402. *Acidity Functions. Part II. The Nature of Hydrogen Ion in Some Aqueous and Non-aqueous Solvents. The Exceptional Solvating Properties of Water.*

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Acidity functions *H* have been determined for solutions of hydrogen chloride in binary mixtures of water, dioxan, ethanol, and acetone, using *m*- and *p*-nitroaniline as indicators. In water–dioxan, water–ethanol, and water–acetone mixtures, *H* varies non-linearly with solvent composition, passing through a minimum in the region of equimolar proportions of the two components. This is in sharp contrast to the behaviour in ethanol–acetone and ethanol–dioxan mixtures, where the change of *H* with solvent composition is gradual. The non-linear variations of *H* in the partly aqueous media are paralleled by the corresponding changes in electrical conductivity, in the catalytic properties, and in the heats of transfer of hydrogen chloride as determined by E.M.F. measurements, and cannot be accounted for merely as dielectric-constant effects. They may be explained, however, in terms of the exceptionally high proton-affinity (cf. Part I, preceding paper) and the exceptional quasi-crystalline structure of water. On the addition of organic solvent to the aqueous medium, the tetrahedral lattice is gradually broken down, and owing to the denser packing and the smaller extent of intermolecular hydrogen-bonding between water molecules, the stability of the hydroxonium ions increases and the proton-donating properties of the medium fall. When the proportion of organic solvent becomes sufficiently large, the hydroxonium ions are finally replaced by organic solvates and *H* rapidly increases with decreasing water content. The value obtained for the equilibrium constant of the reaction $H_3O^+ + EtOH \rightleftharpoons EtOH_2^+ + H_2O$ is in agreement with that obtained from conductivity measurements.

In Part I (preceding paper), measurements were reported of the acidity function *H* for solutions of hydrogen chloride in water, dioxan, ethanol, and acetone. In the present work, the variation of *H* with solvent composition in binary mixtures of these four solvents has been determined. These data were required in connection with kinetic investigations of certain acid-catalysed

Table I.

Indicator ratios for *p*-nitroaniline–hydrochloric acid in water–dioxan, water–ethanol, and water–acetone mixtures: λ_N, ε_N refer to wave-lengths (mμ) and molecular extinction coefficients of the maxima in neutral solution; λ_A, ε_A refer to the acid solutions; ε_S is the extinction coefficient of nitrobenzene at λ_A in the same solvent. $I = (\varepsilon_N - \varepsilon_A)/(\varepsilon_A - \varepsilon_S)$.

Vol. % of organic solvent.*	Neutral.		0·1M-HCl.				1M-HCl.			
	λ_N.	ε_N.	λ_A.	ε_A.	ε_S.	*I*.	λ_A.	ε_A.	ε_S.	*I*.
				Dioxan.						
0	378	12,800	373	6,800	80	0·89	371	715	90	19·3
20	385	14,600	383	9,900	35	0·48	386	2,100	30	6·03
40	383	15,300	382	13,700	35	(0·12)	395	7,100	15	1·15
60	376	16,000	378	15,000	50	(0·07)	386	10,500	30	0·52
70	375	16,200	375	15,200	55	(0·07)	378	8,600	50	0·89
80	370	16,200	369	15,200	70	(0·07)	†	†	†	†
90	366	15,700	366	14,300	85	(0·10)	†	†	†	†
100	353	15,400	353	11,000	150	0·40	340	3,500	180	3·60
				Ethanol.						
0	378	12,800	373	6,800	80	0·89	371	715	90	19·3
20	385	13,800	387	8,700	25	0·59	379	1,500	50	8·50
40	385	15,300	388	12,800	20	(0·20)	385	4,200	30	2·64
60	384	16,200	386	14,000	25	(0·16)	382	7,200	35	1·26
70	380	16,400	382	14,300	35	(0·15)	380	8,200	40	1·04
80	378	16,400	379	15,600	40	(0·05)	380	8,200	40	1·04
90	378	16,200	378	15,300	40	(0·06)	380	6,200	40	1·62
100	374	15,200	373	4,800	60	2·19	368	720	70	22·3
				Acetone.						
0	378	12,800	373	6,800	80	0·89	371	715	90	19·3
20	385	13,800	384	9,700	35	0·42	387	2,000	25	5·98
40	384	15,200	384	14,000	35	(0·09)	386	4,900	25	2·11
60	379	16,200	379	15,300	45	(0·06)	380	7,800	40	1·08
70	377	16,200	379	15,800	45	(0·03)	377	8,100	45	1·01
80	376	16,200	374	16,000	55	(0·01)	375	5,800	50	1·81
90	374	16,000	372	15,300	65	(0·05)	374	950	50	16·7
100	366	15,800	365	2,800	85	4·80	*350*	260	160	155

* For the precise meaning of " vol. % ", see Braude and Stern, this vol., p. 1984.

† The components form a two-phase system in this range.

TABLE II.

Indicator ratios for *m*-nitroaniline–0·1M-hydrochloric acid in water–organic solvent mixtures. For meaning of symbols, see Table I.

Vol. % of organic solvent.	λ_N.	ε_N.	λ_A.	ε_A.	ε_S.	*I*.
			Dioxan.			
40	368	1450	352	350	155	5·7
60	372	1450	370	600	70	1·6
70	373	1550	375	700	55	1·3
80	373	1600	377	780	50	1·1
90	373	1600	370	550	70	2·2
			Ethanol.			
40	364	1450	*348*	310	170	8·1
60	367	1450	362	480	90	2·5
70	369	1450	365	550	85	1·8
80	372	1450	366	640	85	1·5
90	373	1450	366	620	85	1·6
			Acetone.			
20	360	1550	*345*	275	190	15
40	371	1600	*355*	350	130	5·7
60	378	1600	370	610	70	1·8
70	380	1600	375	760	50	1·2
80	380	1650	376	860	45	1·0
90	380	1600	372	810	90	1·1

TABLE II*a*.

Indicator ratios and indicator constant of *m*-nitroaniline in water; c_A = hydrochloric acid concentration; $K_B^{H_2O} = I/c_A$.

c_A.	λ_N.	ε_N.	λ_A.	ε_A.	ε_S.	*I*.	$K_B^{H_2O}$.
0·001	356	1450	355	1020	160	0·27	270
0·005	356	1450	355	750	160	1·35	270
0·01	356	1450	355	510	160	2·7	270

TABLE III.

Indicator ratios for *p*-nitroaniline–0·1M-hydrochloric acid in anhydrous ethanol–dioxan and ethanol–acetone mixtures. For meaning of symbols, see Table I (ε_s has been neglected in calculating *I*).

	Ethanol–dioxan.						Ethanol–acetone.				
Vol. % of dioxan.	λ_N.	ε_N.	λ_A.	ε_A.	*I*.	Vol. % of acetone.	λ_N.	ε_N.	λ_A.	ε_A.	*I*.
0	373	15,200	373	4,800	2·17	0	373	15,200	373	4800	2·17
10	371	16,000	371	4 800	2·34	10	372	15,600	371	4900	2·18
20	371	16,000	371	4 800	2·34	20	372	15,200	371	5000	2·24
30	369	16,300	370	4,800	2·40	30	371	16,300	371	5000	2·26
40	367	16,500	369	5,200	2·17	40	371	16,400	369	5000	2·28
50	366	16,500	368	5,200	2·17	50	370	16,400	369	4800	2·41
60	365	17,100	364	5,400	2·16	60	369	16,400	369	4800	2·41
70	363	17,100	361	5,500	2·09	70	369	16,500	369	4100	3·03
80	362	16,600	359	5,900	1·81	80	369	16,500	369	3800	3·34
90	360	16,300	359	7,700	1·18	90	368	16,200	369	3600	3·50
100	353	15,400	353	11,000	0·40	100	366	15,800	365	2800	4·64

reactions (cf. Braude and Stern, following paper) and it was also hoped that they would throw more light on the abnormally high proton-affinity of water indicated by the earlier work.

As previously, acidity functions were determined spectrophotometrically, *p*-nitroaniline being used as indicator as far as possible. Measurements were made at two acid concentrations, 0·1 and 1M. At the lower concentration the indicator ratios obtained with *p*-nitroaniline for the water–organic solvent mixtures containing 40 to 90% (by vol.) of organic solvent were too small to be of sufficient accuracy (Table I) and for these solutions a more basic indicator was required. *m*-Nitroaniline, which fulfils the desirable condition (cf. Part I) of close structural relationship to *p*-nitroaniline and has a base strength of the required order, was employed, although its light-absorption properties are much less suitable than those of the *p*-isomer, the difference in intensities of the bands due to the base and its conjugate acid being only about one-tenth as great. The spectrometric data and indicator ratios for the various solvent mixtures are collected in Tables I—III. The value of the indicator constant $K_B^{H_2O}$ derived from solutions in dilute aqueous hydrochloric acid (Table II*a*) is 270 for *m*-nitroaniline as compared with 9 for *p*-nitroaniline.

The derived values of the acidity functions are given in Tables V and VI. In water–dioxan, water–ethanol, and water–acetone mixtures, H decreases strongly on the addition of the organic solvent to water, or of water to the organic solvent, and passes through a minimum in the region of equimolar proportion of the two components (Fig. 1). The curves are similar in shape at the two acid concentrations 0·1 and 1M, but the minima occur at somewhat lower proportions of organic solvent at the higher acid concentration. The behaviour of the aqueous solutions is in

TABLE IV.

Acidity functions of hydrogen chloride in aqueous solvent mixtures : m = mols. % of organic solvent ; $H = \log I_{p\text{-nitroaniline}} - 0{\cdot}954$ or $\log I_{m\text{-nitroaniline}} - 2{\cdot}43$.

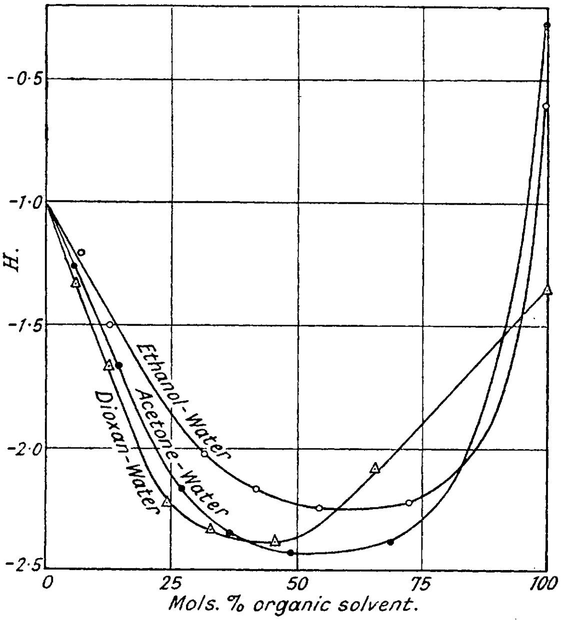
Vol. % of organic solvent.	Water–dioxan.			Water–ethanol.			Water–acetone.		
	m.	H (0·1M-HCl).	H (1M-HCl).	m.	H (0·1M-HCl).	H (1M-HCl).	m.	H (0·1M-HCl).	H (1M-HCl).
0	0	−1·01	+0·33	0	−1·01	+0·33	0	−1·01	+0·33
20	5·0	−1·27	−0·17	7·1	−1·18	−0·03	5·8	−1·33	−0·18
40	12·3	−1·67	−0·89	12·0	−1·52	−0·53	14·0	−1·67	−0·63
60	24·0	−2·23	−1·24	31·8	−2·03	−0·85	27·0	−2·17	−0·92
70	32·9	−2·32	−1·01	42·0	−2·17	−0·94	36·5	−2·35	−0·95
80	45·8	−2·39	—	55·2	−2·25	−0·94	49·5	−2·43	−0·70
90	65·2	−2·09	—	73·8	−2·23	−0·74	69·0	−2·39	+0·27
100	100	−1·35	−0·40	100	−0·61	+0·39	100	−0·27	+1·24

TABLE V.

Acidity functions of hydrogen chloride in non-aqueous solvent mixtures : m = mols. % of dioxan or acetone.

Ethanol–dioxan.				Ethanol–acetone.			
m.	H (0·1M-HCl).	m.	H (0·1M-HCl).	m.	H (0·1M-HCl).	m.	H (0·1M-HCl).
0	−0·61	50·6	−0·62	0	−0·61	54·4	−0·57
7·1	−0·58	61·4	−0·63	8·1	−0·61	64·8	−0·47
14·5	−0·58	73·2	−0·70	17·6	−0·60	76·1	−0·43
22·6	−0·57	86·0	−0·88	24·8	−0·60	88·0	−0·41
31·4	−0·62	100	−1·35	34·2	−0·59	100	−0·27
40·5	−0·62	—	—	44·3	−0·57	—	—

FIG. 1.



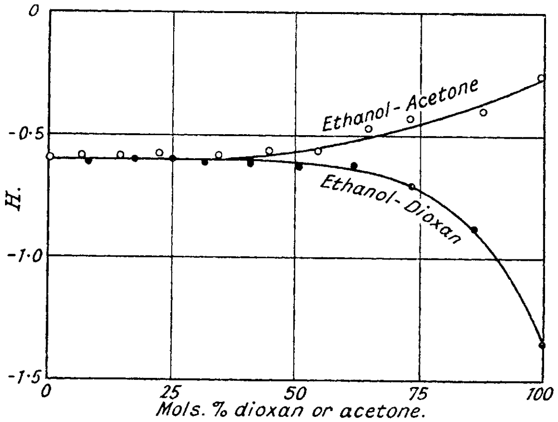
The dependence of acidity function on solvent composition in organic solvent–water mixtures. Concentration of hydrogen chloride 0·1M.

sharp contrast to that of ethanol–acetone and ethanol–dioxan mixtures, where *H* exhibits no minima but varies gradually with solvent composition (Fig. 2).

The striking contrast in the variation of the acidity function with solvent composition in the partly aqueous as compared with the completely non-aqueous media shows that the peculiar features of the former must be associated with the component water. These features cannot be solely due to dielectric-constant or similar effects, since such effects should arise equally in ethanol–dioxan mixtures, the dielectric constants of which also cover a wide range (D = 30 to D = 2).

It has long been known that small concentrations of water have a very pronounced influence on the properties of hydrogen chloride in solvents such as methanol, ethanol, and acetone, both the electrical conductivity (Goldschmidt, *Z. physikal. Chem.*, 1914, **89**, 129; Hughes and Hartley, *Phil. Mag.*, 1933, **26**, 610; Bezman and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1330) and the catalytic effects in certain acid-catalysed reactions (Goldschmidt, *Z. Elektrochem.*, 1914, **20**, 473 and earlier papers; Braude, *J.*, 1944, 443) decreasing rapidly with increasing water content. This phenomenon cannot be due to a decrease in the degree of dissociation of the acid, since the dissociation constant actually increases (Bezman and Verhoek, *loc. cit.*), and was first ascribed by Goldschmidt to the greater basicity of the water as compared with ethanol, and to the replacement of ethoxonium ions ($EtOH_2^+$) by hydroxonium ions (H_3O^+). Lapworth and Partington (*J.*, 1910, **97**, 19) showed that a similar decrease occurs in the indicator ratio of aminoazobenzene when small quantities of water are added to anhydrous solutions of hydrogen chloride in ethanol, and could be explained in the same way, and Kolthoff (*Pharm. Weekblad*, 1923, **60**, 22) employed the corresponding change in the indicator ratio of methyl-orange for the empirical determination of the water content of slightly aqueous ethanol. Some measurements with *p*-nitroaniline in this region of solvent composition are given in Table VI. From these data the equilibrium constant of the reaction

FIG. 2.



The dependence of acidity function on solvent composition in ethanol–dioxan and ethanol–acetone mixtures. Concentration of hydrogen chloride 0·1M.

$$EtOH_2^+ + nH_2O \rightleftharpoons (nH_2O,H^+) + EtOH \quad . \quad . \quad . \quad . \quad . \quad (1)$$

can be calculated, if it is assumed that the minimum value of I (I') which is reached at a water concentration of about 20 vol. % (Table I) represents the point where the conversion of ethoxonium ions into water-solvated protons is complete. The ratio $[(nH_2O,H^+)]/[EtOH_2^+]$ is then given by $x = (I_0 - I)/(I - I')$, where I_0 is the indicator ratio in anhydrous ethanol and I that at a water concentration c_{H_2O}; and the equilibrium constant of reaction (1) is given by

$$K_{H_2O}^{EtOH} = \frac{[(nH_2O,H^+)]}{[EtOH_2^+][H_2O]^n} = \frac{x(x+1)^n}{(c_{H_2O} + xc_{H_2O} - nx\alpha c_A)^n} \quad . \quad . \quad . \quad . \quad (2)$$

where c_A is the acid concentration, and α the degree of dissociation of the acid.

In order to have a physical meaning, $K_{H_2O}^{EtOH}$ must be positive, *i.e.*, $nx\alpha c_A < (c_{H_2O} + xc_{H_2O})$. This condition can only be fulfilled with the present values of x (Table VI) if n, the number of water molecules associated with each hydrogen ion, is less than 2. This must mean that, in fact, $n = 1$ and that in this range the hydroxonium ion is correctly represented by H_3O^+ as was first assumed, but not proved, by Goldschmidt (*loc. cit.*). The values of $K^{EtOH}_{H_2O}$ are satisfactorily constant for water concentrations from 0·05 to 0·5M (Table VI). The mean value of 13 is in reasonably good agreement with the mean value of 17 deduced by Goldschmidt and by Bezman and Verhoek (*loc. cit.*) from conductivity measurements, and in less good agreement with the value of 5 (Goldschmidt, *loc. cit.*) derived from kinetic data. The corresponding constant K^{EtOH}_{B} for the equilbrium between *p*-nitroaniline and ethoxonium ions in ethanol is 31 (Part I, *loc. cit.*) and water is thus a base almost half as strong as *p*-nitroaniline.

TABLE VI.

Indicator ratios for *p*-nitroaniline–0·1M-hydrogen chloride in slightly aqueous ethanol, and equilibrium constants $K^{EtOH}_{H_2O}$ (see text) of the reaction $EtOH_2^+ + H_2O \rightleftharpoons H_3O^+ + EtOH$: $\varepsilon_N = 15{,}200$, $\varepsilon_S = 60$, $x = [H_3O^+]/[EtOH_2^+]$.

Vol. % of ethanol.	H_2O, mols./l.	ε_A.	I.	x.	$K^{EtOH}_{H_2O}$.
100	0·000	4800	2·19	—	—
99·9	0·056	5900	1·57	0·41	16
99·8	0·112	6900	1·22	0·83	13
99·7	0·168	7600	1·01	1·25	11
99·6	0·224	8300	0·83	1·75	11
99·5	0·280	9100	0·67	2·45	12
99·4	0·336	9,800	0·55	3·28	13
99·3	0·392	10,400	0·46	4·22	13
99·2	0·448	10,800	0·41	4·95	14
99·1	0·504	11,200	0·36	5·90	14
99·0	0·560	11,600	0·31	7·25	15
				Mean	13

The decrease in H observed on passing from water to mixtures containing up to about 50 mols. % of organic solvent is again paralleled by a corresponding fall in electrical conductivity (Schukov and Dneprov, *J. Gen. Chem. Russia*, 1938, **8**, 1476; Owen and Waters, *J. Amer. Chem. Soc.*, 1938, **60**, 2371; Hartmann, *Z. physikal. Chem.*, 1941, *A*, **191**, 197), and again cannot be accounted for simply by a decrease in the degree of dissociation of the acid. In the case of water–ethanol mixtures, the dissociation constant (K_A) of hydrochloric acid remains very large up to a 90% molar proportion of ethanol (Bezman and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1330). In water–dioxan mixtures, where the lowering of the dielectric constant is considerably greater, K_A does decrease with increasing concentration of dioxan, but much less rapidly than the corresponding fall in H. Thus, Owen and Waters (*loc. cit.*) give the values of K_A as *ca.* 1 and 0·01 for 45 and 70 weight % dioxan, respectively, corresponding to changes in the degree of dissociation of $\Delta \log \alpha =$ *ca.* $-0{\cdot}15$ and -1 as compared with water ($\alpha = 1$). The corresponding changes in H are *ca.* $-1{\cdot}2$ and $-1{\cdot}9$. Since $H = \log (\alpha c_A K^S_B / K^{H_2O}_B)$ (Part I, *loc. cit.*), and since the acid concentration c_A is a constant, the changes in H must therefore again be partly due to changes in $K^S_B/K^{H_2O}_B$, *i.e.*, in the indicator constant for the solvent relative to that for water. $K^S_B/K^{H_2O}_B$ can be calculated from H, c_A, and the value of α derived from conductivity measurements. The values obtained for water–ethanol mixtures are given in Table VII, α being taken as unity throughout except in 100% ethanol where it is taken as 0·7 (cf. Part I, *loc. cit.*).

TABLE VII.

Indicator constant ratios $K^S_B/K^{H_2O}_B$ for 0·1M-hydrochloric acid–water–ethanol mixtures, and free energies of transfer of hydrogen chloride from infinitely dilute aqueous solution.

Vol. % of ethanol.	$K^S_B/K^{H_2O}_B$.	$-\boldsymbol{R}T\Delta \log K^S_B/K^{H_2O}_B$.	$\Delta(-\Delta H)$.*
0	1	—	—
20	0·66	+ 230	− 150
40	0·30	+ 570	+ 550
60	0·093	+1400	+2300
70	0·068	+1600	+2400
80	0·056	+1700	+2300
90	0·059	+1700	+2000
100	3·1	− 690	−3000

* Butler and Robertson, *Proc. Roy. Soc.*, 1929, *A*, **125**, 694.

If the earlier conclusion is correct, namely, that in media containing more than 20 vol. % of water, the hydrogen ions are exclusively solvated by water, then the change in K^S_B in this range of solvent composition must be due either to a change in the state of solvation or to the inconstancy of the activity-coefficient term (equation 2, Part I, *loc. cit.*), or to both. Even if the activity-coefficient term were not constant, it could only account for a small part of the variation in K^S_B, since the mean activity coefficient of hydrogen chloride itself only changes by a factor of less than 5 on passing from water to ethanol or dioxan (Butler and Robertson, *Proc. Roy. Soc.*, 1929, *A*, **125**, 694; Harned *et al.*, *J. Amer. Chem. Soc.*, 1938, **61**, 59) and since the total variation in the symmetrical term $(f_{SH^+}\ f_B)/(f_{SH^+}\ f_S)$ is likely to be much smaller. It is therefore highly probable that the decrease in K_B^S which accounts for the left-hand part of the H–c_S curves in water–organic solvent mixtures (Fig. 1) is due to a change in the state of solvation of the hydrogen ions, and to an increase in the proton-affinity of water. A qualitative explanation of this effect may be given in terms of the quasi-crystalline tetrahedral structure which conditions the unique properties of water (Bernal and Fowler, *J. Chem. Physics*, 1933, **1**, 515) and in which the proton affinity of the individual water molecules is partly satisfied by hydrogen-bonding with neighbouring molecules. The protons are accommodated in the interstices of the tetrahedral lattice and bonded equally to the surrounding oxygen atoms, a picture in agreement with a solvation number of 4 (Ulich, " Hand- und Jahrbuch der chemischen Physik ", 1933, **6**, 186) for hydrogen ion in water. On the addition of an organic solvent to the purely aqueous medium, the open tetrahedral structure will be gradually broken down through the interposition of organic solvent molecules, and hydrogen-bonding between neighbouring water molecules will be partly replaced by much weaker hydrogen-bonding with organic solvent molecules. The density of packing will increase and the proton will be preferentially surrounded by the smaller water molecules (cf. Rao, *J. Indian Chem. Soc.*, 1945, **22**, 260). As a result of the smaller extent of intermolecular hydrogen bonding and of the closer packing of the solvation shell surrounding the protons, the effective proton affinity of the water molecules will increase, and the equilibrium $(n\text{H}_2\text{O,H}^+) + \text{B} \rightleftharpoons \text{BH}^+ + n\text{H}_2\text{O}$ will be displaced towards the left. As the proportion of organic solvent is increased, the aqueous solvation shell will be gradually dispersed and the aqueous solvates $(n\text{H}_2\text{O,H}^+)$ will be replaced by hydroxonium ions H_3O^+. This state of affairs will correspond to the minima in the H–c_S curves. In the rising (right-hand) parts of the curves (Fig. 1) the hydroxonium ions are in turn replaced by organic oxonium ions of the type EtOH_2^+.

It thus appears that the effective proton-affinity of liquid water, though already unusually large (cf. Part I) is still much smaller than that of water in another solvent, and that the nature of the H–c_S curves in water–organic solvent mixtures is conditioned by the exceptional structure of water on the one hand, and its exceptionally high proton-affinity on the other. The cause of this high proton-affinity is not clear; it may be connected with the threefold symmetry of the hydroxonium ion. In the organic solvents, infra-red absorption and *X*-ray diffraction studies indicate that hydrogen-bonded structure is either much less prevalent, as in the case of ethanol (cf. Gordy, *J. Amer. Chem. Soc.*, 1938, **60**, 605; Pierce and MacMillan, *ibid.*, p. 779; Davies, *Ann. Reports*, 1946, **43**, 5), or largely absent, as presumably in acetone and dioxan, and consequently the deviations from linearity of the H–c_S curves in anhydrous mixtures are much less pronounced.

A measure of the change in the proton-affinity of the solvent will be given by $\boldsymbol{R}T\Delta\log(K_B^S/K_B^{H_2O})$, which is the change in the free energy of the proton-transfer reaction $\text{SH}^+ + \text{B} \rightleftharpoons \text{BH}^+ + \text{S}$. The values obtained for the water–ethanol system are given in Table VII. They are of the same order of magnitude and vary in the same manner with the medium composition as the corresponding changes in the heat content of transfer of hydrogen chloride from water to the ethanolic solvent derived by Butler and Robertson (*loc. cit.*) from E.M.F. measurements of the cell $\text{H}_2|\text{HCl,H}_2\text{O–EtOH,AgCl}|\text{Ag}$. These authors pointed out that $-\Delta H$ should vary linearly with solvent composition if it depended only on changes in electrostatic solvation energy with dielectric constant and that the deviations signify another kind of interaction. The correspondence between $\boldsymbol{R}T\Delta\log K_B^S/K_B^{H_2O}$ and $\Delta(-\Delta H)$ is in agreement with the view that both are controlled primarily by the change in the proton-affinity of the water and by the energy of " chemical " solvation of the proton. The displacement of the maxima in $-\Delta H$ (minima in H) towards lower ethanol proportions with increasing acid concentrations probably arises from the fact that the electrolyte assists in disrupting the quasi-crystalline water structure (cf. Stewart, *J. Chem. Physics*, 1943, **11**, 72; Hasted, Ritson, and Collie, *ibid.*, 1948, **16**, 1). Another indication of this effect is provided by the miscibility gap which occurs in the 1M-hydrogen chloride–water–dioxan system (Table I).

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