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Effect of Water on the Conductance of Hydrogen Halides in Diethylene Glycol

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The effect of addition of small amounts of water on the conductance of hydrogen chloride and hydrogen bromide in diethylene glycol at 25 °C was investigated. The Λ_0 of both acids sharply decreases with the addition of water, passes through a minimum at about 1.23 wt% of water and then increases. This was explained on the basis of the changes in the proton jump mechanism due to shift of the proton transfer equilibrium, $ROH_2^+ + H_2O \rightleftharpoons ROH + H_3O^+$. The role of water in this equilibrium was shown to be similar to the protonation of a Hammett indicator base in acid solutions.

Conductance studies on hydrogen halides in amphiprotic solvents, especially the monohydric alcohols and their aqueous mixtures have received[1-4] some attention in recent years. Such studies are useful[5] in elucidating the effect of solvent structure on the proton migration mechanism in these solvents. Despite this, practically no conductance measurements have been reported[6] in glycols or their aqueous mixtures. The present work, which is in continuation of our earlier work on the subject,[7,8] therefore, deals with the effect of addition of small amounts of water on the conductance of hydrogen chloride and bromide in diethylene glycol in order to elucidate the nature of solute-solvent interactions in these systems.

Experimental

BDH (LR) grade sample of diethylene glycol, purified according to the method described earlier[9] was used. The distilled sample had a bp 120 °C at 10 mmHg, $d^{25\,^\circ C} = 1.115$ g ml^{-1}, and the specific conductivity 9.5×10^{-9} ohm^{-1} cm^{-1} at 25 °C. Conductivity water, obtained by repeatedly distilling double distilled water to which a pinch of permanganate and a trace of sodium hydroxide were added, was used. *p*-Nitroaniline, recrystallised twice from alcohol (mp = 147 °C) was employed as the indicator in H_0 measurements, details of which are given elsewhere.[10] The preparation, purification and standardization of stock HCl and HBr solutions in diethylene glycol are similar to that described[8,9] earlier. The conductance measurements were carried out with a precision conductivity bridge (Model WBR/TAV, WTW, West Germany). A logarithmic indicator amplifier with built-in 1000 Hz generator served as the balance indicator. Further details of the conductance measurements are given[6] elsewhere. All measurements were made at 25.00±0.01 °C employing high boiling liquid paraffin as bath liquid. All solutions were prepared by weight and converted to volume concentrations by appropriate density data. The physical constants of the various solvent mixtures used were identified with the pure solvent in all calculations.

Results and Discussion

The conductance data of the acids are given in Tables 1 and 2. Computer analysis of these data with the Fuoss-Onsager 1965 three parameter equation[11] revealed no significant association of the halides either in the pure solvents[8] or the mixtures. The data were hence analyzed by the Fuoss-Onsager 1965 two parameter equation[11] given by

$$\Lambda = \Lambda_0 - SC^{1/2} + 2EC\log(\tau) + LC \qquad (1)$$

where the various terms have their usual significance. The Λ_0 obtained for the acids in the various solvent mixtures are presented in Table 3. It is seen from this Table that the Λ_0 of the acids decreases continuously as the amount of water added to a solution of HCl or HBr in diethylene glycol increases gradually, passes through a minimum at about 1.23 wt% of water and then increases again with further additions of water. This variation can be qualitatively accounted for in terms of the changes in the proton jump mechanism arising due to the shift of the equilibrium

Table 1. Conductance data of hydrogen chloride in diethylene glycol containing added water at 25 °C

C=concn of acid in eq/l, Λ in ohm^{-1}·cm^2·mol^{-1}

Wt% water	0.2494		0.3737		0.4975	
	$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ
	10.10	7.21	9.90	7.05	9.90	6.85
	15.4	7.20	15.4	6.98	15.30	6.80
	21.6	7.10	21.5	6.96	21.50	6.75
	25.7	7.08	25.7	6.94	25.70	6.73
	37.3	7.07	37.3	6.91	37.20	6.71
	42.4	7.04	42.4	6.84	42.30	6.60
	46.1	6.95	46.0	6.80	46.00	6.52
Wt% water	0.6212		0.7444		0.8676	
	$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ
	9.90	6.70	9.90	6.65	9.90	6.54
	15.30	6.63	15.30	6.58	15.30	6.50
	21.50	6.60	25.60	6.55	21.40	6.49
	25.60	6.57	37.10	6.49	25.60	6.43
	37.20	6.54	42.20	6.43	37.10	6.42
	42.30	6.52	45.80	6.38	42.20	6.40
	45.90	6.48			45.80	6.31
Wt% water	0.9902		1.234		1.356	
	$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ
	9.90	6.49	10.00	6.52	9.80	6.59
	15.30	6.47	15.20	6.46	15.20	6.53
	25.60	6.45	21.30	6.45	21.30	6.47
	37.00	6.39	25.50	6.44	25.50	6.43
	42.10	6.35	36.90	6.38	36.90	6.41
	45.70	6.30	42.00	6.34	42.00	6.37
			45.60	6.30	45.60	6.30

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TABLE 2. CONDUCTANCE DATA OF HYDROGEN BROMIDE IN DIETHYLENE GLYCOL CONTAINING ADDED WATER AT 25 °C

C=concn of acid in eq/l, Λ in $\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$

Wt% water	0.2494		0.3737		0.4975	
	$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ
	11.10	7.52	11.10	7.15	11.10	6.92
	18.30	7.51	18.20	7.13	18.20	6.91
	32.80	7.45	23.90	7.11	23.90	6.90
	40.80	7.44	32.80	7.10	32.70	6.87
	58.60	7.38	40.70	7.09	40.70	6.85
			58.50	7.00	58.40	6.77
Wt% water	0.6212		0.7444		0.9902	
	$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ
	11.10	6.80	11.10	6.63	11.10	6.52
	18.20	6.79	18.20	6.62	18.10	6.51
	23.90	6.78	23.80	6.61	23.80	6.50
	32.70	6.72	32.70	6.58	32.50	6.48
	40.60	6.70	40.60	6.56	40.50	6.42
	58.40	6.68	58.30	6.50	58.20	6.34
Wt% water	1.234		1.356			
	$C\times10^4$	Λ	$C\times10^4$	Λ		
	11.00	6.51	11.00	6.55		
	18.10	6.49	18.00	6.53		
	23.70	6.48	23.70	6.52		
	32.50	6.41	32.50	6.43		
	40.40	6.40	40.30	6.42		
	58.00	6.31	57.90	6.32		

TABLE 3. LIMITING EQUIVALENT CONDUCTANCES, Λ_0, OF HCl AND HBr IN DIETHYLENE GLYCOL–WATER MIXTURE AT 25 °C

Wt% water	Λ_0 (HCl) $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	Λ_0 (HBr) $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$
0.2494	7.62±0.04	7.96±0.06
0.3737	7.44±0.03	7.55±0.05
0.4975	7.29±0.05	7.32±0.05
0.6212	7.06±0.02	7.17±0.03
0.7444	7.04±0.04	7.01±0.04
0.8676	6.92±0.04	—
0.9902	6.90±0.04	6.92±0.04
1.234	6.89±0.03	6.89±0.04
1.356	6.97±0.03	6.95±0.04

$$\text{ROH}_2^+ + \text{H}_2\text{O} \rightleftharpoons \text{ROH} + \text{H}_3\text{O}^+ \qquad (2)$$

in which the initial decrease of Λ_0 is caused by the replacement of protons of abnormal conductance (ROH_2^+) by protons of normal conductance (H_3O^+) at low concentrations of water. At higher concentrations of water, the H_3O^+ ions are increasingly surrounded by water molecules and their proton jump mechanism is restored resulting in abnormal conductance of these ions. Similar observations have been made by Goffredi *et al.* in propanol-water mixtures and Selvarajan and Kalidas[7] in ethylene glycol-water and propylene glycol-water mixtures. The equilibrium constant K, of Reaction (2) was evaluated[12] according to

$$\frac{1}{\Lambda_0^\circ-\Lambda_0} = \frac{1}{\Lambda_0^\circ-\Lambda_0^{\text{w}}} + \frac{1-x}{xK(\Lambda_0^\circ-\Lambda_0^{\text{w}})} \qquad (3)$$

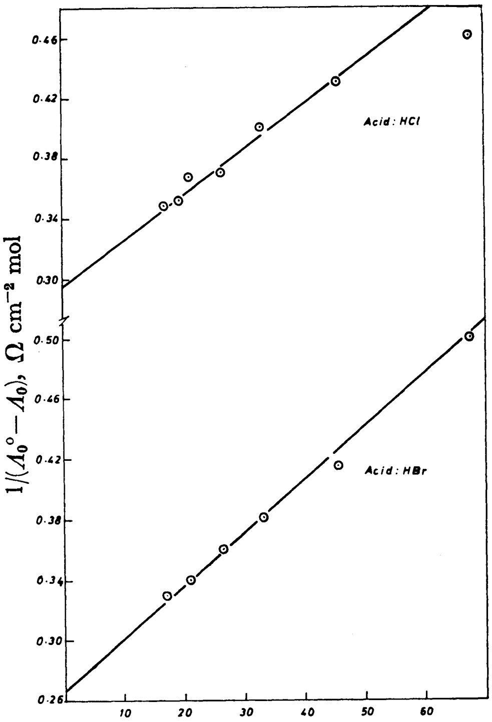

Fig. 1. Plot of $1/(\Lambda_0^\circ-\Lambda_0)$ *vs.* $(1-x)/x$ at 25 °C in diethylene glycol for HCl and HBr.

where Λ_0° represents the conductance of the hydrogen halide in diethylene glycol with the protons in the form of ROH_2^+, Λ_0^{w} is the (hypothetical) conductance of the same acid in the solvent with the protons in the form of H_3O^+ and Λ_0 is the conductance at a mole fraction x of water. A plot of $1/(\Lambda_0^\circ-\Lambda_0)$ *vs.* $(1-x)/x$ for the two acids is shown in Fig. 1. The average value of K obtained (from the slopes of these plots) corresponding to the least squares fitting of the best straight lines (for the two acids) is 88±12. Although it might be expected that the equilibrium constant of Reaction (2) in different alcohols is related to the basic strengths of these molecules, a comparison of the values in different alcohols shows that this is not true. This is most probably due to the structural influence of the solvent on the proton migration mechanism in amphiprotic solvents, *viz.*, through the free solvent molecules and through hydrogen bonded net works in the solvents as proposed by Goffredi *et al.*[5] It is, however, significant that the role of water in Reaction (2) can be likened to that of a Hammett indicator base in protonation equilibria according to

$$\text{SH}^+ + \text{B} \rightleftharpoons \text{S} + \text{BH}^+ \qquad (4)$$

and hence the H_0 difference between two solvents S_1 and S_2 can be related to

$$H_{0(S_2)} - H_{0(S_1)} = \log\frac{K_{(S_2)}}{K_{(S_1)}} \qquad (5)$$

where $K_{(S_2)}$ and $K_{(S_1)}$ are the equilibrium constants of Reaction (2) in the two solvents. Considering S_1 and S_2 to be diethylene glycol and propylene glycol respectively, the H_0 difference was found to be 0.22 (at 0.1 mol/kg concn) while the log ratio of equilibrium constants is 0.31 ($K_{\text{P,G}}=43$)[7] which shows the approximate validity of Equation(5) and hence of the assumption made above.

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