Conductance of Hydrogen Halides (HCl and HBr) in Water-Dimethylformamide Mixtures at 25 °C

D. Muralimohan Rao and C. Kalidas
Department of Chemistry, Indian Institute of Technology, Madras-600 036.

Z. Naturforsch. **45a,** 1006–1008 (1990); received May 22, 1990

The conductance of HCl and HBr in water-dimethylformamide (DMF) mixtures of 10–80 wt % DMF at 25 °C has been measured and discussed, using the three parameter conductance equation suggested by Fuoss et al. in 1965. The ionic conductances and Walden products of the H^+, Cl^- and Br^- ions have been determined and explained. No appreciable ion-association of these acids in these media has been found.

Introduction

Previous studies deal with the conductance of hydrogen halides in water-amphiprotic solvent mixtures [1–4] and water-dipolar aprotic solvent mixtures [5–7]. The present work, which is a continuation of our earlier investigations on the ion solvation in water-dimethylformamide (DMF) mixtures, deals with the conductance of HCl and HBr in these mixtures.

Experimental

The purification of DMF (Merck, India), the preparation of conductivity water and the various solutions, and the determination of the dielectric constant and density of water-DMF mixtures have been described earlier [8]. The purified sample of DMF had a conductance of 1.02×10^{-7} ohm^{-1} cm^{-1} at 25 °C (lit. value [9] 0.5×10^{-7} ohm^{-1} cm^{-1}), refractive index $n_D^{25} = 1.4300$ and density, $d^{25} = 0.9445$ g cm^{-3} (lit. values [10] 1.4269 and 0.9443 g cm^{-3} respectively). The conductance of the conductivity water was about 5×10^{-7} ohm^{-1} cm^{-1}, in agreement with the literature value [11]. It was stored in an always closed bottle. The temperature was maintained at 25 ± 0.02 °C with an ultra cryostat (Lauda-Tischkryostat, TUK 30, Lauda, West Germany). The viscosity data were taken from [12] after converting the molefractions to weight percent. The conductance measurements were made with a precision conductivity bridge (model WBR/TAV, WTW GmbH, West Germany) which has a logarithmic indicator amplifier with a built-in 1000 c/s generator serving as balance-indicator. The resistance measurements are generally accurate to ±0.1%.

Results and Discussion

The conductance data, when analysed with the Fuoss-Onsager-Skinner three parameter equation [13], using an IBM 360 computer, did not indicate any appreciable association of the acids. Hence the data were further analysed with the Fuoss-Onsager-Skinner two parameter equation ((2.7b) in [13])

$$\Lambda = \Lambda_0 - S c^{1/2} + E' c \ln \tau^2 + J' c. \qquad (1)$$

The equivalent conductances, Λ_0, of the acids at infinite dilution at various compositions of water-DMF mixtures are recorded in Table 1. The viscosities of the solvent mixtures and the Walden products of the acids at various compositions are recorded in Table 2. The results show that the acids are practically completely dissociated in these solvent mixtures, which is further supported by the linear plots obtained when plotting Λ' given by ((2) in [13])

$$\Lambda' = \Lambda - \Lambda_0 + S c^{1/2} - E c \log c \qquad (2)$$

against c_{acid} for all compositions of the water-DMF mixtures. If there is appreciable association, the plots of Λ' against c_{acid} should not be linear but rather curved [14a, b].

Variation of Λ_0 and the Walden Product, $\Lambda_0 \eta_0$, of the Acids with Solvent Composition

It is seen (Table 1) that Λ_0 of both acids decreases with increasing DMF concentration, reaches a mini-

---

Reprint requests to Prof. Dr. C. Kalidas, Department of Chemistry, Indian Institute of Technology, Madras-600036, India.

0932-0784 / 90 / 0800-1006 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 1. Λ_0(HCl) and Λ_0(HBr) values with standard deviations σ for HCl and HBr in water-DMF mixtures at 25 °C. Λ_0 in ohm^{-1} cm^2 mol^{-1}.

wt % DMF	0	10	20	40	60	80	100
HCl	426.75[a]	335.45 ± 0.18	253.38 ± 0.40	145.50 ± 0.25	82.18 ± 0.21	50.56 ± 0.13	65.30[c]
σ		0.16	0.30	0.28	0.23	0.17	
HBr	428.22[b]	329.43 ± 0.19	238.92 ± 0.61	142.16 ± 0.32	86.45 ± 0.04	56.51 ± 0.08	88.70[d]
σ		0.16	0.40	0.23	0.03	0.11	

[a] = data from R. H. Stokes, J. Phys. Chem. **65,** 1242 (1961).

[b] = data from Table XIII of [16], using ionic conductance values.

[c] and [d] = data from L. R. Dawson, M. Golben, G. R. Leader, and H. K. Zimmerman, J. Electrochem. Soc. **99,** 28 (1952).

Table 2. Viscosities of H_2O-DMF mixtures at 25 °C (η_0) and corresponding Walden products ($\Lambda_0 \eta_0$) for HCl and HBr. η_0 in poise, Λ_0 in ohm^{-1} cm^2 mol^{-1}.

wt % DMF	0	10	20	40	60	80	100
$\eta_0 \times 10^2$	0.895	1.075	1.360	2.110	2.490	1.880	0.800
$\Lambda_0 \eta_0$(HCl)	3.82	3.61	3.45	3.07	2.05	0.95	0.52
$\Lambda_0 \eta_0$(HBr)	3.83	3.54	3.25	2.99	2.15	1.06	0.71

mum around 80 wt % of DMF and thereafter increases upto pure DMF. This is in agreement [7, 12] with the variation of the viscosities of the solvent mixtures. The existence of a maximum of η_0 can lead to a minimum in equivalent conductance [7], as observed in the present case. However, these two do not correspond to the same composition of the solvent mixture ($\eta_{(\max)}$ at $\simeq 60$ wt % of DMF, $\Lambda_{0\,(\min)}$ at $\simeq 80$ wt % DMF). This may be attributed to the larger size of the solvated ions (specially proton) in the DMF-rich region, which can be inferred from the size of the DMF molecule ($r_{\mathrm{DMF}} = 3.13$ Å) which is greater than [7] that of water ($r_{H_2O} = 1.93$ Å). It has also been established [12] that DMF · $n\,H_2O$ complexes are more bulky than either of the pure solvents, and that solvation of the ions by the bulkier DMF · $n\,H_2O$ complexes leads to an even greater decrease of Λ_0.

The Walden products ($\Lambda_0\,\eta_0$) of the two acids (Table 2) continuously decrease with increasing composition of DMF and may be explained as follows. Upto 60 wt % of DMF, the larger decrease of the Λ_0 of the acids more than compensates the increase η_0 of the solvent mixture, while at higher compositions (60 to 80 wt % of DMF) both Λ_0 and η_0 decrease, resulting in a continuous decrease of $\Lambda_0\,\eta_0$. From 80 wt % DMF and beyond, the decrease in viscosity of the solvent mixture overweighs the small increase of equivalent conductance, resulting in a decreasing trend in the Walden product.

Variation of Ionic Conductances and Ionic Walden Products with Solvent Composition

By combining the Λ_0 ($HClO_4$) data obtained from conductance measurements on $HClO_4$ at 30 °C in the composition range 10–80 wt % of DMF with the ion conductance data of ClO_4^- in these mixtures determined previously [15], the ionic conductances of H^+ in various water-DMF mixtures at 30 °C were obtained. The ion conductance of H^+ at 25 °C in the various water-DMF mixtures was then obtained by applying a correction for the temperature difference via an equation given in [16]. The ion conductances of Cl^- and Br^- were then calculated by combining the Λ_0 of the corresponding acids with the ion conductance data on H^+ at 25 °C in the usual manner. These data together with the ionic Walden products for different water-DMF compositions are given in Table 3. It is seen that $\lambda^0_{H^+}$ decreases continuously upto 80 wt % DMF. It is well known [2] that the large $\lambda^0_{H^+}$ in water depends on the abnormal proton transfer mechanism among the associated solvent molecules. The addition of DMF results in a rapid decrease of the anomalous proton conductivity due to a break up of H-bonded water net work and hence the breakdown of the abnormal proton transfer mechanism. A further possibility for the decrease of $\lambda^0_{H^+}$ arises from the increase of the solvation radius of H^+ with the addition of DMF, as DMF is known to solvate smaller cations in general and H^+ in particular [17], which results in a decrease of its mobility. Between 40 to 60 wt % DMF, the formation of the bulky DMF · $n\,H_2O^{12}$ type complexes and the solvation of H^+ ion by these complexes increases this effect further, resulting in a decrease of the mobility of H^+. The λ^0 of Cl^- and Br^- decreases with the addition of DMF upto 60 wt % DMF and thereafter increases upto 80 wt % DMF. This is in accordance with that expected from the variation of the viscosity of the

Table 3. Single ion conductances and ionic Walden products at infinite dilution for H^+, Cl^- and Br^- in water-DMF mixtures at 25 °C.

wt % DMF	λ^0/ohm^{-1} cm^2 mol^{-1}			$\lambda^0\,\eta_0$/ohm^{-1} mol^{-1} cm^2 poise			$R=(\lambda^0\,\eta_0)$ mixture/ $(\lambda^0\,\eta_0)$ water	
	H^+	Cl^-	Br^-	H^+	Cl^-	Br^-	Cl^-	Br^-
0	349.82	76.95	78.40	3.13	0.69	0.70	1.00	1.000
10	272.37	63.08	57.06	2.93	0.68	0.61	0.986	0.871
20	197.24	56.14	41.68	2.68	0.76	0.57	1.102	0.814
40	111.12	34.38	31.04	2.34	0.72	0.65	1.043	0.929
60	75.80	6.38	10.65	1.89	0.16	0.26	0.232	0.371
80	35.97	14.59	20.54	0.68	0.27	0.39	0.391	0.557

solvent mixtures, which increases upto 60 wt % DMF and then decreases. It is noteworthy that the λ^0_{min} of these ions coincides with the viscosity maximum of the solvent mixtures.

It is seen (Table 3) that the Walden product of H^+ decreases continuously with increasing concentration of DMF.

The non-constancy of the Walden product and its decrease for this ion on the addition of DMF indicates an increase of the solvodynamic radius of H^+ by the entry of DMF molecules ($r_{H_2O} = 1.93$ Å and $r_{DMF} = 3.13$ Å, calculated assuming that the molecules are spherical) into the solvation shell of H^+ as already mentioned earlier.

The Walden products of anions generally decrease upto 60 wt % DMF (except at 20 and 40 wt % of DMF in the case of Cl^- and 40 wt % of DMF in the case of Br^-, where there is a slight increase). The values reach a minimum around 60 wt % DMF and then increase upto 80 wt % DMF. This is in general agreement with the observed increase of the viscosity of the solvent and may be ascribed to strong solvent-solvent interactions giving DMF · $n\,H_2O$ type complexes. The minimum in the Walden product coincides with the maximum viscosity ($\simeq 60$ wt % DMF) of the solvent mixture. From 60 wt % DMF onwards, the viscosity of the solvent mixture decreases, whereby the ionic mobilities will increase, giving rise to an increase in the Walden product of the anions. It is seen that $R < 1$ ($R = (\lambda^0\,\eta_0)$ mixed solvent/$(\lambda^0\,\eta_0)$ water) for Br^- in all solvent mixtures and that R generally decreases with the addition of DMF while the R for Cl^- slightly increases beyond unity in the 20–40 wt % DMF region and subsequently decreases below unity. The R values which are less than unity and their decrease with the addition of DMF is in agreement [18] with the results obtained for the same ions in water-DMSO mixtures. Considering the conductance behaviour of halide ions as indicative of the degree of solvent structure, DMF will be classified as a structure breaker of water, which is in agreement with the results reported previously [19].

[1] L. Wolf, J. Phys. Chem. **64,** 500 (1960).
[2] R. L. Kay and T. Shedlovsky, J. Phys. Chem. **60,** 151 (1956).
[3] H. O. Spivey and T. Shedlovsky, J. Phys. Chem. **71,** 2165 (1967).
[4] V. V. Sastry and C. Kalidas, Indian J. Chem. **24 A,** 658 (1985).
[5] C. Cooke, C. McCallum, A. D. Pethybridge, and J. E. Prue, Electrochim. Acta **20,** 591 (1978).
[6] G. Kortüm and Ch. Hebestreit, Z. Phys. Chem. Frankfurt **95,** 65 (1975).
[7] D. Singh, L. Bahadur, and M. V. Ramanamurthy, J. Soln. Chem. **6,** 703 (1977).
[8] D. Muralimohan Rao and C. Kalidas, J. Chem. Engg. Data. **32,** 158 (1987).
[9] S. B. Brummer, J. Chem. Phys. **42,** 1636 (1965).
[10] B. E. Geller, Russ. J. Phys. Chem. **7,** 1146 (1969).
[11] H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolyte Solutions, Reinhold, New York (1958).
[12] P. K. Tikoo and R. D. Singh, Electrochim. Acta **26,** 1057 (1981).
[13] R. M. Fuoss, L. Onsager, and J. L. Skinner, J. Phys. Chem. **69,** 2581 (1965).
[14] a) D. F. Evans and R. L. Kay, J. Phys. Chem. **70,** 366 (1966). – b) O. Popovych and R. P. T. Tomkins, Non Aqueous Solution Chemistry, John Wiley and Sons, New York 1981, Chapt. VII, p. 264.
[15] V. V. Giridhar, Ph.D. Thesis (1986), IIT, Madras.
[16] S. Glasstone, Introduction to Electrochemistry, D. Van Nostrand Company Inc., New York, 1960, p. 61.
[17] A. K. Das and K. K. Kundu, Electrochim. Acta **23,** 685 (1978).
[18] G. Petrella, M. Petrella, M. Castagnolo, A. D. Atti, and A. D. Giglio, J. Soln. Chem. **10,** 129 (1981).
[19] C. de Visser and G. Somsen, Z. Phys. Chem. (N.F.) **92,** 159 (1974).