The Electrical Conductivity of the System $HClO_4$-H_2O

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An investigation of the systems formed by perchloric acid with CH_3COOH and its chlorine derivatives[1] has shown that $HClO_4$ interacts not with CCl_3COOH, but with $CHCl_2COOH$, $CH_2ClCOOH$ and CH_3COOH, yielding molecular compounds. This interaction is most pronounced in the system $HClO_4$—CH_3COOH and has been interpreted by the present authors as the formation of acid salts wherein $CHCl_2COOH$, $CH_2ClCOOH$ and CH_3COOH perform the part of bases. The system $HClO_4$—CCl_3COOH has its analogues [2] in the system H_2SO_4—CCl_3COOH, as well as in the system $HClO_4$—H_2SO_4, where interaction between the constituents is likewise lacking[3]. To confirm the correctness of this view it would be interesting to study the system $HClO_4$—H_2O where an acid-base interaction undoubtedly occurs and to compare the results of studying this system with those obtained for previous systems, especially for $HClO_4$—CH_3COOH.

Van Wyk[4] studied the fusibility of the system $HClO_4$—H_2O and also measured the viscosity and density of this system at 20 and 50°. Linde[5] investigated the electrical conductivity of the aqueous solutions of $HClO_4$ at 25 and 50°, going as far as 50 molar per cent, *i. e.* up to a monohydrate.

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[1] T. Sumarokova and M. Usanovich, J. Gen. Chem. (Russ.), in press.

[2] M. Usanovich and V. Tartakovskaya, J. Gen. Chem. (Russ.), in press.

[3] M. Usanovich, T. Sumarokova and V. Udovenko, Acta Phys. Chim., **11**, 505 (1939).

[4] Van Wyk, Z. anorg. Chem., **48**, 42 (1906).

[5] Linde, Z. Elektrochem., **30**, 55 (1924).

Bearing in mind that such experimental data are available, we decided to confine ourselves to obtaining complete electrical conductance diagrams.

Experimental part

In our study the conductance diagram was obtained at the temperatures 20, 50 and 60°; the 50° isotherm was investigated at great length.

The diagram plotted on the basis of the results of the conductivity measurements is shown[6] in Fig. 1. Examination of the graph shows that with gradual addition of water to $HClO_4$ the conductivity at first increases, becoming as high as $\varkappa_{50} = 0.2654$ at 54.3 molar p. c. of perchloric acid, whereupon it again starts to decrease, passing through a minimum corresponding approximately to 45° molar per cent of perchloric acid, next steeply rises, attaining the maximum value of electrical conductivity, $\varkappa_{50} = 0.7828$, at about 10 molar per cent of perchloric acid, and then abruptly falls off to the conductivity of perchloric acid which is 0.0106. The minimum conductance corresponds to the maximum viscosity as studied by Van Wyk[4].

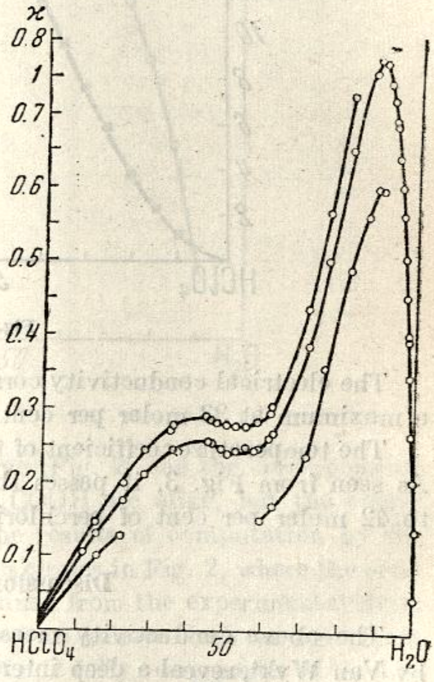

Fig. 1.

Comparison of our conductivity measurements with Linde's data shows a considerable discrepancy in the absolute values, though in both cases the curves qualitatively follow the same course.

Linde's conductivity values are much higher than those of the present authors, the conductivity isotherm at 25° (Linde) approaching

[6] For the numerical data, see a forthcoming paper, J. Gen. Chem. (Russ.).

closely our isotherm obtained at 50°, whilst his data referring to 50° are much above our data for 60°.

The good agreement between the results of the different runs as well as their lower absolute values suggest the conclusion that our data are correct.

Using Van Wyk's data[4] the conductivity was corrected for viscosity; the results are shown in Fig. 2.

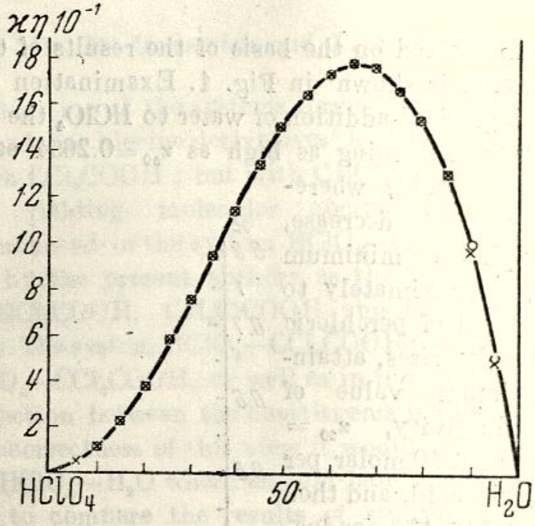

Fig. 2.

The electrical conductivity corrected for viscosity passes through a maximum at 33 molar per cent.

The temperature coefficient of the conductivity, α, was computed. As seen from Fig. 3, it passes through a maximum corresponding to 42 molar per cent of perchloric acid.

Discussion of results

The above conductivity measurements, as well as those made by Van Wyk[4], reveal a deep interaction between the constituents of the system under consideration in the liquid phase. The conductivity and viscosity diagrams bear a general resemblance to those obtained by the present authors[1] for the system $HClO_4$—CH_3COOH, the difference being, however, that in the latter system the viscosity maximum and the corresponding conductivity minimum correspond to the rational composition $2CH_3COOH.HClO_4$, whereas in the system $HClO_4$—H_2O they correspond to a composition intermediate between $HClO_4.H_2O$ and $HClO_4.2H_2O$.

In the system $HClO_4$—H_2O the temperature coefficient of conductivity, the course of which in the system $HClO_4$—CH_3COOH indicates two compounds, passes only through a maximum whose position is also intermediate between the mono- and dihydrate of perchloric acid (Fig. 3).

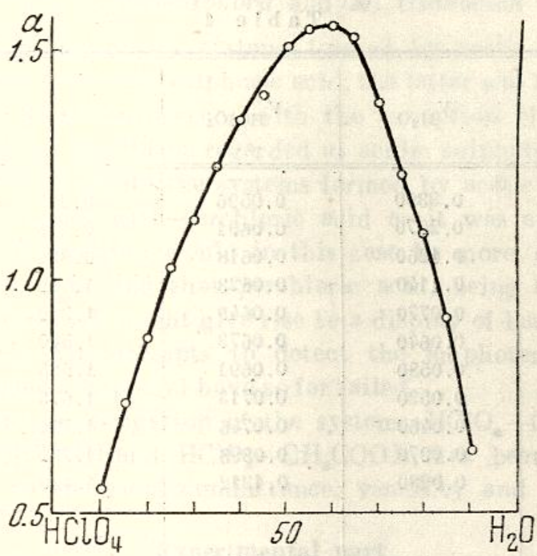

Fig. 3.

The corrected conductivity curve (Fig. 2) and the corresponding curve for the system $HClO_4$—CH_3COOH are alike, but the course of the former is more regular. The results of computation by the formula $\varkappa\eta = Ax(1-x)^2$ are shown as circles in Fig. 2, where the crosses represent the values of $\varkappa\eta$ obtained from the experimental data.

It would, however, be erroneous to believe such an agreement to be the proof that the curve in Fig. 2 fully corresponds to the law of mass action and that the conductivity of our system is therefore determined by the dihydrate of perchloric acid. As has been pointed out in our previous paper, the formula used in the computations takes no account of the change in volume, though in our system[4] an appreciable compression occurs.

It was therefore decided to make com utations by some other formula that would allow for the change in volume. It was found that the quantity $\varkappa\eta V_1 V_2$ remains constant throughout a wide concentration range (Table 1), whilst the product $\varkappa\eta V_1 V_2^2$ undergoe a certain variation.

It follows that the results of the two formulae lead to contradictory conclusions, because Table 1 is in favour of $HClO_2 \cdot H_2O$ being the electrolyte of our system.

Table 1

Molar ercentage $HClO_4$	V_{H_2O}	V_{HClO_4}	$\varkappa\eta$	$K \times 10^3$
84.7	0.3300	0.0596	0.225	4.4
77.7	0.2070	0.0601	0.445	5.5
67.0	0.1260	0.0618	0.820	6.4
64.3	0.1140	0.0623	1.920	6.5
54.3	0.0770	0.0649	1.310	6.5
48.8	0.0640	0.0673	1.540	6.3
45.5	0.0580	0.0691	1.625	6.6
42.6	0.0530	0.0713	1.675	6.7
38.1	0.0460	0.0746	1.760	5.9
29.0	0.0370	0.0898	1.730	5.8
17.3	0.0280	0.1312	1.420	5.2
			Mean	6.0

Summary

1. The electrical conductivity of the system $HClO_4$—H_2O has been studied at temperatures 20, 50 and 60°.

2. The conductivity diagram, as well as those of other properties, is indicative of chemical interaction going on in the system; of the hydrates of perchloric acid, $HClO_4.H_2O$ and $HClO_4.2H_2O$ appear to manifest themselves in the liquid phase.

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