

## Conductance behaviour of HCl in water-ethylene glycol, water-diethylene glycol and ethylene glycol-diethylene glycol mixtures

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**Abstract.** The conductance behaviour of HCl in water-ethylene glycol, water-diethylene glycol and ethylene glycol-diethylene glycol mixtures was investigated in the complete range of solvent compositions of 25°C by applying the three-parameter conductance equation. No appreciable association of the acid was observed in any of the mixed solvents. The large decrease of  $\Lambda_0$  and  $\Lambda_0\eta_0$  of the acid in the early and end composition region of the mixed solvents has been attributed to the drastic structural changes brought about by the addition of the organic component in the aqueous solvent mixtures and by the addition of diethylene glycol in the case of ethylene glycol-diethylene glycol mixtures.

**Keywords.** Conductance; hydrogen chloride; glycol mixtures.

### 1. Introduction

Several studies on the conductance behaviour of HCl in amphiprotic solvents in presence of small amounts of added water (Strehlow 1960; De Lisi and Goffredi 1971; Selvarajan and Kalidas 1974; Srinivas Rao and Kalidas 1976) have been reported. However, relatively few reports (Shedlovsky and Spirey 1967; Shedlovsky and Kay 1956, Goffredi and Shedlovsky 1967) are available on the conductance of HCl in aqueous organic solvent mixtures over the complete range of solvent compositions. As part of a programme of work on ion-solvent interactions in amphiprotic media, we have undertaken a comprehensive conductance study of HCl in water-ethylene glycol (EG) and water-diethylene glycol (DEG) mixtures covering the entire range of solvent compositions. Further, the effect of replacement of a highly structured liquid like water in water-EG mixtures by an organic component, *i.e.*, diethylene glycol, has also been studied by conductance measurements on the acid in EG-DEG mixtures over the complete range of solvent compositions. Such studies dealing with conductance in binary non-aqueous mixed solvents on HCl have not been reported earlier.

### 2. Experimental

Ethylene glycol (EG) and diethylene glycol (DEG) were purified according to the methods described earlier (Kalidas and Palit 1961; Kalidas and Rao 1974).

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Specific conductances of  $2 \times 10^{-8}$  mho  $\text{cm}^{-1}$  (EG) and  $9.5 \times 10^{-9}$  mho  $\text{cm}^{-1}$  (DEG) were observed at 25°C. Conductivity water was prepared by distilling doubly-distilled water, to which a trace of permanganate and a few sodium hydroxide pellets were added, over an all-glass apparatus. Hydrogen chloride gas, generated according to the method described earlier (Kalidas and Palit 1961), was bubbled into the solvent mixture of the desired composition and standardised against a freshly standardised solution of aqueous NaOH and solutions of HCl of the desired concentration were prepared from this stock solution. A precision conductance bridge model WBR/TAV (Wissenschaftliche Technische Werkstätten GmbH, West Germany) operating on 220 V and 50 cycles/sec was used for all conductance measurements. A logarithmic indicator amplifier with a built-in 1000 cycles/sec generator was used as the balance indicator. The resistance measurements are generally accurate to  $\pm 0.1\%$ . A conductance cell similar to that reported by Daggett and Kraus (1951) with a cell constant  $0.5524 \text{ cm}^{-1}$  was used. The temperature was maintained to within  $\pm 0.01^\circ\text{C}$  by circulating liquid paraffin at the given temperature through the annular space of the double-walled cell used in the measurements. The viscosities and dielectric constants of EG-DEG mixtures were determined at 25°C (Sivaprasad and Kalidas 1979) by an Ostwald viscometer and a DK meter 60 GK respectively while the same data for water-EG and water-DEG mixtures were taken from literature (Gallant 1967; Akerlof 1932). The general procedure in the conductance measurements has been described earlier (Kalidas and Rao 1976) and usually HCl concentrations in the range  $1$  to  $7 \pm 10^{-3}$  eqv/l were employed.

### 3. Results and discussion

The conductance data on the acid in the various solvent mixtures were analysed by the Fuoss-Onsager (1965) three parameter equation given by (Fuoss *et al* 1965)

$$A = A_0 - SC^{1/2}\gamma^{1/2} + 2EC\gamma \log(\tau\gamma^{1/2}) + LC\gamma - AC\gamma \exp(-2T\gamma^{1/2})A \quad (1)$$

wherein the various terms have their usual significance. The calculations were performed on an IBM 360 computer. The results analysed showed no appreciable association of the acid ( $K_A < 10$ ) in all the three systems and hence the 1965 Fuoss-Onsager two-parameter equation given by (Fuoss *et al* 1965)

$$A = A_0 - SC^{1/2} + 2EC \log(\tau) + LC \quad (2)$$

was used in further analysis of the data. The terms in (2) have been explained elsewhere (Fuoss *et al* 1965). The correction for the solvent conductance was small and hence neglected. The conductance data, the  $A_0$  values and the standard deviation for each run obtained from the computer analysis of the data at

**Table 1.** Conductance data of HCl in water-EG mixtures at 25°C.

$c \times 10^4$ mol lit <sup>-1</sup>	$A$	$\Delta A^*$	$c \times 10^4$ mol lit <sup>-1</sup>	$A$	$\Delta A^*$
	20 wt % EG			40 wt % EG	
9.397	196.95	0.06	11.49	120.32	0.07
14.17	196.14	-0.05	15.14	119.90	-0.02
20.65	195.36	-0.05	20.60	119.46	-0.05
28.59	194.68	0.07	27.38	119.08	0.01
36.94	193.82	-0.06	34.33	118.67	-0.01
48.63	193.00	0.00	42.86	118.26	-0.00
66.16	191.89	0.01	59.23	117.57	0.01
	60 wt % EG			80 wt % EG	
13.75	65.81	-0.01	15.82	29.87	-0.02
19.20	65.53	0.00	24.34	29.58	-0.03
24.55	65.28	-0.01	31.83	29.44	0.03
29.90	65.10	0.02	38.95	29.30	0.05
37.91	64.81	0.01	44.40	29.14	0.00
46.19	64.55	0.01	53.86	28.96	-0.02
57.06	64.21	-0.02	62.19	28.77	0.04
			68.91	28.56	0.04

\* represents the difference between the measured  $A$  and that calculated from (2).  $A$  and  $\Delta A$  are given in ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

**Table 2.** Conductance data of HCl in water-DEG mixtures at 25°C.

$c \times 10^4$ mol lit <sup>-1</sup>	$A$	$\Delta A^*$	$c \times 10^4$ mol lit <sup>-1</sup>	$A$	$\Delta A^*$
	20 wt % DEG			40 wt % DEG	
18.17	182.94	0.09	19.81	94.30	0.04
26.40	181.84	-0.02	22.69	94.01	-0.04
34.33	180.97	-0.04	28.58	93.65	0.01
43.85	180.00	-0.10	34.57	93.22	-0.06
52.96	179.34	0.03	48.85	92.57	0.10
61.89	178.58	0.00	56.15	92.07	-0.03
68.46	178.11	0.05	68.13	91.51	-0.02
	60 wt % DEG			80 wt % DEG	
11.91	45.40	-0.04	18.35	16.62	0.05
14.84	45.31	0.00	25.49	16.39	-0.03
20.98	45.05	-0.01	33.35	16.23	-0.04
31.43	44.78	0.06	45.13	16.06	-0.01
38.07	44.56	0.02	53.40	15.95	0.00
46.38	44.32	-0.01	61.38	15.82	-0.01
53.24	44.19	0.01	68.90	15.76	0.03
61.47	43.97	0.03			

\* represents difference between the measured  $A$  and that calculated from (2).  $A$  and  $\Delta A$  are given in ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

**Table 3.** Conductance data of HCl in EG-DEG mixtures at 25°C.

$c \times 10^4$ mol lit <sup>-1</sup>	$A$	$\Delta A^*$	$c \times 10^4$ mol lit <sup>-1</sup>	$A$	$\Delta A^*$
20 wt % DEG			40 wt % DEG		
10.83	16.39	0.01	13.17	13.69	0.11
18.74	16.10	-0.01	18.15	13.31	-0.07
27.97	15.86	0.00	23.80	13.09	-0.08
35.52	15.70	0.01	34.38	12.81	-0.02
44.58	15.52	0.00	44.99	12.53	0.02
52.32	15.38	-0.01	55.52	12.27	0.04
62.61	15.26	0.03	66.03	11.95	-0.01
69.44	15.12	0.02			
60 wt % DEG			80 wt % DEG		
12.48	9.82	0.05	15.47	7.66	-0.01
19.43	9.63	0.00	29.27	7.46	0.08
24.52	9.51	-0.03	33.65	7.31	0.02
31.34	9.37	-0.07	37.99	7.16	-0.06
45.83	9.29	0.04	46.18	7.01	-0.07
53.65	9.17	0.01	54.15	6.94	-0.01
62.18	9.07	0.00	62.18	6.85	0.02
			68.79	6.76	0.03

\* Represents the difference between the measured  $A$  and that calculated from (2).  $A$  and  $\Delta A$  are given in ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

**Table 4.** Data of  $A_0(\text{HCl})$  and  $\sigma A^*$  in the various mixtures of water-EG, water-DEG and EG-DEG mixtures at 25°C.  $A_0$  given in ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

Wt % DEG/EG	0	20	40	60	80	100
Water-EG	426.75 <sup>a</sup>	199.89	122.39	67.35	30.93 ± 0.03	32.77 <sup>b</sup>
wt % EG		± 0.05	± 0.03	± 0.01		
$\sigma A$		0.06	0.04	0.02	0.03	
Water-DEG	426.75 <sup>a</sup>	187.07	96.97	46.54	17.35 ± 0.03	9.76 ± 0.05 <sup>c</sup>
wt % DEG		± 0.07	± 0.06	± 0.03		
$\sigma A$		0.07	0.06	0.04	0.03	0.05
EG-DEG	32.77 <sup>b</sup>	17.01	14.43	10.26	8.28 ± 0.05	9.76 ± 0.05 <sup>c</sup>
wt % DEG		± 0.02	± 0.06	± 0.04		
$\sigma A$		0.02	0.07	0.04	0.05	0.05

\*  $\sigma A$ 's represent standard deviation of the individual points; <sup>a</sup> Stokes (1961); <sup>b</sup> Convington and Dickinson (1973); <sup>c</sup> Srinivas Rao and Kalidas (1976).

25°C are recorded in tables 1 to 4. The walden products  $A_0\eta_0$  in all the solvent mixtures and their viscosities at 25°C are given in table 5. The two-parameter equation fits the data fairly well as evidenced from the small differences in  $\Delta A$  and the small values of  $\sigma A$  for each run (tables 1-3). Further the plots of  $A'$  given by

$$A' = A - A_0 + SC^{1/2} - EC \log C \quad (3)$$

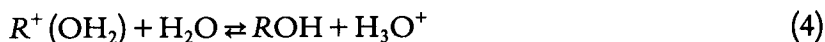
**Table 5.** Viscosities of the solvent mixtures ( $\eta_0$ ) and walden products ( $A_0\eta_0$ ) of HCl in various water-EG, water-DEG and EG-DEG mixtures at 25°C.  $\eta_0$  is given in poise,  $A_0\eta_0$  is given in  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  poise.

Wt% DEG/EG		0	20	40	60	80	100
water-EG system	$\eta_0$	0.0089	0.0135	0.025	0.042	0.080	0.169
wt % EG	$\eta_0 A_0$ (HCl)	3.80	2.70	3.06	2.83	2.43	5.54
Water-DEG system	$\eta_0$	0.0089	0.017	0.03	0.066	0.147	0.3055
wt % DEG	$\eta_0 A_0$ (HCl)	3.8	3.18	2.91	3.07	2.55	2.98
EG-DEG system	$\eta_0$	0.169	0.1945	0.2138	0.2295	0.2485	0.3055
wt % DEG	$\eta_0 A_0$ (HCl)	5.54	3.31	3.09	2.34	2.06	2.98

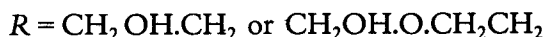
against concentration of the acid in all the mixed solvents are fairly linear lending further support (Evans and Kay 1966) to the complete dissociation of the acid in all solvent mixtures.

### 3.1 Variation of $A_0$ and $A_0\eta_0$ as a function of solvent composition

It is seen from table 4 that a small minimum observed for  $A_0$  of HCl at 80 wt % EG in water-EG mixtures is not observed in water-DEG mixtures which is most possibly due to the large differences in the viscosity and dielectric constant of EG and DEG which affect the conductance values in the pure solvents to widely varying extent. Selvarajan and Kalidas (1974) and Srinivas Rao and Kalidas (1976) observed that  $A_0$  (HCl) (taking into account the glycol-rich region) passes through a minimum at 2.5 wt % water and 1.4 wt % water in mixtures of water-EG and water-DEG respectively and this sharp decrease in  $A_0$  (HCl) on the addition of small amount of water was interpreted on the basis of the abnormal conductance in EG or DEG according to



where



In the water-rich region, the large decrease in  $A_0$  on the addition of organic solvent to an infinitely dilute solution of HCl in water may be attributed to the breakdown of the H-bonded structure of water resulting in the disruption of the abnormal proton conductance in spite of the fact that the protons are virtually present as  $\text{H}_3\text{O}^+$  ions right up to 90 wt % organic solvent in these mixtures as shown by our earlier studies (Selvarajan and Kalidas 1974). Shedlovsky and Kay (1956) arrived at similar conclusions in their conductance studies on HCl in methanol-water mixtures.

Examination of  $A_0\eta_0$  data (table 5) in water-EG mixtures shows that it decreases initially up to 20 wt % EG and then increases slightly up to 40 wt % EG. The region from 40-80 wt % EG is marked by a gradual decrease and finally an increase in pure EG. The variation in water-DEG mixtures is in general similar to that in water-EG mixtures. The viscosity of the solvent mixtures, however, (table 5) increases continuously with the addition of the organic component in both water-EG and water-DEG mixtures. The large decrease in  $A_0\eta_0$  in water-EG mixtures parallels the decrease of  $A_0$  observed on the addition of small amounts of water (in the region of 80 wt % EG) to an infinitely dilute solution of HCl in EG. It is plausible to conclude that the changes in  $A_0\eta_0$  in this region are not predominantly controlled by the changes in the viscosity of the medium but only by the structural changes occurring on addition of water. Similar conclusions apply for the variation of  $A_0\eta_0$  with solvent composition in the water-rich region up to about 40 wt % organic solvent.

To get further information on the variation of the walden product with solvent composition, the cationic and anionic walden products were estimated in water-EG mixtures assuming

$$\lambda_{K^+}^0 \approx \lambda_{NO_3^-}^0 \approx \lambda_{Cl^-}^0 \quad (5)$$

which was found to be valid (within  $\pm 5\%$ ) from an examination of the conductance data for these ions in water (Robinson and Stokes 1959), EG, ethanol and methanol (Covington and Dickinson 1973). For obtaining the ionic walden products in the mixture of water-EG, the  $A_0$  ( $KNO_3$ ) data of Beradelli and Sesta (1972) in water-EG mixtures were utilised and the results so obtained are given in table 6. It is seen from this table that the changes in the walden product for chloride ion are more gradual with a small maximum at 40 wt % EG while considerable decrease of the same for  $H^+$  ion is observed at the extreme compositions. It may be mentioned that the walden product variation of chloride ion in water-EG mixtures is similar to that observed in water-ethanol mixtures (Shedlovsky and Spivey 1967). Thus the variation of  $A_0\eta_0$  of HCl in water-EG mixtures (and possibly in water-DEG) is largely dictated by the changes occurring in the value for the proton.

**Table 6.** Limiting single ion conductances and walden products of  $H^+$  and  $Cl^-$  ions in water-EG mixtures at 25°C.  $\lambda^0$ 's are given in  $ohm^{-1} cm^2 mol^{-1}$  and  $\lambda^0\eta_0$  are given in  $ohm^{-1} cm^2 mol^{-1}$  poise.

Wt % EG	0	20	40	60	80	100
$\lambda^0 H^+$	349.80	150.69	83.39	48.60	21.68	27.70
$\lambda^0 Cl^-$	76.35	49.20	39.00	18.75	9.25	5.07
$\lambda^0 H^+ \eta_0$	3.11	2.03	2.09	2.04	1.73	4.68
$\lambda^0 Cl^- \eta_0$	0.68	0.66	0.98	0.79	0.74	0.86

The results in EG-DEG mixtures show (table 4) that  $\Lambda_0$  (HCl) initially decreases up to 80 wt % DEG on the addition of small amounts of EG to an infinitely dilute solution of HCl in DEG and then gradually increases up to pure EG the rise being steep in the region of pure EG. The variation of the walden product with solvent composition is similar to that of  $\Lambda_0$ .

The decrease of  $\Lambda_0$  may be attributed to the decrease of the abnormal conductance of the proton in DEG caused by the addition of small amounts of EG due to the proton partition equilibrium between DEG and EG. The proton jump mechanism is restored due to  $\text{EGH}^+$  formation when considerable amount of EG is added and  $\Lambda_0$  increases rather steeply as pure EG is approached.

In the EG-rich region, the continuous decrease of  $\Lambda_0$  up to 80 wt % EG may thus be attributed to the disruption of hydrogen bonded structure of EG and hence the decrease of the abnormal proton conductance. It may be added that this explanation is also supported (Sivaprasad 1978) by considerable decrease of enthalpy of transfer of HCl from EG to EG-DEG mixtures.

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