PHYSICOCHEMICAL STUDY OF AQUEOUS-DIOXANE SOLUTIONS

VII. ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF HYDROGEN CHLORIDE IN AQUEOUS DIOXANE *

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Some physicochemical properties of hydrogen chloride solutions in dioxane were described previously [1]. The present study consisted of an investigation of the electrical conductivity of hydrogen chloride in dioxane-water mixtures with different dielectric constants. The values of the dielectric constants of a number of such mixtures of the same composition as those used by Kraus and Fuoss [2] were taken from that paper. Values for mixtures not given by Kraus and Fuoss were determined graphically. The hydrogen chloride solutions in these solvents were prepared as described previously [1]. The concentrations of the solutions obtained were determined by the usual titration with caustic soda solution in presence of phenolphpthalein. Systems with very high dioxane content, and also in anhydrous dioxane, were diluted with water before titration. The solutions of hydrogen chloride in dioxane-water solvent were used in the following dilutions: 10, 100, and 1000 liters/g-equiv. This choice of dilutions made it possible to plot the equivalent conductivity – dilution curves in the region which approached a horizontal line, which was the region of greatest interest in this study. The electrical conductivity of each system was studied at 20, 30, and 40°.

The results of Table 1 show that as the dioxane content of the medium increases and the dielectric constant DC decreases, λ of the HCl solutions decreases, and when the dielectric constant of the medium falls to 8 (10 times as small as DC for water), the equivalent conductivity of the hydrogen chloride solutions is only a few units (that is, its value decreases nearly 100 times). In this medium, the dielectric constant of which is 8, 0.1 N hydrogen chloride solution has lower equivalent conductivity than 0.1 N acetic acid in water. The conductivity of 0.01 N acetic acid in water is, however, about 5 times the conductivity of hydrogen chloride in aqueous dioxane, which has DC equal to 8. If we take hydrogen chloride solutions in anhydrous dioxane, when DC = 2.21, then, as was shown previously [1], the electrical conductivity of such a solution at dilutions of 1000-10 liters/g-equiv. is negligible. Only at dilutions of the order of 0.2 does the equivalent conductivity reach values of the order of tenths of a unit, and the value falls with dilution according to the so-called "anomalous" curve $\lambda = f(v)$. Thus, here also, as for the various solvents studied by Kablukov, the electrical conductivity of hydrogen chloride solutions entirely depends on the dielectric constant of the aqueous dioxane medium. It is also interesting to note that similar values for the electrical conductivities of hydrogen chloride solutions are obtained irrespective of whether the solvent is pure or a mixture. Kablukov found, for solutions in methyl alcohol, the dielectric constant of which is 35.4, an equivalent conductivity of 117 at a dilution of 91.16; for a dioxane-water mixture (DC = 37) at the same dilution we have an equivalent conductivity of about 123.

The variation of the electrical conductivity of HCl solutions in dioxane-water mixtures on temperature (in the temperature range studied) is approximately represented by a linear function with different slopes to the temperature axis: it is greatest for systems with DC = 37; in systems with DC = 12, the temperature coefficient remains positive but has a lower absolute value.

λ_0 of hydrogen chloride solutions

As Table 1 shows, the $\lambda = f(v)$ curves for dioxane-water solutions of hydrogen chloride lie lower with decreasing DC of the medium (Fig. 1).

As is known, by transformation of the function $\lambda = f(v)$ into the function $\lambda = f(\sqrt{c})$ values of λ_0 may be obtained by extrapolation, that is, values of equivalent conductivity corresponding to $\alpha = 1$ (the classical theory).

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But, as Fig. 2 shows, the $\lambda = f(\sqrt{c})$ curves also lie lower with decreasing DC of the medium, and so the values of λ_0 decrease also, and when DC $\longrightarrow$ 1, $\lambda_0 \longrightarrow$ 0.

TABLE 1

Electrical Conductivity of Hydrogen Chloride in Aqueous Dioxane Media

Percentage of water in the dioxane mixture	DC	Dilution, liters/g-equiv.	Temperature	$\chi \cdot 10^3$	λ
82	60	10	20°	16.3	163
	60	100	20	2.02	202
	60	1000	20	0.215	215
53	37	10	20	8.76	87.6
	37	10	30	8.95	89.5
		10	40	12.0	120.0
	37	100	20	1.275	127.5
		100	30	1.523	152.3
		100	40	1.752	175.2
	37	1000	20	0.132	132.0
		1000	30	0.163	163.2
		1000	40	0.204	204.0
20.2	12	10	20	0.867	8.67
		10	30	1.05	10.5
	12	100	20	0.0936	9.36
		100	30	0.1027	10.27
		100	40	0.1062	10.62
	12	1000	20	0.011	11.0
		1000	30	0.021	21
		1000	40	0.025	25
14	8	10	20	0.261	2.61
		10	25	0.288	2.88
		10	30	0.303	3.03
		10	40	0.316	3.16
	8	100	20	0.0376	3.76
		100	25	0.0432	4.32
		100	30	0.0473	4.73
		100	40	0.0521	5.21
	8	1000	18	0.00405	4.05
		1000	20	0.00427	4.27
		1000	25	0.00452	4.52

It is known from the work of Owen and Waters [4], who measured the electrical conductivity of hydrogen chloride solutions in dioxane-water mixtures at DC = 60, 79, 38, 48, 27 and 9.53 at 25° (these results are also quoted in the book by Harned and Owen [5], p. 326) * that the equivalent conductivity curves plotted against the square root of the concentration also form a group of curves which lie lower with decreasing DC of the medium. This tendency of $\lambda_0 \longrightarrow$ 0 as DC of the medium tends to unity, follows both from Kablukov's data [3] and from the data of other workers (Table 2).

These results can be explained only if we admit the possibility of the process $H^+ + Cl^- \longrightarrow HCl$ which goes increasingly toward the right as the dielectric constant of the medium decreases, even in very dilute solutions.

* Although Chapter 11 of this book is exclusively devoted to the properties of HCl solutions, it makes no mention whatever of the classic investigations by the Russian scientist I. A. Kablukov, who was the first to study the electrical conductivity of non-aqueous solutions of hydrogen chloride.

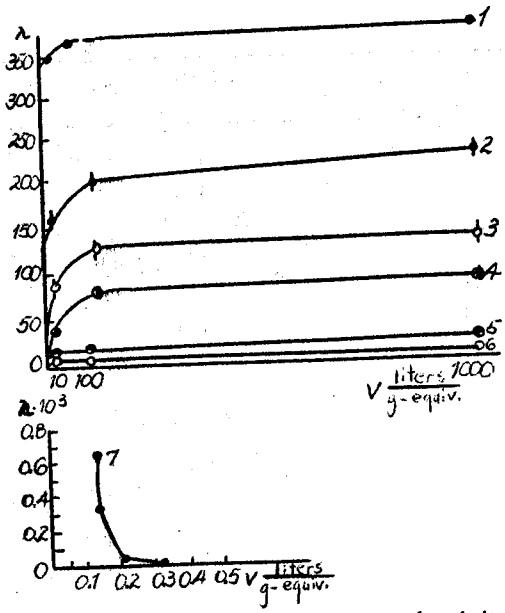

Fig. 1. Variation of the equivalent conductivity of HCl solutions in dioxane-water medium at 20°.
1) In water (DC = 80), 2) in dioxane-water medium (DC = 60), 3) in dioxane-water medium (DC = 37), 4) the same for DC = 20, 5, 6) the same, with increase of dioxane content and decrease of DC to 12 and 8 respectively, 7) the same for pure dioxane, with DC = 2.1.

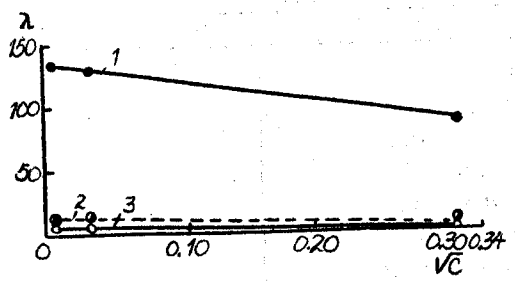

Fig. 2. $\lambda = f(\sqrt{c})$ for dioxane-water solutions of hydrogen chloride.
1) At DC = 37, 2) at DC = 12, 3) at DC = 8.

The values for λ_0 determined by ourselves from Fig. 2 for media with low dielectric constants, like the values obtained by Owen and Harned [5], are meaningless, as these values for the equivalent conductivity do not correspond to that state of the electrolyte ($\alpha = 1$) which is necessary for λ_0 and which the theory of strong electrolytes demands for all media. Semenchenko [6] was right in pointing out "that in solvents with low dielectric constants molecularization of ions, and even formation of complex ions and molecules is possible, which is completely ignored by the Debye-Onsager theory" (italics ours). This is also indicated by the $\lambda = f\ \frac{1}{D}$ curve for solutions of HCl in any medium (Fig. 3).

If the data obtained in the present study are used to plot the graph for the function

$$\log \frac{\lambda_u}{\lambda_p} = f\ \frac{1}{D} \quad . \tag{1}$$

then this will be a straight line which does not pass through the origin; therefore, for hydrogen chloride solutions, the equation for the relationship between λ and D may be given in the form

$$\lambda_p = \lambda_u \cdot 10^{-(20.5 \cdot \frac{1}{D} + 0.5)} \tag{2}$$

or

$$\lambda_p = 1500 \cdot 10^{-(20.5 \cdot \frac{1}{D} + 0.5)}$$

Quite obviously this equation loses its meaning when $\frac{1}{D} \approx 0$, since when $D \longrightarrow \infty$ and $\frac{1}{D} \longrightarrow 0$, not only ionic triads but simple undissociated molecules are absent, as is the mobility-decreasing action of the charge of one ion on another; therefore in such conditions the equations (2) become

$$\log \frac{\lambda_u}{\lambda_p} = k \cdot \frac{1}{D} \tag{3}$$

or

$$\lambda_p = \lambda_u \cdot e^{-k \cdot \frac{1}{D}} \quad . \tag{4}$$

TABLE 2

Decrease of the Values of λ_0 of HCl Solutions with Decrease of DC of the Medium

Medium		t°	λ_0	Sources
Substance	DC			
Water	80	25	≈ 425	[11]
Methyl alcohol	33	25	133.1	[6]
Dioxane + water	37	18	137	Our data
Ethyl alcohol	25	25	62 (66.5)	[7]
Propyl alcohol	20.1	25	46.6	[9]
Butyl alcohol	17.8	25	20	[9]
Dioxane + water	8	20	≈ 5	Our data
Benzene	2.2	18	≈ 0	[3]
Dioxane	2.1	18	≈ 0	Our data

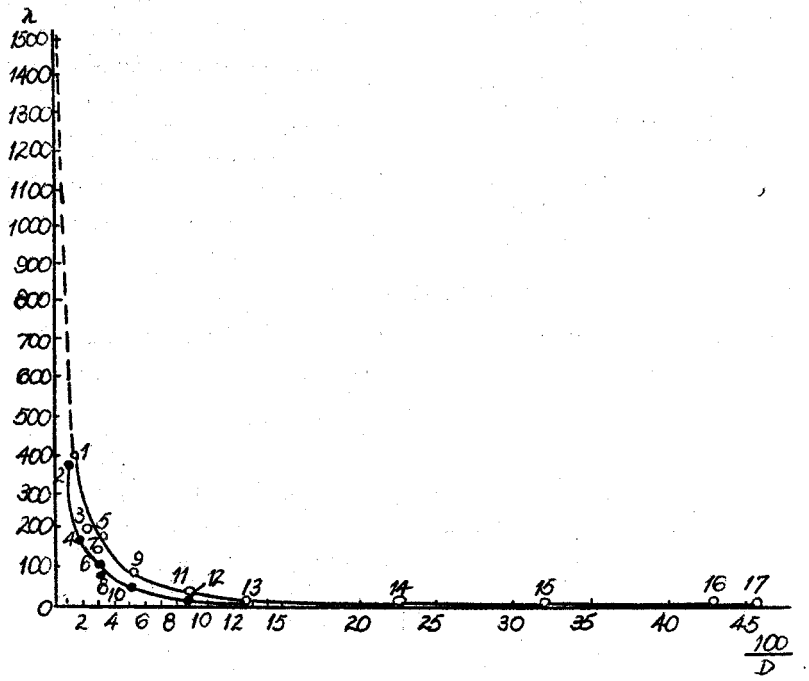

Fig. 3. $\lambda = f\left(\frac{1}{D}\right)$ for hydrogen chloride solutions.

1) Aqueous solution, v = 1000 liters/g-equiv., 2) aqueous solution, v = 10 liters/g-equiv., 3) dioxane-water solution for DC = 60 and v = 1000 liters/g-equiv., 4) dioxane-water solutions for DC = 60 and v = 10 liters/g-equiv., 5) in methyl alcohol for DC = 33 and v = 1000 liters/g-equiv. [9], 6) in methyl alcohol for DC = 33 and v = 10 liters/g-equiv., 7) dioxane-water solution for DC = 37 and v = 1000 l/g-equiv., 8) dioxane-water solution for DC = 37 and v = 10 liters/g-equiv., 9) dioxane-water solution for DC = 20 and v = 1000 liters/g-equiv., 10) dioxane-water solution for DC = 20 and v = 10 liters/g-equiv., 11, 12) dioxane-water solutions for DC = 12 and v = 1000 and 10 liters/g-equiv., 13) dioxane-water solution for DC = 8 and v = 1000 liters/g-equiv., 14) in ethyl ether for DC = 4.5 [3], 15) dioxane- water solution for DC = 2.12 [10], 16) in benzene for DC = 2.28 [3], 17) in dioxane for DC = 2.1.

The results of a check of the agreement between data calculated from Equations 1-3 and experimental data obtained both by ourselves and by other workers in various media are shown in Table 3.

TABLE 3

Comparison of Theoretically Calculated and Experimentally Determined Values of the Equivalent Conductivity of Hydrogen Chloride

Substance	Medium DC	$\lambda_{calc.}$	$\lambda_{exp.}$	Source	Relative deviation (%)
Water	80	264	370	Tech. Encyclopedia	40
Dioxane + water	37	137	132	Our data	− 3
	20	44	58		30
	12	9.8	11		12
	8	4.52	4.05		−10
Methyl alcohol	33	113	133	[12]	17
Ethyl alcohol	25	72	74		2
Propyl alcohol	20.1	44.2	37.26	[13]	−20
Butyl alcohol	17.8	33	18.53		−44
Ethyl ether	4.45	$1.7 \cdot 10^{-2}$	$0.58 \cdot 10^{-2}$	[8]	−60
Dioxane	2.1	$10^{-6.5}$	Very small for v = 1000	Our data	Same order of magnitude

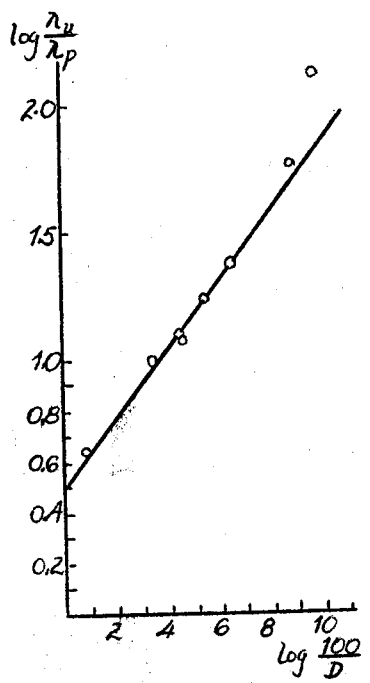

Fig. 4. Variation of $\log \frac{\lambda_u}{\lambda_p}$ with $\frac{1}{D}$ for hydrogen chloride solutions.

The data of Table 3 shows that the order of magnitude of the equivalent conductivity of hydrogen chloride solutions may be predicted with the aid of the mathematical relationships (1, 3).

In 11 instances when the theoretically calculated and experimentally found values of the electrical conductivity were compared, 2 showed a relative deviation from 3 to 2%; 4 gave relative deviations from −20 to 30%, 2 gave relative deviations from −40 to 40%, and only one gave a relative deviation of −60%; here, as was already pointed out for media with larger values of DC (80), the term B in equation (3) should increasingly lose its meaning, and therefore it is better to use equation (4) for such media.

The agreement, shown in Table 3, between the calculated and the experimental values of electrical conductivity confirms the validity of the view that the ions of a strong electrolyte form molecules when it is transferred to media with decreasing values of the dielectric constant, even in greatly diluted solutions.

As is known [6], the Kohlrausch-Onsager equation, even with such a conveniently investigated electrolyte as an aqueous solution of potassium chloride (which is nonvolatile, non-hygroscopic, stable to oxidation and reduction, etc.), gives results which deviate by 32.2 to 21.4% from the experimental results, and therefore the agreement of our experimental data with those calculated with the aid of equations (1, 2) should be regarded as satisfactory.

SUMMARY

1. The specific and equivalent conductivities of hydrogen chloride in aqueous dioxane solutions at DC between 80 and 2.1 have been measured.

2. It is shown that the equivalent conductivity of hydrogen chloride solutions decreases regularly with decreasing DC of the medium. The explanation for this is that when DC $\longrightarrow$ 1, $a \longrightarrow 0$ and $\lambda_0 \longrightarrow 0$.

3. The agreement between the values of the equivalent conductivity calculated with the aid of the proposed equation and the experimental values has been checked. Satisfactory agreement was found.

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