

Effects of Water on Proton Migration in Alcoholic Solvents

Part 5.—Conductance of Hydrogen Chloride in Methanol at 15, 25 and 35°C and in Ethanol and Pentan-1-ol at 15 and 35°C

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Conductance data are reported for hydrogen chloride in water+methanol mixtures at 15, 25 and 35°C and in water+ethanol and in water+pentan-1-ol mixtures at 15 and 35°C. Measurements were carried out in alcohol-rich mixtures over a water composition range up to about 20 % by weight. The results have been analysed in terms of the Fuoss-Onsager conductance theory. The temperature dependence of the limiting molar conductance/viscosity product for hydrochloric acid in anhydrous methanol, ethanol and pentan-1-ol, respectively, is considered and discussed with respect to the influence of molecular solvent structure on the proton transfer mechanism.

In earlier papers ^{1, 2} on the molar conductances at infinite dilution of hydrogen chloride in anhydrous and wet aliphatic alcohols at 25°C, we pointed out that in these amphiprotic media the proton limiting conductance/viscosity product is strictly dependent on the size and geometry of the hydrocarbon side chain of the alcohol molecule, at least for side chains containing no more than five carbon atoms.

To rationalize this experimental evidence we advanced the hypothesis that anomalous proton mobility is the result of two contributions whose magnitude depends on the degree of hydrogen bonding in the solvent. In the present investigation we have examined the conductance behaviour of hydrogen chloride in some monofunctional aliphatic alcohols as a function of temperature in an effort to obtain, through a modification of the short range structure of the solvent media, further information on proton transfer.

EXPERIMENTAL

The electrical apparatus, conductance equipment and experimental procedures employed in the present work were described in our previous paper.³

Cell constants were determined at $25 \pm 0.005^\circ\text{C}$ by using the conductance parameters of the molar conductivity of aqueous potassium chloride solutions determined by Lind, Zwolenik and Fuoss.⁴ Oil thermostats at 15 and 35°C were also regulated to within $\pm 0.005^\circ\text{C}$ and each temperature was established by a carefully calibrated Beckmann differential thermometer.

Successive additions of stock solution of hydrogen chloride to the solvent in the conductivity cell were made gravimetrically and vacuum corrected. Molar concentrations were determined using solvent-mixture densities for the water+methanol and water+ethanol systems. For the water+pentan-1-ol system the density of the pure alcohol was used. In the case of both methanol+water and ethanol+water mixtures all the solvent properties, *i.e.*, densities,^{5, 6} viscosities⁶⁻⁸ and dielectric constants^{9, 10} were taken from the literature.

Densities of pentan-1-ol at 15 and 35°C were determined in a 20 cm³ single-necked pycnometer while viscosities were measured in an Ubbelohde suspended-level viscometer which did not require kinetic-energy correction. Both types of instruments were calibrated with conductance water and the measurements were carried out in a water bath controlled to $\pm 0.01^\circ\text{C}$. Dielectric constants were measured at 1 MHz using a Boonton Electr. Corp.

capacitance bridge type 75D and a stainless steel cylindrical cell. During the measurements the temperature was controlled to $\pm 0.01^\circ\text{C}$ by keeping the cell in a closely fitting grounded copper jacket through which thermostated oil was pumped. The cell was calibrated with propan-1-ol,¹¹ methanol⁹ and water¹² of high purity at both temperatures. These data are given in table 1 along with the physical properties utilised for pure methanol and ethanol. The preparation of conductivity grade water and purification of alcohols were described previously.³ The vapour phase chromatograph of each purified solvent sample showed a single peak and its water content, as determined by the K. Fischer titration method, never exceeded 0.01 %.

TABLE 1.—PHYSICAL PROPERTIES OF METHANOL, ETHANOL AND PENTAN-1-OL AT DIFFERENT TEMPERATURES

solvent	$T/^\circ\text{C}$	dielectric constant	viscosity/P	density/g cm ⁻³
methanol	15	34.70 ^a	0.00634 ^b	0.7958 ^c
	25	32.66 ^a	0.005445 ^d	0.78658 ^d
	35	30.74 ^a	0.00474 ^d	0.7771 ^d
ethanol	15	25.77 ^e	0.01332 ^f	0.79363 ^c
	35	22.82 ^e	0.00914 ^f	0.77643 ^c
pentan-1-ol	15	16.20 ± 0.06	$0.04680 \pm 3 \times 10^{-5}$	$0.81804 \pm 2 \times 10^{-5}$
	35	14.20 ± 0.03	$0.02638 \pm 4 \times 10^{-5}$	$0.80397 \pm 4 \times 10^{-5}$

^a ref. (9); ^b ref. (7); ^c ref. (5); ^d ref. (6); ^e ref. (10); ^f ref. (8).

RESULTS AND DISCUSSION

The molar concentrations and corresponding molar conductances for the three systems analysed are assembled in table 2, where each group of data is tabulated in order of decreasing stoichiometric concentration of water in the solvent mixture.

As before, the data in table 2 were analysed in terms of the Fuoss–Onsager conductance theory in the form of eqn (1)¹³

$$\Lambda = \Lambda_\infty - S\sqrt{c\alpha} + E'c\alpha \ln \tau^2\alpha + Lc\alpha - K_A c\alpha\gamma_\pm^2 \Lambda \quad (1)$$

where each term has its usual meaning.

TABLE 2.—CONDUCTANCE DATA FOR HYDROGEN CHLORIDE IN SOME WATER + ALCOHOL MIXTURES AT 15, 25 AND 35°C

$10^2 n_{\text{H}_2\text{O}}$ /mol dm ⁻³	$10^4 c$ /mol dm ⁻³	Λ/cm^2 $\Omega^{-1} \text{mol}^{-1}$	$10^2 n_{\text{H}_2\text{O}}$ /mol dm ⁻³	$10^4 c$ /mol dm ⁻³	Λ/cm^2 $\Omega^{-1} \text{mol}^{-1}$
water + methanol					
15°C					
944	8.010	85.32	699	10.82	82.02
	10.41	84.88		14.84	81.38
	15.47	84.14		20.24	80.65
	18.92	83.68		23.80	80.23
	21.46	83.36		30.96	79.46
	25.71	82.87			
456	4.981	82.72	364	4.706	83.53
	8.165	81.85		9.169	82.29
	15.11	80.47		12.10	81.65
	17.96	80.00		16.99	80.74
	20.26	79.64		20.45	80.17
	23.10	79.24		25.77	79.43
				30.94	78.76

TABLE 2.—*contd.*

$10^2 n_{\text{H}_2\text{O}}$ /mol dm ⁻³	$10^4 c$ /mol dm ⁻³	A/cm^2 $\Omega^{-1} \text{ mol}^{-1}$	$10^2 n_{\text{H}_2\text{O}}$ /mol dm ⁻³	$10^4 c$ /mol dm ⁻³	A/cm^2 $\Omega^{-1} \text{ mol}^{-1}$
270	9.738	83.86	185	4.766	88.38
	14.03	82.92		9.897	86.72
	17.37	82.28		12.91	85.95
	20.95	81.66		16.73	85.11
	26.33	80.66		20.66	84.35
				23.36	83.88
				28.52	83.08
92.5	4.727	95.52	44.3	6.462	106.11
	7.456	94.41		10.12	104.69
	11.33	93.18		13.29	103.67
	14.69	92.31		18.17	102.32
	18.30	91.48		20.19	101.83
	20.82	90.94			
	23.67	90.38			
37.6	9.190	108.68	26.6	2.986	118.29
	11.64	107.87		5.626	116.78
	13.78	107.23		9.128	115.23
	15.23	106.80		11.72	114.29
	17.85	106.15		14.58	113.34
				17.07	112.60
				19.42	111.98
18.7	3.583	126.53	9.55	4.549	140.33
	5.726	125.25		8.170	138.27
	8.091	124.09		11.00	136.96
	11.16	122.86		13.99	135.79
	14.61	121.64		15.96	135.05
	18.09	120.58		17.76	134.44
	21.96	119.53		20.69	133.54
4.42	4.599	152.58	2.25	7.074	158.84
	7.920	150.51		9.826	157.28
	11.45	148.74		13.04	155.71
	14.37	147.46		16.43	154.26
	16.73	146.53		19.70	153.04
	18.90	145.75		23.69	151.66
	20.95	145.05			
1.37	3.016	164.72	0.44	8.680	164.45
	9.956	160.08		10.82	163.28
	12.50	158.74		13.43	162.05
	14.38	157.88		16.12	160.81
	16.97	156.78		17.60	160.19
	21.35	155.14			
25°C					
824	11.85	102.79	514	20.76	97.46
	19.86	101.29		31.16	95.88
	42.61	98.21		36.51	95.20
	47.30	97.62		46.85	93.94
	53.81	96.97		53.58	93.28
254	17.36	98.38	167	13.41	102.71
	25.07	96.81		22.57	100.45
	33.29	95.42		32.95	98.49
	41.29	94.29		40.40	97.31
	47.42	93.49		48.04	96.27
				57.09	95.20

TABLE 2.—*contd.*

$10^2 n_{\text{H}_2\text{O}}$ /mol dm ⁻³	$10^4 c$ /mol dm ⁻³	A/cm^2 $\Omega^{-1} \text{ mol}^{-1}$	$10^2 n_{\text{H}_2\text{O}}$ /mol dm ⁻³	$10^4 c$ /mol dm ⁻³	A/cm^2 $\Omega^{-1} \text{ mol}^{-1}$
86.2	6.665	113.32	43.6	23.54	119.38
	15.28	110.15		30.60	117.74
	21.96	108.30		38.12	116.22
	59.96	102.04		44.87	115.04
	70.36	100.83		49.72	114.26
	80.94	99.75			
21.2	5.511	141.99	9.87	14.90	154.34
	10.80	139.30		24.29	150.91
	15.93	137.22		29.08	149.45
	21.64	135.33		39.90	146.74
	25.52	134.23		48.51	144.93
6.33	13.83	163.15	5.11	19.08	164.35
	20.48	160.52		22.76	162.95
	24.75	159.05		30.00	160.64
	28.38	157.95		34.84	159.23
	35.20	156.09		43.53	157.11
4.06	6.369	173.39	2.58	6.378	178.80
	11.91	170.05		14.14	174.25
	21.95	167.60		20.86	171.27
	25.99	164.15		27.06	169.01
	31.42	162.34		32.23	167.31
1.66	7.314	181.78	1.53	12.62	178.90
	16.17	176.69		18.09	176.33
	23.77	173.54		23.99	173.39
	29.50	171.50		29.62	172.01
	35.97	169.51		34.51	170.53
1.05	44.72	167.13	0.52		
	15.43	179.72		18.01	180.58
	22.51	176.68		24.33	177.97
	26.78	175.06		34.83	174.50
	34.76	172.58		41.67	172.51
	40.36	171.02		54.52	169.31
	57.54	166.95			
35°C					
925	7.398	125.28	682	6.504	119.96
	9.656	124.61		8.798	119.16
	12.59	123.86		11.55	118.31
	17.25	122.79		14.42	117.56
	21.13	121.99		17.56	116.81
	25.32	121.26		26.76	115.02
355	6.252	117.61	447	7.739	116.55
	8.578	116.61		12.53	115.06
	14.45	114.59		15.97	114.16
	16.97	113.85		19.88	113.22
	19.13	113.28		22.84	112.57
265	5.868	118.02	175	7.309	120.84
	8.304	117.05		10.71	119.39
	12.53	115.68		14.33	118.13
	16.29	114.57		17.27	117.20
	18.50	113.96		19.93	116.46

TABLE 2.—*contd.*

$10^2 n_{H_2O}$ /mol dm ⁻³	$10^4 c$ /mol dm ⁻³	A/cm^2 $\Omega^{-1} \text{ mol}^{-1}$	$10^2 n_{H_2O}$ /mol dm ⁻³	$10^4 c$ /mol dm ⁻³	A/cm^2 $\Omega^{-1} \text{ mol}^{-1}$
86.9	5.103	132.08	43.3	5.650	145.47
	11.35	128.80		9.599	143.12
	14.77	127.41		11.92	141.97
	17.51	126.40		14.67	140.73
	19.80	125.67		21.70	138.08
36.2	4.271	152.01	25.8	5.690	158.49
	7.192	150.01		8.670	156.46
	10.90	147.87		17.59	151.95
	14.69	146.10		21.12	150.59
	18.18	144.65		24.06	149.57
17.4	21.72	143.36	8.20		
	5.586	168.66		1.968	189.32
	7.532	167.16		4.586	186.09
	11.90	164.41		7.066	183.74
	15.47	162.58		9.337	181.99
4.14	17.40	161.61	3.49	13.84	179.04
	19.32	160.79			
	3.291	197.97		2.896	200.39
	7.769	193.67		4.435	198.62
	10.98	191.34		9.557	194.26
2.89	13.08	189.98	1.51	11.60	192.85
	16.00	188.32		13.84	191.40
	17.87	187.24		15.85	190.28
	19.52	186.40			
	6.980	198.26		3.449	207.30
1.21	9.373	196.35	0.82	6.573	204.01
	12.53	194.11		12.79	199.18
	17.64	191.09		16.83	196.77
	20.37	189.71		20.94	194.62
	5.818	204.93		2.800	209.94
0.52	9.612	201.76		5.704	206.54
	13.02	199.31		8.321	204.11
	17.20	196.74		11.95	201.33
	19.38	195.52		15.52	199.03
	22.27	194.04		18.37	197.30
				21.04	195.93
	6.517	207.64			
	9.605	204.99			
	11.02	203.91			
	14.33	201.72			
111	16.53	200.34			
			water+ethanol 15°C		
	5.022	34.48	88.8	9.174	33.54
	8.984	33.54		11.88	33.02
	12.46	32.92		17.08	32.23
	18.86	31.99		23.79	31.39
	23.97	31.40		33.72	30.41
	30.16	30.77		39.64	29.92
	36.51	30.21			

TABLE 2.—*contd.*

$10^2 n_{\text{H}_2\text{O}}$ /mol dm ⁻³	$10^4 c$ /mol dm ⁻³	A/cm^2 $\Omega^{-1} \text{mol}^{-1}$	$10^2 n_{\text{H}_2\text{O}}$ /mol dm ⁻³	$10^4 c$ /mol dm ⁻³	A/cm^2 $\Omega^{-1} \text{mol}^{-1}$
79.4	10.80	33.20	77.2	5.111	34.46
	17.86	32.14		12.37	33.00
	21.53	31.66		19.05	32.03
	24.70	31.31		23.97 _i	31.43
	27.87	30.97		31.57	30.66
	31.51	30.62		35.20	30.33
				39.64	29.96
66.4	10.60	33.46	53.1	5.940	35.08
	17.77	32.33		10.63	34.04
	22.96	31.68		15.21	33.24
	27.43	31.20		20.61	32.46
	31.83	30.76		27.12	31.68
	38.25	30.20		32.60	31.12
				37.58	30.67
44.7	11.66	34.21	34.0	5.147	36.57
	18.11	33.16		10.78	35.24
	24.63	32.31		15.94	34.30
	31.25	31.59		20.17	33.65
	38.86	30.88		24.64	33.07
	46.31	30.27		27.68	32.70
				35.99	31.84
22.1	5.045	38.65	8.82	7.506	44.35
	14.68	36.42		12.23	43.12
	19.59	35.60		18.18	41.89
	25.31	34.80		23.49	40.97
	33.31	33.87		27.89	40.31
	36.99	33.51		33.61	39.56
5.69	5.122	48.86	4.67	12.63	48.47
	9.118	47.61		17.08	47.37
	13.14	46.56		22.76	46.18
	18.20	45.42		28.74	45.17
	21.19	44.84		35.13	44.22
	26.13	43.97		39.94	43.58
	30.91	43.25			
3.39	10.58	51.86	2.56	5.044	56.40
	13.87	50.90		17.36	52.22
	21.54	49.08		25.65	50.35
	27.46	47.95		30.91	49.37
	33.05	47.04		35.84	48.57
	37.96	46.33		42.33	47.64
1.41	11.67	57.57	0.35	4.705	65.45
	16.03	56.19		9.493	62.87
	20.00	55.10		12.62	61.56
	25.94	53.71		17.31	59.91
	30.53	52.78		26.18	57.47
	38.24	51.42		31.09	56.34

TABLE 2.—*contd.*

$10^2 n_{H_2O}$ /mol dm ⁻³	$10^4 c$ /mol dm ⁻³	A/cm^2 $\Omega^{-1} \text{ mol}^{-1}$	$10^2 n_{H_2O}$ /mol dm ⁻³	$10^4 c$ /mol dm ⁻³	A/cm^2 $\Omega^{-1} \text{ mol}^{-1}$
35°C					
104	5.487	52.79	95.2	5.796	52.47
	10.55	50.86		10.18	50.90
	14.36	49.75		15.34	49.43
	18.99	48.61		21.06	48.11
	23.54	47.68		26.98	46.96
	28.49	46.75		31.56	46.20
	34.56	45.79		36.07	45.51
86.9	5.788	52.50	85.5	9.016	51.62
	10.21	50.81		13.24	50.30
	16.59	49.05		19.13	48.82
	20.83	48.08		24.68	47.66
	27.78	46.75		29.65	46.78
	32.33	45.99		34.88	45.94
	38.00	45.17			
75.9	5.060	52.97	63.7	4.638	53.83
	13.45	50.03		15.26	50.12
	17.41	48.99		21.68	48.56
	22.09	47.93		26.52	47.59
	26.42	47.08		31.07	46.76
	35.33	45.62		35.89	45.99
52.8	7.676	52.71	43.7	10.06	52.57
	13.18	50.78		14.90	51.01
	22.47	48.41		20.38	49.58
	26.57	47.56		25.74	48.39
	33.60	46.33		32.11	47.22
				37.93	46.28
31.5	5.770	56.24	21.6	10.35	56.90
	11.30	53.85		14.70	55.25
	15.67	52.42		19.10	53.89
	21.49	50.85		24.58	52.47
	27.02	49.64		29.59	51.37
	35.13	48.12		36.16	50.14
8.19	4.764	69.97	4.01	9.853	74.41
	16.56	63.69		15.17	71.59
	20.47	62.27		20.90	69.19
	24.75	60.96		31.01	65.94
	29.58	59.67		39.64	63.80
	36.64	58.06			
2.02	4.667	84.72	1.21	7.157	85.94
	8.234	81.62		11.49	82.62
	12.65	78.66		15.85	79.96
	23.17	73.61		21.59	77.15
	28.76	71.57		27.63	74.73
	34.67	69.77		33.55	72.74
0.34	8.364	88.89			
	15.31	83.70			
	18.65	81.74			
	21.97	80.09			
	27.09	77.85			
	31.61	76.15			

TABLE 2.—*contd.*

$10^2 n_{\text{H}_2\text{O}}$ /mol dm ⁻³	$10^4 c$ /mol dm ⁻³	A/cm^2 $\Omega^{-1} \text{mol}^{-1}$	$10^2 n_{\text{H}_2\text{O}}$ /mol dm ⁻³	$10^4 c$ /mol dm ⁻³	A/cm^2 $\Omega^{-1} \text{mol}^{-1}$
water + pentan-1-ol 15°C					
46.0	2.683	7.347	39.4	2.906	7.151
	8.742	5.852		8.286	5.849
	11.60	5.473		12.13	5.348
	17.04	4.971		15.46	5.033
	21.16	4.693		19.70	4.713
	28.40	4.330		26.85	4.343
	33.14	4.146			
32.2	6.426	6.078	29.5	3.059	6.979
	13.80	5.069		5.440	6.291
	17.49	4.769		8.576	5.707
	22.34	4.465		12.98	5.167
	27.92	4.196		17.37	4.796
	34.03	3.968		21.02	4.558
				27.24	4.243
23.6	4.158	6.612	18.3	2.982	6.926
	7.669	5.845		6.461	5.980
	12.26	5.237		9.421	5.486
	15.32	4.951		15.13	4.871
	18.75	4.697		19.72	4.538
	25.45	4.321		24.28	4.283
13.1	2.511	7.242	9.08	2.661	7.309
	4.764	6.474		7.186	6.022
	6.922	5.982		10.84	5.454
	10.70	5.398		15.60	4.961
	13.49	5.089		21.30	4.556
	16.65	4.814		26.34	4.290
	24.42	4.332		32.36	4.045
5.40	4.596	7.078	3.41	3.180	8.130
	9.078	6.088		6.758	6.980
	13.08	5.548		11.24	6.162
	18.82	5.030		17.02	5.516
	22.99	4.756		21.23	5.185
	32.25	4.318		26.53	4.866
2.09	4.708	8.185	1.50	4.472	8.832
	9.975	6.862		7.992	7.726
	14.76	6.185		12.19	6.934
	20.40	5.649		14.94	6.560
	25.36	5.308		22.84	5.812
	30.47	5.033		28.25	5.462
0.99	6.304	8.945	0.36	5.002	10.96
	9.771	8.007		11.18	8.843
	12.80	7.434		16.44	7.882
	16.14	6.953		23.56	7.050
	23.19	6.241		27.69	6.700
	29.86	5.774		33.08	6.332

TABLE 2.—*contd.*

$10^2 n_{H_2O}$ /mol dm ⁻³	$10^4 c$ /mol dm ⁻³	A/cm^2 Ω^{-1} mol ⁻¹	$10^2 n_{H_2O}$ /mol dm ⁻³	$10^4 c$ /mol dm ⁻³	A/cm^2 Ω^{-1} mol ⁻¹
35°C					
42.5	9.000	8.595	35.8	5.793	9.513
	16.15	7.245		12.77	7.616
	21.43	6.641		15.88	7.129
	28.18	6.092		21.06	6.530
	34.69	5.704		26.05	6.105
29.4			26.3	31.70	5.734
	4.670	9.940		7.069	8.995
	9.893	8.108		12.67	7.608
	13.16	7.450		16.73	6.984
	23.60	6.216		22.73	6.344
22.2	29.72	5.774	14.8	26.20	6.062
	3.907	10.43		2.719	11.47
	8.427	8.500		7.266	8.885
	13.02	7.474		12.66	7.554
	19.33	6.608		17.43	6.837
10.9	24.50	6.129	9.10	22.97	6.260
	27.85	5.881		28.80	5.817
	2.689	11.77		2.549	12.11
	6.490	9.388		8.468	8.802
	10.48	8.156		12.82	7.759
6.20	14.11	7.440	4.06	15.88	7.250
	18.00	6.887		18.90	6.854
	22.66	6.395		23.22	6.411
	27.93	5.974			
	3.447	12.36		6.319	10.61
2.63	10.48	9.102	1.96	10.94	8.969
	14.10	8.296		14.92	8.114
	18.71	7.574		18.25	7.596
	23.02	7.076		23.43	6.993
				29.23	6.497
1.43	2.377	14.98	0.85	3.538	14.02
	5.667	11.76		12.17	9.593
	9.300	10.08		16.94	8.588
	15.61	8.511		23.51	7.683
	18.14	8.090		28.32	7.215
0.40	22.44	7.528		32.53	6.886
	9.528	11.03		2.893	17.29
	13.20	9.895		5.959	13.91
	16.16	9.244		9.080	12.10
	18.94	8.754		12.33	10.91
	24.63	8.000		15.90	9.981
	31.67	7.339		18.95	9.384
				24.06	8.624
	5.746	15.16			
	8.661	13.20			
	11.57	11.94			
	15.88	10.67			
	19.83	9.846			
	24.57	9.108			

A least square computer program was used to obtain the values of Λ_{∞} , K_A , a and σ_A , the standard deviation of fit, for each set of data. The best-fit parameters are reported in tables 3, 4 and 5, where each group of data is tabulated in order of decreasing stoichiometric concentration of water in the solvent mixture. In table 6 the results of the HCl + water + pentan-1-ol system at 35°C refer to a computer analysis performed by the Shedlovsky equation ¹⁴ owing to the considerable association shown by the hydrogen chloride in these solvent media. The method of calculation has already been described.²

Inspection of the above tables shows that the variation of Λ_{∞} as the water content increases resembles that observed in previous investigations on similar solvent systems, *i.e.* when small amounts of water are added to the anhydrous alcohol, the limiting molar conductance decreases rapidly, passes through a minimum, and then

TABLE 3.—CONDUCTANCE PARAMETERS FOR HYDROGEN CHLORIDE IN SOME WATER + METHANOL MIXTURES AT 15, 25 AND 35°C

$10^2 n_{H_2O}$ /mol dm ⁻³	$\Lambda_{\infty}/\text{cm}^2$ $\Omega^{-1} \text{mol}^{-1}$	$a/10^{-10} \text{ m}$	σ_A/cm^2 $\Omega^{-1} \text{mol}^{-1}$
water + methanol			
15°C			
0.44	173.86 ± 0.04	2.43 ± 0.05	0.02
1.37	170.00 ± 0.03	2.41 ± 0.04	0.03
2.25	166.98 ± 0.02	2.54 ± 0.02	0.02
4.42	158.84 ± 0.01	2.64 ± 0.01	0.009
9.55	146.16 ± 0.01	2.98 ± 0.02	0.01
18.7	131.29 ± 0.01	3.38 ± 0.01	0.009
26.6	122.45 ± 0.02	3.53 ± 0.05	0.03
37.6	115.55 ± 0.03	4.00 ± 0.07	0.01
44.3	111.85 ± 0.01	3.44 ± 0.03	0.009
92.5	99.92 ± 0.01	3.81 ± 0.03	0.02
185	92.33 ± 0.01	3.71 ± 0.03	0.01
270	88.94 ± 0.02	3.81 ± 0.05	0.01
364	86.84 ± 0.02	3.72 ± 0.05	0.02
456	85.87 ± 0.01	3.64 ± 0.04	0.01
699	86.02 ± 0.02	3.69 ± 0.07	0.01
944	88.48 ± 0.03	3.1 ± 0.1	0.02
25°C			
0.52	196.40 ± 0.04	2.89 ± 0.02	0.03
1.05	194.10 ± 0.04	2.99 ± 0.02	0.03
1.53	191.80 ± 0.06	2.97 ± 0.04	0.04
1.66	191.49 ± 0.04	2.85 ± 0.02	0.05
2.58	187.78 ± 0.02	2.89 ± 0.01	0.02
4.06	182.21 ± 0.03	2.86 ± 0.02	0.03
5.11	179.36 ± 0.04	3.12 ± 0.02	0.03
6.33	175.64 ± 0.02	3.32 ± 0.01	0.01
9.87	166.88 ± 0.04	3.21 ± 0.02	0.03
21.2	149.01 ± 0.05	3.52 ± 0.06	0.05
43.6	132.43 ± 0.02	3.50 ± 0.02	0.01
86.2	119.81 ± 0.04	3.50 ± 0.02	0.06
167	110.88 ± 0.01	3.52 ± 0.01	0.01
254	106.87 ± 0.02	3.52 ± 0.02	0.01
514	105.33 ± 0.06	3.37 ± 0.07	0.04
824	108.32 ± 0.07	3.03 ± 0.08	0.06

TABLE 3.—*contd.*

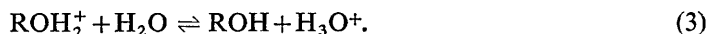
$10^2 n_{\text{H}_2\text{O}}$ /mol dm ⁻³	$\Lambda_\infty/\text{cm}^2$ $\Omega^{-1} \text{mol}^{-1}$	$a/10^{-10} \text{ m}$	$\sigma\Lambda/\text{cm}^2$ $\Omega^{-1} \text{mol}^{-1}$
35°C			
0.52	218.82±0.05	2.34±0.04	0.04
0.82	217.01±0.05	2.17±0.04	0.06
1.21	215.41±0.03	2.33±0.02	0.02
1.51	215.13±0.07	2.39±0.05	0.07
2.89	209.50±0.04	2.43±0.03	0.03
3.49	207.34±0.02	2.56±0.02	0.02
4.14	205.36±0.02	2.51±0.02	0.02
8.20	194.79±0.05	2.02±0.07	0.05
17.4	177.44±0.02	2.77±0.03	0.02
25.8	166.88±0.04	3.07±0.04	0.04
36.2	159.01±0.04	3.31±0.06	0.04
43.3	153.29±0.03	3.30±0.04	0.03
86.9	138.83±0.02	3.40±0.04	0.02
175	127.94±0.02	3.80±0.04	0.01
265	123.80±0.08	4.6 ±0.2	0.07
447	122.52±0.06	3.9 ±0.01	0.04
572	123.43±0.01	3.09±0.02	0.006
682	124.91±0.01	3.32±0.02	0.007
925	130.14±0.02	3.20±0.06	0.02

increases again with increasing water concentration. Moreover, at constant water content, Λ_∞ increases with temperature.

By free-hand extrapolation of the curves Λ_∞ plotted against the weight fraction of water in the solvent mixture, a rough estimate of the limiting molar conductance values in anhydrous alcohols was obtained. Following the procedure reported in a previous paper,¹ the evaluation of more accurate values of Λ_∞ was made by successive approximations using the Thomas and Marum equation¹⁵

$$n_{\text{H}_2\text{O}} = -N/K_r + \Delta\lambda_\infty^+ n_{\text{H}_2\text{O}} / (\Lambda_{\text{ROH}}^\infty - \Lambda_n^\infty) \quad (2)$$

where $n_{\text{H}_2\text{O}}$ (mol dm⁻³) is the stoichiometric concentration of water in the solvent mixture, N the molar concentration of pure alcohol and K_r the equilibrium constant of the proton exchange reaction



$\Delta\lambda_\infty^+$ represents the excess of mobility, that is, the difference between the $\lambda_{\text{ROH}_2^+}^\infty$ value in pure alcohol and the $\lambda_{\text{H}_3\text{O}^+}^\infty$ value at the minimum, $\Lambda_{\text{ROH}}^\infty$ is the limiting conductance in the pure alcohol and Λ_n^∞ that in a water+alcohol mixture containing n moles per dm³ of water.

The $\Lambda_{\text{ROH}}^\infty$ and K_r values derived from this analysis are assembled in table 6 together with the limiting conductance/viscosity products and the standard thermodynamic functions ΔG_T° , ΔH_{298}° and ΔS_{298}° for reaction (3). These quantities were derived from K_r values and their temperature dependence according to the relation $R \ln K_r = \Delta S^\circ - \Delta H^\circ/T$. All the errors quoted in table 6 are [standard deviations.

To our knowledge only one of the results presented here can be compared with literature data, *i.e.* the limiting molar conductance of HCl in pure methanol at 25°C. The agreement between our value and that obtained by Shedlovsky and Kay¹⁶ of 198.5 is excellent.

By examining the results in table 6 the following features emerge: (a) the temperature dependence of $\Lambda_{\text{ROH}}^{\infty}\eta$ in methanol and ethanol is in the opposite direction with respect to that in pentan-1-ol; (b) within experimental accuracy the values of the standard thermodynamic functions decrease as the size of the solvent molecule increases.

TABLE 4.—CONDUCTANCE PARAMETERS FOR HYDROGEN CHLORIDE IN SOME WATER+ETHANOL MIXTURES AT 15 AND 35°C

$10^2 n_{\text{H}_2\text{O}}$ /mol dm ⁻³	Λ_{∞} /cm ² Ω ⁻¹ mol ⁻¹	$a/10^{-10}$ m	K_A / mol ⁻¹ dm ⁻³	σ_A /cm ² Ω ⁻¹ mol ⁻¹
water+ethanol 15°C				
0.35	70.68±0.01	3.47±0.02	47.3±0.4	0.003
1.41	65.11±0.02	3.12±0.04	25.8±0.9	0.004
2.56	60.84±0.02	3.21±0.06	22 ±1	0.01
3.39	58.17±0.01	3.34±0.03	20.1±0.7	0.003
4.67	55.04±0.08	3.4 ±0.1	18 ±3	0.01
5.64	52.61±0.03	2.85±0.04	—	0.03
8.82	48.62±0.01	2.97±0.01	—	0.01
22.1	41.76±0.01	3.22±0.01	—	0.008
34.0	39.59±0.01	3.29±0.02	—	0.01
44.7	38.65±0.01	3.35±0.01	—	0.008
53.1	38.19±0.01	3.40±0.01	—	0.006
66.4	37.51±0.01	3.55±0.02	—	0.01
77.2	37.27±0.02	3.59±0.04	—	0.03
79.4	37.22±0.02	3.59±0.04	—	0.01
88.8	37.23±0.01	3.48±0.01	—	0.008
111	37.14±0.01	3.48±0.02	—	0.01
35°C				
0.34	102.43±0.07	3.80±0.09	107 ±2	0.01
1.21	96.99±0.04	3.52±0.05	81 ±1	0.009
2.02	98.81±0.02	3.44±0.04	70.8±0.8	0.008
4.01	85.42±0.03	3.51±0.03	58.1±0.9	0.006
8.19	76.59±0.03	3.74±0.05	54 ±1	0.01
21.6	65.31±0.05	3.75±0.08	37 ±2	0.009
31.5	61.89±0.02	3.50±0.05	22 ±1	0.008
43.7	59.70±0.06	3.4 ±0.1	13 ±3	0.01
52.8	58.77±0.02	3.36±0.04	11.4±0.9	0.005
63.7	58.28±0.01	3.10±0.01	—	0.01
75.9	57.54±0.01	3.16±0.01	—	0.01
85.5	57.73±0.01	3.17±0.01	—	0.01
86.9	57.31±0.02	3.20±0.02	—	0.02
95.2	57.31±0.01	3.21±0.01	—	0.01
104	57.43±0.02	3.10±0.03	—	0.03

Let us consider first the effect of temperature (*i.e.* of a modification of the solvent hydrogen-bonding equilibrium) on the anomalous proton mobility.

As outlined above it was shown in previous studies¹⁷ that if we take into account the viscous frictional force acting on the solvent molecules involved in the rotational process (rate-determining step of the proton-transfer mechanism)^{18, 19} the expected direct proportionality between $\lambda_{\text{H}^+}^{\infty}\eta$ and ω , where ω is the angular velocity of a rotating solvent molecule, does not occur. Using this approach the structural effects of the

TABLE 5.—CONDUCTANCE PARAMETERS FOR HYDROGEN CHLORIDE IN SOME WATER+PENTAN-1-OL MIXTURES AT 15 AND 35°C

$10^2 n_{H_2O}$ /mol dm ⁻³	Λ_{∞} /cm ² Ω ⁻¹ mol ⁻¹	K_A / mol ⁻¹ dm ⁻³	$a/10^{-10}$ m	σ_A /cm ² Ω ⁻¹ mol ⁻¹
water+pentan-1-ol				
15°C				
0.36	17.75±0.03	2132±13	3.95±0.04	0.005
0.99	14.48±0.04	1618±18	3.78±0.05	0.004
1.50	13.04±0.05	1508±26	4.2 ±0.1	0.008
2.09	12.15±0.02	1447±9	4.32±0.04	0.003
3.41	11.02±0.01	1296±10	4.23±0.05	0.003
5.40	10.19±0.01	1204±8	4.22±0.03	0.002
9.08	9.55±0.01	1190±9	4.31±0.05	0.004
13.1	9.33±0.01	1136±6	4.34±0.04	0.002
18.3	9.13±0.02	1097±13	4.38±0.08	0.004
23.6	9.10±0.02	982±17	4.29±0.09	0.005
29.5	9.13±0.02	1002±15	4.31±0.08	0.006
32.2	9.16±0.05	1016±31	4.2 ±0.1	0.008
39.4	9.29±0.03	1014±22	4.4 ±0.1	0.009
46.0	9.44±0.03	1026±22	4.4 ±0.1	0.01
35°C				
0.40	36.77±0.05	7823±28	4.71	0.005
0.85	32.20±0.05	6646±29	4.66	0.009
1.43	28.93±0.04	6212±21	2.49	0.002
1.96	26.22±0.08	5572±43	2.77	0.008
2.63	24.81±0.02	5256±10	3.44	0.002
4.06	22.06±0.04	4527±20	3.40	0.004
6.20	20.09±0.02	3325±12	6.74	0.004
9.10	18.73±0.01	3636±8	4.45	0.002
10.9	18.30±0.02	3517±10	4.29	0.004
14.8	17.72±0.05	3391±27	3.91	0.010
22.2	17.21±0.02	3094±8	4.65	0.003
26.3	17.04±0.03	2909±15	5.05	0.004
29.4	16.93±0.01	2943±3	4.62	0.001
35.8	17.03±0.02	2881±11	4.72	0.003
42.5	17.15±0.02	2781±11	4.49	0.002

TABLE 6.—LIMITING MOLAR CONDUCTANCES OF HCl AND DERIVED PARAMETERS IN METHANOL, ETHANOL AND PENTAN-1-OL AT 15, 25 AND 35°C

solvent	$T/^{\circ}\text{C}$	$\Lambda_{\text{HCl}}^{\infty}$ /cm ² Ω ⁻¹ mol ⁻¹	$\Lambda_{\text{HCl}}^{\infty}\eta$ /P cm ² Ω ⁻¹ mol ⁻¹	K_r	ΔG_r° /K J mol ⁻¹	ΔH_{298}° /K J mol ⁻¹	ΔS_{298}° /J mol ⁻¹ deg ⁻¹
methanol	15	175.85±0.08	1.115	124±3	11.55±0.05		
	25	198.84±0.06	1.083	121±1	11.89±0.02	-1.2±0.6	36±2
	35	221.1 ±0.2	1.048	122±6	12.3 ±0.1		
ethanol	15	72.96±0.09	0.972	287±9	13.56±0.08		
	25	89.16±0.09 ^a	0.967	285±7	14.01±0.06	-3.8±0.9	34±3
	35	105.08±0.02	0.960	266±1	14.31±0.01		
pentan-1-ol	15	23.0±0.2	1.076	1455±43	17.45±0.07		
	25	31.9±0.2 ^b	1.112	911±18	16.89±0.04	-26 ±2	-32±7
	35	43.4±0.2	1.145	710±18	16.82±0.07		

^a ref. (2); ^b ref. (1).

solvent were pointed out through the correlation found between the proton limiting conductance/viscosity products and the monomer concentration of the alcohols.

This suggested the idea that the excess proton mobility can be related to the molecular nature and to the degree of self-association of the solvent system. Actually the results derived from the present analysis give new support to this hypothesis owing to the additional fact that by increasing the temperature the expected direct proportionality is partially verified.

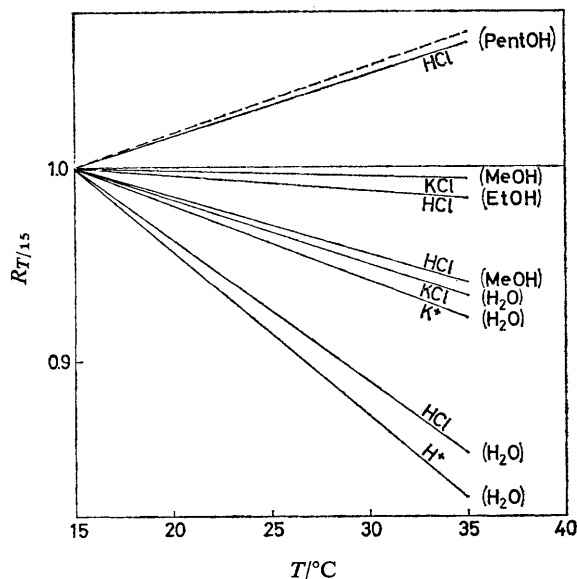


FIG. 1.—Variation of single-ion and solute limiting conductance/viscosity product ratios with temperature for hydrogen chloride and potassium chloride in some amphiprotic media.

Since limiting transference numbers and their temperature coefficients are not available for all the HCl-solvent systems considered here, the temperature-mobility dependence was analysed by employing the ratio of the limiting conductance/viscosity products, $R_{T/15} = (\Lambda_{\text{ROH}}^\infty)_T / (\Lambda_{\text{ROH}}^\infty)_{15}$. The effect of temperature on $R_{T/15}$, is shown in fig. 1 where for comparison purposes data for hydrogen chloride in water²⁰ and potassium chloride in water²¹ and in methanol²² are also reported. Despite the approximation of this approach, the correlation among $R_{T/15}$ values is still qualitatively correct as the reported trends of $(\lambda_{\text{H}^+}^\infty)_T / (\lambda_{\text{H}^+}^\infty)_{15}$ and $(\lambda_{\text{K}^+}^\infty)_T / (\lambda_{\text{K}^+}^\infty)_{15}$ in water suggest.

As can be seen from fig. 1 the $R_{T/15}$ values increase as the temperature increases only in the solvent which is expected to have the lowest degree of internal structure. However, in water, the solvent with the highest degree of intermolecular association, the conductance/viscosity product ratio decreases rapidly as the temperature increases showing an enhanced temperature dependence.

From this comparison we note that the magnitude of the temperature coefficient of $R_{T/15}$, whether positive or negative, accounts well for the structural contribution of the solvent media to the excess proton mobility.

According to our hypothesis, if we use the sign of the above quantity as a criterion for classifying the structural state favourable to proton transfer in this series of amphiprotic solvents we find: (i) in water and in methanol the contribution to the

anomalous proton mobility related to the increase in monomer concentration due to the structural melting is dominated by the parallel decrease in the contribution related to the proton binding to the large aggregates; (ii) in ethanol, a less structured solvent, the decrease due to the proton binding to the linear polymeric chains is well compensated by the increase of the contribution due to the monomer concentration and, of course, to the increased rate of the rotational process; (iii) as the number of carbon atoms increases, a systematic change in the steric environment of the hydroxyl group is expected which will produce a decrease in the extent of association and in the length of the open polymeric chains. Consequently, the magnitude of the contribution due to the structured form will decrease more and more and temperature changes will influence mainly the rotational process.

At this point we may assume that for an alcohol without any internal structure the change in $R_{T/15}$ with temperature should be related only to a decrease in the overall reorientation time of the solvent molecules. If this is the case one can use the relation $\omega = kT/8\pi ab^2\eta$ (the angular velocity of an anisometric particle of molecular axial ratio a/b) to evaluate the dependence of the limiting ratio on temperature in this hypothetical alcohol. This is shown by the dashed line reported in fig. 1.

Finally we deal with the thermodynamic data for the proton transfer reaction (3). It may be recalled that the total free energy change involved in the proton exchange process between alcohol and water molecules is negative at all three temperatures and for all three alcohols becomes more negative as the alkyl chain length of the alcohol molecule increases. This is in line with the results obtained in earlier studies.¹⁻³ Furthermore the ΔH_{298}° value of the process, as a result of a balance between breaking and forming of hydrogen bonds, appears to depend markedly on the molecular nature of the alcohol. The negative values of the enthalpy and the entropy change associated with the proton exchange in pentan-1-ol support the view that the increase in the degree of order in the system could be ascribed largely to the hydrogen bonding of alcohol molecules around the hydronium ion. Moreover the positive values of ΔS_{298}° and the small negative values of ΔH_{298}° found for this process in methanol and ethanol could be considered as a manifestation of a structural collapse which in turn involves an hydrogen bonding of greater strength.

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