A CONDUCTANCE INVESTIGATION OF SULFAMIC ACID IN AQUEOUS SOLUTIONS OF METHANOL, ETHANOL AND ISOPROPANOL AT 25 °C

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The conductance of dilute solutions of sulfamic acid in water–methanol, water–ethanol and water–isopropanol mixture were measured at 25 °C. The experimental data were processed using the Lee and Wheaton equation to evaluate the limiting conductance Λ_0 and association constant K_a. The lowest dielectric constant for each type of water–alcohol mixture was about 20.

Studies of the structure of electrolyte solutions in aqueous and nonaqueous solutions have important and various practical applications[1]. The determination of the dissociation constant of an acid in a binary mixed solvent provides useful data for the theoretical understanding of the ionization process and provides the necessary data concerning buffers for the calibration of pH-meters in these systems. The numerous factors that influence acid-base equilibria include the structure of the solute and solvent species, especially their hydrogen bonding capabilities and any specific solute–solvent interactions which affect ionization, the ionic charges and the basicity and dielectric constant of the solvent[2,3]. The use of solvent mixtures permits a range of dielectric constants to be obtained but this procedure introduces the added complication of the preferential solvation of the species participating in the ionization process.

Conductivity measurements in mixed aqueous solvent systems provide a convenient and accurate means for determining acid ionization constants of a relatively strong acid[4] and have several advantages over other methods since they are precise, relatively easy to perform and a wide range of ionization constants can be determined.

The present investigation was carried out to determine the association constant of sulfamic acid, a strong acid, in the chemically similar binary solvent systems water–methanol, water–ethanol and water–isopropanol at 25 °C from conductance measurements.

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EXPERIMENTAL

Conductivity water was obtained from a Millipore ion exchange appparatus. The specific conductance was better than 1 . 10^{-8} S cm^{-1}. After equilibrium with atmospheric CO_2 the water conductivity increased to 2 . 10^{-7} S cm^{-1}.

Sulfamic acid was Fluka product of high degree of purity (puriss. p.a.) and was used without further purification. Methanol and absolute ethanol were from Fluka, while isopropanol was purchased from Merck. All the alcohols were of puriss. p.a. quality and they were distilled from sulfanilic acid (in order to remove the basic impurities) and the middle fraction was collected. The specific conductance was about 1 . 10^{-8} S cm^{-1}.

The alcohol–water mixtures were prepared directly in the conductivity cell, which was maintained at 25 ± 0.002 °C in a thermostat. All the solutions were prepared by weight. The Erlenmeyer type cells were used and were similar to those proposed by Kraus et al.[5]. The resistance measurements were carried out using a Beckman alternating current conductivity bridge. The conductance measurement techniques have been described elsewhere[6]. No solvent correction was made during the calculation, since the specific conductance of the solvent is mainly due to atmospheric CO_2 contamination whose ionization in the presence of a stronger acid is largely suppressed.

RESULTS AND DISCUSSION

The experimental data were treated by the method proposed by Pethybridge and Taba[7], which uses the Lee and Wheaton equation in its series form[8]. The model, upon which the Lee–Wheaton equation is based, is an improvement of the restricted primitive model. In this model, a layer of solvent in contact with the ion is assumed to have different properties from the bulk solvent . The distance of closest approach is defined as the distance from the reference ion, beyond which the solvent can be treated as a continuum, and within which ions are treated as being paired.

In Table I the experimental values are given for the equivalent conductance Λ at different molarities C of sulfamic acid in the various alcohol–water mixtures. Resistance measurements of alcohol–water mixtures containing more than 90% (w/w) alcohol were impossible since resistance changed continuously during the measurement. This may be attributed to changes in ion solvation. The values of the physical properties of the solvent mixtures given in Table I were taken from the literature[9,10]. The conductance data given in Table II were analysed by a least-square procedure using the following set of equations:

$$\Lambda = \gamma\,[\Lambda_0\,(1 - \Delta X / X) - \Delta\Lambda] \tag{1}$$

$$K_a = (1 - \gamma) / \gamma^2 y^2 C \tag{2}$$

$$\ln y \approx \ln f = -\kappa b / 2\,(1 + \kappa R) \tag{3}$$

$$b = e^2 / 2DkT \tag{4}$$

for Λ_0 and K_a values which minimize

$$\sigma_\Lambda^2 = \Sigma_j \left[\Lambda_j(\mathrm{calc}) - \Lambda_j(\mathrm{obs})\right]^2 / (n - 2)\,, \qquad (5)$$

where Λ_0 is the molar conductance at infinite dilution, σ_Λ (%) the standard deviation based on the experimental and the calculated values of Λ, K_a the asssociation constant and b a quantity known as the Bjerrum distance. In the very dilute range of concentration used in the conductance measurements, we have neglected the numerical difference between the activity coeffiicient f of the rational (mole fraction) scale and the activity coefficient y of the molarity scale[11,12]. The remaining symbols have their usual meaning.

TABLE I

Equivalent conductance of sulfamic acid in alcohol–water mixtures at 25 °C[a]

Water D = 78.5 η = 0.8937		20% MeOH–water D = 70.01 η = 1.400		40% MeOH–water D = 60.91 η = 1.593	
$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ
7.316	386.62	6.879	243.99	4.732	171.71
12.414	383.71	17.089	240.85	12.727	166.70
22.463	379.11	27.196	238.39	21.220	162.34
33.771	374.40	36.916	236.26	28.490	159.12
44.049	370.53	45.576	234.58	37.138	155.72
54.896	366.81	54.438	232.89	44.753	152.95
65.539	363.37	63.809	231.30	51.387	150.76
75.297	360.52	73.736	229.73	60.888	147.91

60% MeOH–water D = 51.71 η = 1.403		80% MeOH–water D = 42.60 η = 1.006		90% MeOH–water D = 37.88 η = 0.767	
$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ
5.173	120.74	3.899	86.00	5.560	52.685
12.382	114.25	10.885	73.06	12.392	41.317
20.177	109.09	18.075	65.36	19.988	34.980
27.558	104.71	25.493	59.80	25.904	31.854
34.534	101.42	32.340	55.93	33.102	28.998
41.987	98.25	41.257	52.06	40.850	26.771
49.223	95.64	48.577	49.45	49.340	24.819
60.213	92.05	55.964	47.24	57.539	23.346

TABLE I
(*Continued*)

20% EtOH–water		40% EtOH–water		60% EtOH–water	
D = 66.99		D = 55.02		D = 32.84	
η = 1.808		η = 2.374		η = 2.232	
$C \,.\, 10^4$	Λ	$C \,.\, 10^4$	Λ	$C \,.\, 10^4$	Λ
11.059	220.72	8.128	137.60	5.662	48.60
19.401	217.10	13.884	135.18	10.607	43.55
27.354	214.12	23.810	131.46	18.244	38.66
35.826	211.30	31.904	128.82	27.444	34.83
47.978	207.70	42.917	125.60	36.987	32.04
62.133	203.80	55.731	122.34	45.716	30.11
72.251	201.35	64.954	120.23	56.326	28.26
80.25	199.47	75.251	118.08	66.677	26.80

80% EtOH–water		90% EtOH–water	
D = 32.84		D = 27.8	
η = 1.738		η = 1.40	
$C \,.\, 10^4$	Λ	$C \,.\, 10^4$	Λ
5.662	48.605	5.224	28.012
10.607	43.558	10.027	23.075
18.244	38.660	18.047	18.994
27.444	34.834	25.339	16.869
36.987	32.042	33.884	15.120
45.715	30.119	43.321	13.776
56.326	28.263	54.209	12.697
66.676	26.800	65.109	11.758

20% i-PrOH–water		40% i-PrOH–water		60% i-PrOH–water	
D = 65.33		D = 49.33		D = 35.33	
η = 1.93		η = 2.60		η = 2.99	
$C \,.\, 10^4$	Λ	$C \,.\, 10^4$	Λ	$C \,.\, 10^4$	Λ
5.434	215.54	10.681	121.86	5.048	69.992
11.556	212.79	20.313	118.62	10.080	67.408
20.628	209.43	29.853	116.00	19.324	63.628

TABLE I
(*Continued*)

30.126	206.38	33.920	115.01	28.404	60.876
38.355	203.99	44.866	112.54	38.251	58.435
46.619	201.76	52.548	110.99	45.998	56.794
54.688	199.75	59.666	109.65	55.890	54.997
62.226	197.90	66.070	108.55	63.785	53.756

80% i-PrOH–water $D = 23.33$ $\eta = 2.57$		90% i-PrOH–water $D = 20$ $\eta = 2.25$	
$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ
4.784	31.207	8.717	11.548
9.126	27.463	14.236	9.601
18.262	23.160	19.684	8.492
23.736	21.432	27.872	7.412
30.198	20.200	35.999	6.703
35.535	19.205	44.499	6.167
44.042	17.982	53.342	5.744
49.774	17.308	63.494	5.367

[a] Weight percentage is given for the amount of alcohol in the mixtures. Units: C, mol dm^{-3}; Λ, S cm^2 mol^{-1}; η, m Pa s.

Equation (*2*) was solved by least-squares method using the experimental values of C and Λ for various R, which is the distance of closest approach. No minimum was observed in the R vs σ_Λ (%) plot. As R was varried, the accompanying values of Λ_0 and K_a that minimize σ_Λ (%) also changed. In the final analysis, the value of 6 Å was accepted as the distance of closest approach, a value which is very close to the mean molecular diameter of sulfamic acid[13].

The dissociation of a neutral acid HA creates ions and is sensitive to changes in dielectric permittivity of the solvent SH. The acid dissociation may be complicated by significant ion pair formation and interactions with the solvent,

$$\mathrm{HA + SH} \overset{K_i}{\rightleftharpoons} \mathrm{SH_2^+A^-} \overset{K_d}{\rightleftharpoons} \mathrm{SH_2^+ + A^-}$$

where K_i is the ionization constant and K_d the dissociation constant, which depends mainly on the dielectric permittivity of the solvent. The acid dissociation constant K_a characterizes the overall process ($K_a = K_i\, K_d$).

As D decreases, K_a can be determined with precision for ever decreasing concentration ranges, while Λ_0 becomes more and more difficult to evaluate. The lowest dielectric permittivity for each type of solvent mixture was about 20. The experimental measurements were made in solvent mixtures where K_a was greater than 10^{-5} and the error of extrapolation to Λ_0 value was small.

The standard free energy of dissociation is made up of two terms: an electrostatic one, which can be estimated by the Born equation[14], and a non-electrostatic one, which includes specific solute–solvent interactions and solvation phenomena. When the electrostatic effects predominate, then in accordance with the Born equation

$$\Delta G_{el} = \frac{N z^2 e^2}{2 r} (1/D_s - 1/D_w) \qquad (6)$$

the plot of pK_a vs ($1/D_s - 1/D_w$) should give a straight line.

The experimental pK_a values of sulfamic acid plotted as a function of the reciprocal dielectric permittivity of the alcohol–water mixture are shown in Fig. 1. The plots are close to be linear, and the strength of the acid diminishes as the solvent is enriched with alcohol, due to a decrease in dielectric permittivity of the mixture. This drop in the acid strength is greatest for methanol and follows the sequence methanol > ethanol > isopropanol. The Born equation can not predict more than the electrostatic work of transferring an ion from one medium to another of having a different dielectric permittivity. Superimposed on this electrostatic energy is a solvation energy, with which the Born model is unable to deal. There have been several attempts to improve the Born equation with the objective of deriving a formula, by which more reliable values of transfer could be obtained[15 - 18]. These have been partly successful.

When dealing with mixed solvents one has to realize 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, namely, by water in partially aqueous organic media. However, this is not always true. For example the work of Grundwald et al.[19] shows that simple inorganic ions are, on the contrary, appreciably solvated by dioxane in dioxane–water solvents.

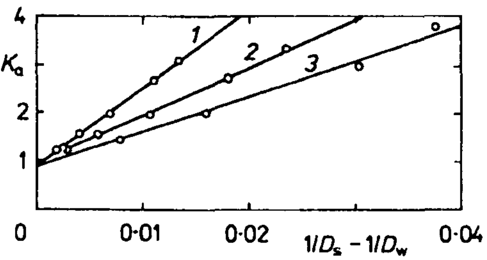

FIG. 1

The dependence of pK_a on $1/D_s - 1/D_w$ for sulfamic acid in alcohol–water mixtures at 25 °C: *1* MeOH–water, *2* EtOH–water, *3* i-PrOH–water

In Fig. 2 the limiting conductances Λ_0 are given for sulfamic acid in the alcohol–water mixtures. Conductance data for sulfamic acid in water have been reported by Taylor et al.[20]. They obtained $K_a = 1.01 \, . \, 10^{-1}$ and $\Lambda_0 = 391.31$, very close to our results. The very small difference between their results and ours may be attributed to the different method of analysis of the experimental data. The value of Λ_0 decreases on increasing the alcohol content in the solvent mixture. This decrease is due to reducing of proton mobility as a function of mole fraction of the alcohol. There is a correlation between the mobilities of the complex ions and the magnitude of the various equilibrium constants with ion–solvent and ion–ion interaction. The loss of the proton mobility resulting from the proton-jump-mechanism that dominates in aqueous solutions, has been determined in other alcohol–water mixtures[21,22]. The decrease is similar

TABLE II

Conductance parameters of sulfamic acid–alcohol–water mixtures at 25 °C

Alcohol	wt. %	Λ_0	K_a	σ_Λ, %
MeOH	20	248.39	16	0.05
	40	176.48	34.6	0.03
	60	128.05	91.6	0.08
	80	100.82	470.2	0.04
	90	86.68	1 259	0.03
EtOH	20	227.71	17.7	0.06
	40	143.36	32.8	0.09
	60	92.71	86.2	0.07
	80	60.48	510	0.03
	90	46.38	2 125	0.05
i-PrOH	20	219.58	16	0.007
	40	128.04	26	0.01
	60	74.69	92.9	0.04
	80	41.37	908	0.06
	90	30.88	6 005	0.02

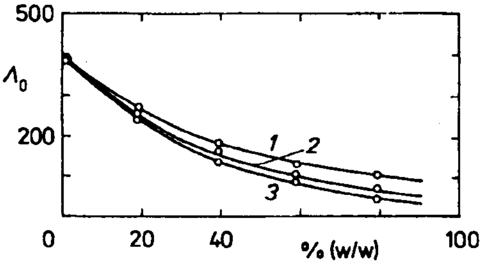

FIG. 2

The dependence of equivalent conductance of sulfamic acid on the weight percentage of: *1* MeOH, *2* EtOH or *3* i-PrOH in the alcohol–water mixture for the three alcohol–water systems, and is greater for isopropanol than ethanol or methanol. This difference is attributed to the different basicity of the alcohol–water mixtures of the same alcohol content that leads to different proton mobilities.

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