_a$  value of phenols upon changing the DMSO content in the solvent is strongly dependent upon the  $pK_a$  value of the phenol in  $H_2O$ . Poh showed that Eqn(1) is only modestly successful for carboxylic acids, with an average error of 0.43  $pK_a$  units for the systems investigated. This first model of Poh is thus inappropriate for the study of the  $pK_a$  values of phenols in DMSO- $H_2O$  mixtures.

One shortcoming of Poh's first method is that specific solute–solvent interactions are excluded. He addressed this problem with his second method <sup>12</sup> by comparing the empirical Hammett–Taft relationship: <sup>17–20</sup>

$$\log(K_{\rm a}/K_0) = \rho^* \sigma^* \tag{2}$$

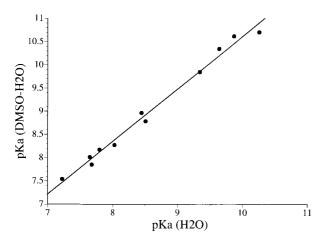
which implicitly accounts for all experimental variables, to the Kirkwood–Westheimer cavity<sup>14</sup> model:

$$\log(K_{\rm a}/K_0) = e\mu\cos\phi/2.303k_{\rm B}TD_{\rm E}l^2 \qquad (3)$$

The  $K_a$  and  $K_0$  values in Eqn (2) represent the dissociation constants of the substituted and unsubstituted acids, respectively,  $\sigma^*$  is the substituent constant and  $\rho^*$  is the reaction constant. For systems where resonance effects are important,  $\sigma^*$  can be replaced by the appropriate substituent constant ( $\sigma^-$ , for example).

In the Kirkwood–Westheimer equation [Eqn (3)], e is the electronic charge,  $\mu$  is the bond dipole moment,  $\phi$  is the angle between the dipole axis and the line joining the reaction site to the midpoint of the dipole axis,  $D_{\rm E}$  is the effective dielectric constant (which is used to make allowances for deviations in the local dielectric constant of the solvent around the solute molecules from its macroscopic value,  $\varepsilon_{\rm r}$ ),  $k_{\rm B}$  is the Boltzmann constant, T is the absolute temperature, and l is the distance between the reaction site and the midpoint of the dipole. It is noted that this model does not account for specific interactions such as hydrogen bonding.

The following equation is obtained from Eqns (2) and



**Figure 1.** Plots of the p $K_a$  values of phenols in 9.7 mol% DMSO vs p $K_a$  values in  $H_2O$ 

(3) if the solvents have no effect on  $\mu$ , and if the ionized molecule has a reasonably fixed geometry (e.g. phenols):

$$\rho_{\rm s}/\rho_{\rm w} = (D_{\rm E})_{\rm w}/(D_{\rm E})_{\rm S} \tag{4}$$

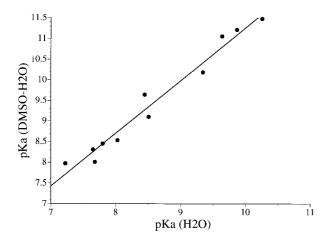
In solvents in which hydrogen bonding effects are important,  $\rho_s/\rho_w$  values were found to be significantly different to the values that can be calculated from Eqns (3) and (4). To account for these discrepancies, a hydrogen bonding factor,  $F_{\rm HB}$ , was introduced, such that

$$\rho_{\rm S}/\rho_{\rm W} = F_{\rm HB}(D_{\rm E})_{\rm W}/(D_{\rm E})_{\rm S} \tag{5}$$

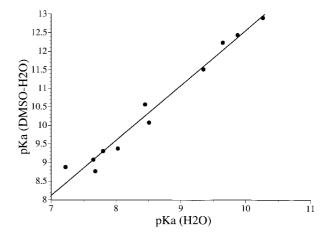
Halle et al.  $^{13}$  used a similar approach to model the acidities of organic acids in DMSO- $\rm H_2O$  mixtures. It was shown that

$$(pK_{a})_{S} = [(\rho)_{S}/(\rho)_{W}](pK_{a})_{W} - [(\rho)_{S}/(\rho)_{W}](pK_{0})_{W} + (pK_{0})_{S}$$
(6)

Combining the approaches of Poh<sup>12</sup> and Halle *et al.*<sup>13</sup> and simplifying leads to



**Figure 2.** Plots of the  $pK_a$  values of phenols in 19.5 mol% DMSO vs  $pK_a$  values in  $H_2O$ 



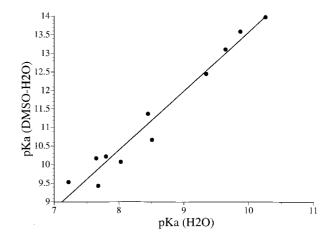
**Figure 3.** Plots of the p $K_a$  values of phenols in 35.5 mol% DMSO vs p $K_a$  values in H<sub>2</sub>O

$$(pK_a)_S = F_{HB}[(D_E)_W/(D_E)_S](pK_a)_W + constant \quad (7)$$

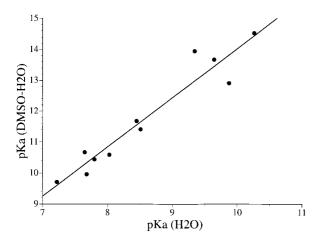
which predicts that a plot of  $pK_a$  values in a mixed solvent against  $pK_a$  values in  $H_2O$  will be linear.

The validity of the Eqn (7) can be tested using the  $pK_a$  values of phenols in DMSO– $H_2O$  mixtures. Plots of  $pK_a$  values of substituted phenols in DMSO– $H_2O$  mixtures against their  $pK_a$  values in  $H_2O$ , using the data in Table1,  $^{7,9,10}$  are shown in Figs. 1–5. The solvent mixtures used in these studies were 30, 50, 70, 80 and 85 vol.%. In the present work, we chose to use mole % DMSO rather than volume % DMSO because mole % has a readily understood physical significance and because mole % DMSO values do not vary with temperature. Thus, 30, 50, 70, 80 and 85 vol.% correspond to 9.7, 19.5, 35.5, 48.6 and 59.3 mol%, respectively.

Each of Figs 1–5 is described by a simple equation of the form y = mx + b, where x is the p $K_a$  value of the phenol in  $H_2O$  and y is the p $K_a$  at a given DMSO– $H_2O$  composition. For these specific solvent mixtures, the p $K_a$ 



**Figure 4.** Plots of the p $K_a$  values of phenols in 48.6 mol% DMSO vs p $K_a$  values in H<sub>2</sub>O



**Figure 5.** Plots of the  $pK_a$  values of phenols in 59.3 mol% DMSO vs  $pK_a$  values in  $H_2O$ 

values can be fitted to the following set of equations:

$$pK_a(9.7 \text{ mol}\%\text{DMSO}) =$$

$$1.13 \,\mathrm{p} K_{\mathrm{a}}(\mathrm{H}_2\mathrm{O}) - 0.659 (r^2 = 0.998) \quad (8)$$

 $pK_a(19.5 \text{ mol}\% \text{DMSO}) =$ 

$$1.27 \,\mathrm{p} K_{\mathrm{a}}(\mathrm{H}_{2}\mathrm{O}) - 1.45(r^{2} = 0.970) \quad (9)$$

 $pK_a(35.5 \text{ mol}\% \text{DMSO}) =$ 

$$1.47pK_a(H_2O) - 2.23(r^2 = 0.975)$$
 (10)

 $pK_a(48.6 \text{ mol}\% \text{DMSO}) =$ 

$$1.58 \,\mathrm{p} K_{\mathrm{a}}(\mathrm{H}_2\mathrm{O}) - 2.27(r^2 = 0.963) \quad (11)$$

 $pK_a(59.3 \text{ mol}\% \text{DMSO}) =$ 

$$1.59 \,\mathrm{p} K_{\rm a}(\mathrm{H}_2\mathrm{O}) - 1.86(r^2 = 0.922) \quad (12)$$

One of the motivations of these investigations was the desire to obtain a general expression, valid for any solvent composition, which can predict  $pK_a$  values of substituted phenols in binary solvent mixtures. Since the plots in Figs 1–5 are all linear, it seemed reasonable that a universal expression may exist for all solvent compositions if a relationship can be found between the 'slope' term,  $F_{\rm HB}[(D_{\rm E})_{\rm W}/(D_{\rm E})_{\rm S}$ , and the 'intercept' term and solvent composition, i.e.

$$p\textit{K}_{a}(DMSO-H_{2}O) = slope[p\textit{K}_{a}(H_{2}O)] + intercept \eqno(13)$$

Plots of the slope terms against solvent composition and intercept terms against solvent composition were therefore constructed (Figs 5 and 6 respectively) and were found to be reasonably linear up to approximately 35.5 mol% DMSO. In these water-rich solvent compositions, the slope terms and intercept terms can be described by

slope = 
$$1.36\chi + 1.00(r^2 = 0.999)$$
 (14)

intercept = 
$$-6.33\chi - 0.061(r^2 = 0.987)$$
 (15)

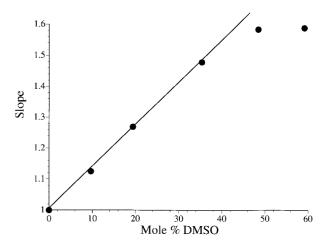
where  $\chi$  represents the mole fraction of DMSO (0.01 × mol% DMSO). Substituting Eqns, (14) and (9) into Eqn, (13) yields

$$pK_a(DMSO-H_2O) = [(1.36\chi + 1.00)pK_a(H_2O)] - 6.33\chi - 0.061$$
 (16)

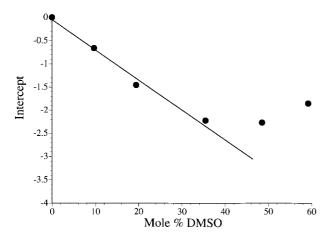
which predicts the  $pK_a$  value of any phenol in DMSO– $H_2O$  mixtures in the  $H_2O$ -rich region (DMSO < 35.5 mol%), given the  $pK_a$  value in  $H_2O$ . The validity of Eqn (16) for media up to 35.5 mol% DMSO is demonstrated by comparison of the experimental values to the calculated values, as shown in Table 1. There is excellent agreement between the empirically and experimentally determined values with the average absolute error being only 0.17  $pK_a$  units.

The finding in this work of an equation that predicts the  $pK_a$  value of phenols in DMSO-H<sub>2</sub>O mixtures based on the  $pK_a$  value in water looks toward extension to other ionization equilibria (carboxylic acids, anilinium ions, etc.), *i.e.* whether these processes will be subject to similar behavior. It is planned to undertake such studies in the future.

Some further comments are necessary concerning the 35.5 mol% DMSO composition as the limit of the applicability of Eqn (16). Figures 6 and 7 show that as the DMSO-rich region is approached (>35.5 mol% DMSO), curvature sets in: neither the 'slope' terms nor the 'intercept' terms are linear outside the water-rich region. At present, a physical description of why the slope varies in a non-linear way (or even why it varies in a linear way in the water-rich region) is not fully apparent. However, it is not surprising that there is a progressive change of behavior between the water-rich region and the DMSO-



**Figure 6.** Dependence on the solvent composition of the 'slope' term of the  $pK_a(DMSO-H_2O)$  vs  $pK_a(H_2O)$  plots



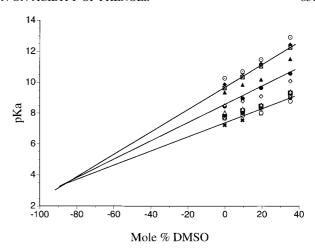
**Figure 7.** Dependence on the solvent composition of the 'intercept term' of the p $K_a(DMSO-H_2O)$  vs p $K_a(H_2O)$  plots

rich region. DMSO and H<sub>2</sub>O are known to have a very strong tendency to form aggregated complexes. The 2:1 complex (33.3 mol% DMSO) is particularly stable. Evidence for this phenomenon is that many physical properties of DMSO–H<sub>2</sub>O are known to exhibit extrema at 33.3 mol% DMSO, including heat of mixing, viscosity, density, <sup>22</sup> energy–volume coefficient, <sup>23</sup> partial molal entropy, the heat of solution of hydrogen <sup>24</sup>, freezing point <sup>25</sup> and adiabatic compressibility. <sup>26</sup>

Turning to the behavior in DMSO-rich mixtures, much fewer data are available here concerning equilibrium processes, but a number of kinetic studies of nucleophilic processes, e.g. reactions of phenoxide anions with carbon, <sup>6a,b</sup> sulfur <sup>6d</sup> and phosphorus <sup>6e,f</sup> esters, have been reported. In these instances a smooth dependence of the log(rate) on mol% DMSO has been found, which does not correlate, however, with solvent composition in the water-rich region. Again, this break in the observed behavior occurs around 35 mol% DMSO, thus providing further evidence for the key significance of this solvent composition in discussions of reactivity relationships in DMSO-H<sub>2</sub>O mixtures.

#### Supersolvent

An interesting phenomenon was discovered during the development of this model. Extrapolation of the plots of  $pK_a$  vs solvent composition into the hypothetical region of negative DMSO content shows that the plots may intersect at a fixed point of approximately -90 mol% DMSO and  $pK_a = 3$  (Fig. 8). At this hypothetical solvent composition, which we have called 'supersolvent,' all phenols have the same  $pK_a$  value, regardless of substituent. Although the common intercept point may in fact be fortuitous, and other lines may be drawn such that no common intercept point occurs, we nonetheless believe that this phenomenon is interesting and worthy of discussion.



**Figure 8.** 'Supersolvent' plot. Plots of the  $pK_a$  values of phenols in DMSO $-H_2O$  mixtures vs mol% DMSO, with plots extended into the region of imaginary solvent composition, to show the common intersection point

The question that the supersolvent poses is, 'what is the physical property of the solvent which causes all phenols to have the same acidity?' In other words, all phenols have the same  $pK_a$  value as the reference phenol in that solvent. This idea is represented by the equation

$$(pK_a)_s = (pK_0)_s \tag{17}$$

Examination of Eqns (4) and (6) shows that for the relationship in Eqn (17) to be true,  $[(D)_E)_W/(D_E)_S]$  must be zero, which holds when  $(D_E)_s$  the effective dielectric constant, is infinitely large. Under these conditions, an electronic effect exerted by the substituent plays no role in the ionization of the organic acid: the solvent does all of the work.

# Applicability to other rate-equilibria relationships and solvent mixtures

The linear relationship that we have observed between  $pK_a$  values of substituted phenols in DMSO-H<sub>2</sub>O mixtures and the corresponding  $pK_a$  values in H<sub>2</sub>O [Figs 1–5 and Eq (16)] will be of value in the main because if its predictive capability. A partial survey indicates that other properties, such as ionizations of different classes of organic acids and bases, as well as reaction rates, show in many cases (e.g. proton transfer from carbon acids, <sup>27</sup> heats of transfer<sup>28</sup> and anionic  $\sigma$ -complex formation <sup>28,29</sup>) similar behavior. Moreover, available evidence shows that this type of behavior persists in mixtures of DMSO with common alcohols.

A theoretical basis of the relationship [Eqn (16)] is at present only imperfectly understood. A primary condition is clearly that plots of the given property (e.g.  $pK_a$ ) are a linear function of mol% DMSO in the H<sub>2</sub>O-rich region. The classical instance of this is the plot of the H<sub> $\perp$ </sub> acidity function <sup>31,32</sup> *versus* mol% DMSO, which after an

almost linear portion in the H<sub>2</sub>O-rich region displays a sharply upward deviation in the DMSO-rich region. This is generally accounted for in terms of a combination of factors: strong H-bonding between H<sub>2</sub>O and DMSO molecules and the progressive desolvation of  $OH^-$  with decreasing  $H_2O$  content.  $^{32,33}$  A similar reasoning may be used in accounting for the increasing values of the slope parameters in the p $K_a$  (DMSO- $H_2O$ ) vs p $K_a$ ( $H_2O$ ) plots as the p $K_a$  of the phenol increases [Eqns (8)–(12)]. Here, also, the corresponding individual plots of  $pK_a vs$  mol% DMSO show an increasing upward deviation in the DMSO-rich region. A plausible explanation is that with relatively strongly acidic phenols where the negative charge on the conjugate base is delocalized over the benzene ring as well as residing in part on the anionic oxygen, efficient solvation can persist in the DMSO-rich region since DMSO is known to interact efficiently with charge dispersed species through dipole-dipole interactions. On the other hand, in the case of weakly acidic phenols with less charge dispersal in the corresponding anions, solvation through H-bonding with H<sub>2</sub>O molecules will be the predominant stabilization mechanism, and in the DMSO-rich media where this stabilization is not available, substituents on the benzene ring will assume a correspondingly greater role. This in turn will be reflected in a greater sensitivity of the  $pK_a$  to medium effect (mol% DMSO) changes; hence the increasing slope parameters in Eqns (8)–(12).

Although the perhaps unique properties of DMSO and its mixtures with water and alcohols have been of immense value in both mechanistic and synthetic chemistry,<sup>2</sup> adequate theoretical treatments of these (and by and large other) mixed solvents have yet to be published, to the authors' knowledge. Hence the empirical relationships observed here, and that can be anticipated from the present study, will continue to be used as a predictive tool in organic chemistry.

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