1946 ACTA PHYSICOCHIMICA U.R.S.S. VOL. XXI. No. 5

The Systems Formed by Perchloric Acid with Acetic Acid and its Chlorine Derivatives

By *T. Sumarokova* and *M. Usanovich*

In studying the binary systems formed by acetic acid and its chlorine derivatives with sulphuric acid, the latter was found [1],[2],[3],[4],[5] to form with these substances with the exception of CCl_3COOH, compounds which should be regarded as acidic sulphates. It seemed of interest to investigate the systems formed by acetic acid and its chlorine derivatives with perchloric acid as it was expected that the chemical interaction would in this case be more distinct than with sulphuric acid and that perchloric acid, being the strongest of all protonic acids[6], might give rise to a display of basic properties in CCl_3COOH. All attempts to detect the amphoteric character of the last named compound have so far failed.

The present investigation of the systems $HClO_4$—$CHCl_2COOH$, $HClO_4$—$CH_2ClCOOH$ and $HClO_4$—CH_3COOH, has been carried out with respect to electrical conductance, viscosity and density.

Experimental part

1. Specimens

(a) The perchloric acid was prepared in the same manner as previously[7].

---

[1] A. Hantzsch, Z. physik. Chem., **61**, 257 (1908).

[2] Bergius, Z. physik. Chem., **72**, 338 (1910).

[3] M. Usanovich and A. Naumova, J. Gen. Chem. (Russ.), **5**, 712 (1935).

[4] Tartakowskaya, Bondarenko and Emeljanova, Acta Phys. Chim., **6** 609 (1937).

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

[6] According to Khodakov (C. R. Acad. Sci. URSS, **41**, 117, 1943), perchloric acid is 10^6 times as strong as sulphuric acid.

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

(b) The trichloracetic acid was recrystallized from a small amount of benzene and then fractionated three times. The fraction with the boiling point 193° at 720 mm Hg pressure was collected and sealed in ampoules.

(c) The dichloracetic acid, synthesized and carefully purified in the Organic Chemistry Laboratory of the Middle Asia State University, was distilled and sealed in ampoules without additional purification.

(d) The monochloracetic acid was fractionated three times; the fraction with the boiling point 187° at 729 mm pressure was collected and sealed in ampoules.

(e) The acetic acid prepared from glacial acetic acid and acetic oxide was subjected to fractional distillation and then fractionally frozen out; the acid with the fusion point 16.5° was sealed in ampoules.

2. Results of measurements[8]

(a) The system $HClO_4$—CCl_3COOH

In Fig. 1 are given the curves for the electrical conductance, viscosity and specific volume. The steady course of the conductance curves retained after correcting for viscosity evidences that no interaction occurs between $HClO_4$ and CCl_3COOH. The system undergoes expansion.

(b) The system $HClO_4$—$CHCl_2COOH$

The measurements were made at 20, 35 and 50°.

The curves for the electrical conductance, viscosity and specific volume are given in Fig. 2. The viscosity curves are S-shaped, the inflexion point being at 50 molal per cent and indicating the formation of a compound of equimolecular composition. The temperature coefficient being small, the electrical conductance isotherm is given for 20° only. The curve passes through a maximum at 80 molal per cent of $HClO_4$, which gives no indication as to the composition of the compound formed. The corrected electrical conductance isotherms (Fig. 5) reproduce the course of the electrical conductivity qualitatively, but its maximum occurs at 67 molal per cent of HCl_4 and is indicative of a compound with the composition $2HClO_4$, $CHCl_2COOH$.

---

[8] The tabulated data are presented in papers to appear shortly in the J. Gen. Chem. (Russ.).

A considerable compression is observed in the system.

(c) The system $HClO_4$—$CH_2ClCOOH$

The system was investigated at temperatures of 20, 35 and 60°. The results are represented in Fig. 3.

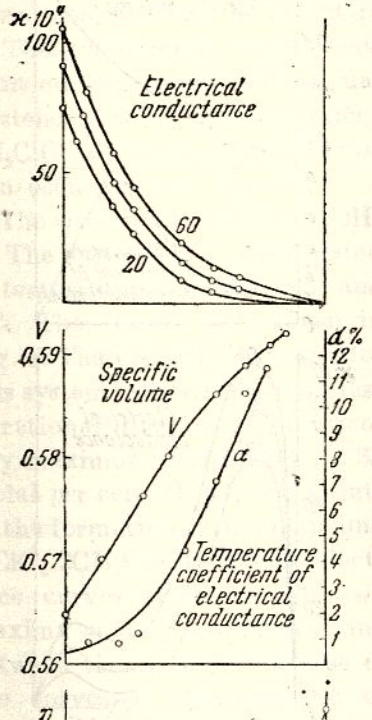

Fig. 1.

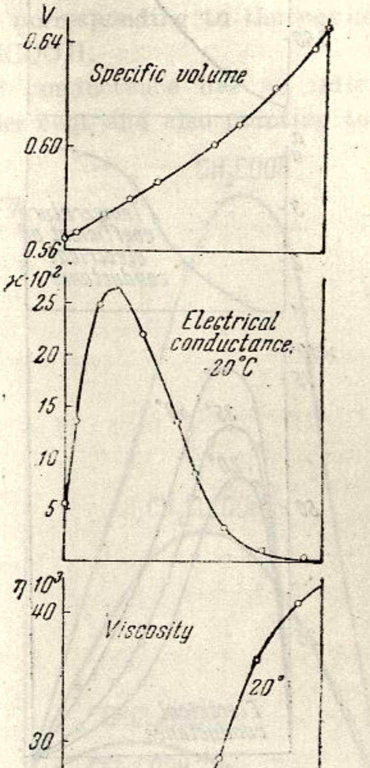

Fig. 2.

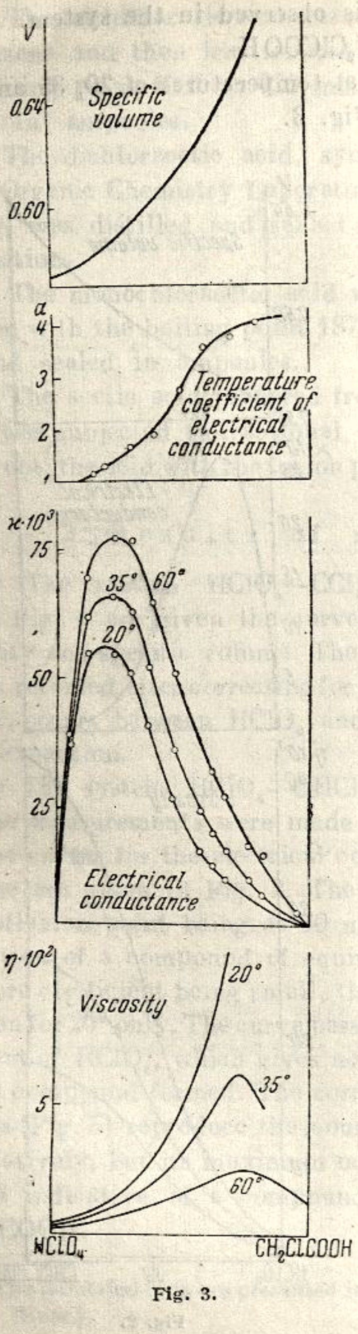
V
0.64
0.60
Specific volume
a
4
3
2
1
Temperature coefficient of electrical conductance
ϰ·10³
75
50
25
35°
60°
20°
Electrical conductance
η·10²
5
20°
35°
60°
Viscosity
HClO₄
CH₂ClCOOH

Fig. 3.

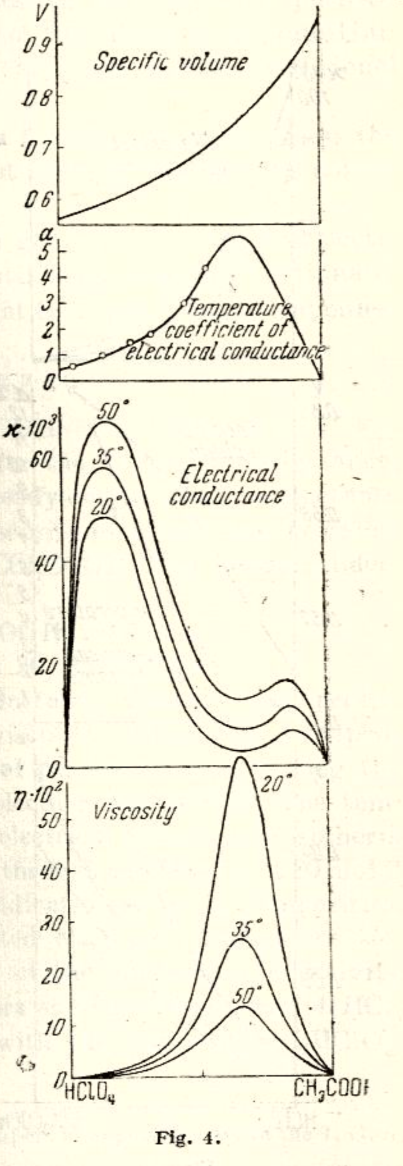
V
0.9
0.8
0.7
0.6
Specific volume
a
5
4
3
2
1
0
Temperature coefficient of electrical conductance
ϰ·10³
60
40
20
0
50°
35°
20°
Electrical conductance
η·10²
50
40
30
20
10
0
20°
35°
50°
Viscosity
HClO₄
CH₃COOH

Fig. 4.

The viscosity isotherms pass through an irrational maximum. The conductance isotherms also pass through a maximum which corresponds to 80 molal per cent of $HClO_4$ and, as the temperature rises, shifts towards monochloracetic acid. On correcting the electrical conductance for viscosity a symmetrical curve is obtained which passes through a maximum corresponding to the equimolecular composition $HClO_4$, $CH_2ClCOOH$.

The temperature coefficient of conductance has an inflexion point corresponding to 50 molal per cent and also pointing to the existence of the compound $HClO_4$, CH_2ClOOH. A marked compression occurs in the system.

(d) The system $HClO_4-CH_3COOH$.

The system was investigated at temperatures of 20, 35 and 50°. The results are shown in Fig. 4. The viscosity diagram for this system falls within the class of rational diagrams. The viscosity maximum corresponds to 33 molal per cent $HClO_4$ and points to the formation of the compound $HClO_4.2CH_3COOH$. The conductance curves pass through two maxima and a minimum lying between them; such a course of the curves is characteristic of systems with a deep interaction between the constituents. The positions of the maxima are 83 and 15 molal per cent of $HClO_4$ and that of the minimum, 33 molal per cent of $HClO_4$. The maximum of corrected conductance (Fig. 5). and that of the temperature coefficient (Fig. 4) correspond to the conductance minimum.

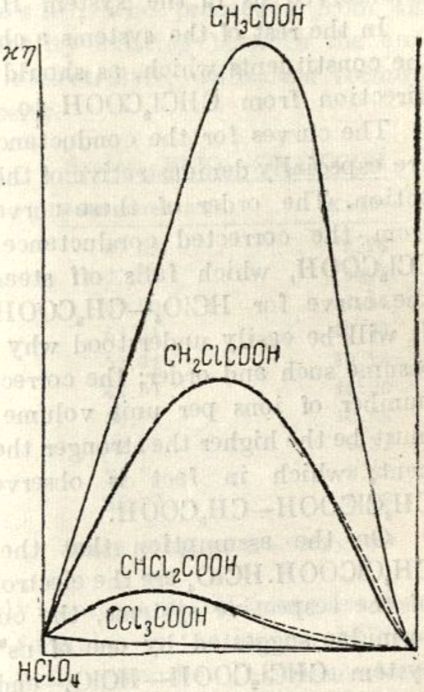

Fig. 5.

On the curve for the temperature coefficient of electrical conductance, apart from the maximum, an inflexion point is observed corresponding to 50 molal per cent and pointing to a compound of the composition $HClO_4-CH_3COOH$. A strong compression occurs in the system.

Discussion of results

Comparison of the data obtained shows in the first place that for the system $HClO_4$—CCl_3COOH the diagrams of all its properties are distinctly different from those of the other systems. In particular, the mixing of the components of this system is accompanied by expansion, whereas in the other systems compression occurs. It follows that $HClO_4$ does not interact with CCl_3COOH in the same way as it does with H_2SO_4[7]; in these two systems the same picture is observed as in the system H_2SO_4—CCl_3COOH[8].

In the rest of the systems a chemical interaction occurs between the constituents which, as should be expected, is intensified in the direction from $CHCl_2COOH$ to CH_3COOH.

The curves for the conductance corrected for viscosity (Fig. 5) are especially demonstrative of the intensity of this chemical interaction. The order of these curves is seen to be regular, starting from the corrected conductance curve for the system $HClO_4$—CCl_3COOH, which falls off steadily from $HClO_4$ and ending with the curve for $HClO_4$—CH_3COOH which is situated uppermost. It will be easily understood why the corrected conductance curves assume such and order; the corrected conductance characterizes the number of ions per unit volume and, for a given acid ($HClO_4$), must be the higher the stronger the base taken as the second component, which in fact is observed in the series $CHCl_2COOH$—$CH_2ClCOOH$—CH_3COOH.

On the assumption that the compounds $CHCl_2.2HClO_4$ and $CH_2ClCOOH.HClO_4$ are the electrolytes determining the conductance of the respective systems, the conductance was computed by the formulae suggested by one of us[9], namely $\varkappa\eta = Ax^2(1-x)$ for the system $CHCl_2COOH$—$HClO_4$ and $\varkappa\eta = Ax(1-x)$ for the system $CH_2ClCOOH$—$HClO_4$.

The results of computations are shown in Fig. 5 by dotted lines. As is seen from the figure, the agreement between the results computed by the above formulae and the recalculated experimental data does not extend over the entire course of the curves. This discrepancy may be accounted for by the considerable change in density occurring in the systems under consideration and disregarded in our

---

[9] M. Usanovich, Acta Phys. Chim., 7, 871 (1936).

formulae. To allow for the change in density, the formulae should be written as follows:

$$\varkappa\eta V_1^2 V_2 = K$$

where V_1^2 is the dilution of $HClO_4$, V_2 is the dilution of $CHCl_2COOH$, and

$$\varkappa\eta V_1 V_2 = K$$

where V_1 is the dilution of $HClO_4$ and V_2 is the dilution of $CH_2ClCOOH$.

A similar computation is encountered in the work of Steele, Archibald and McIntosh[10], who proceeded from the assumption of a direct proportionality existing between the conductivity and concentration of the electrolyte, whilst our formula involves a correction for viscosity.

System $HClO_4$—$CHCl_2COOH$

Molal percentage	$K \times 10^4$
96.69	2.99
86.49	2.24
79.52	2.41
69.75	2.75
56.75	2.94
50.36	2.92
38.41	2.68
24.32	2.17
8.42	3.67

Mean value of $K = 2.72 \times 10^{-4}$

System $HClO_4$—$CH_2ClCOOH$

Molal percentage	$K \times 10^6$
87.05	8.24
77.75	9.98
69.90	11.54
62.74	10.78
52.31	10.96
42.61	10.90
36.72	10.86
32.73	9.37
23.34	8.92
17.67	8.03

Mean value of $K = 9.62 \times 10^{-6}$

In both cases K remains fairly constant at all concentrations. All attempts to apply the same formulae to the system $HClO_4$—CH_3COOH have failed to yield positive results. This seems to be due to the fact that in the given system not one, but two compounds are formed; in fact, our data supply evidence mainly for the existence of $HClO_4.2CH_3COOH$, which is analogous to a dihydrate[11], and not for the equimolecular compound obtained by Hantzsh and Langbein[12] in the crystalline form. An equimolecular com-

---

[10] Steele, Archibald and McIntosh, Z. physik. Chem., 55, 129 (1906).

[11] van Wyk, Z. anorg. Chem., 48, 42 (1906).

[12] Hantzsh u. Langbein, Z. anorg. Chem., 204, 197 (1932).

pound not reflected in the form of any particular point on the viscosity and electrical conductivity curves may be thought of as affecting the magnitude of these properties and their concentration dependence. The more complex nature of the interaction in the system $HClO_4—CH_3COOH$ does not permit the formulae to be applied to this system, for they take account of the formation of one compound only.

Summary

1. The electrical conductivity, viscosity and density of the systems $HClO_4—CCl_3COOH$, $HClO_4—CHCl_2COOH$, $HCCl_4—ClCOOH$ and $HClO_4—CH_3COOH$ have been studied.

2. It is established that $HClO_4$ does not form any complex compounds with CCl_3COOH.

3. The compounds $CHCl_2COOH.2HClO_4$, $CHCl_2COOH.HClO_4$, $CH_2ClCOOH$ and $2CH_3COOH.HClO_4$ have been detected.

3. The formation of these compounds is indicative of the basic properties of $CHCl_2COOH$, $CH_2ClCOOH$ and CH_3COOH.

5. The data obtained confirm the fact that the strength of the acidic bases increases in the series: $CHCl_2COOH < CH_2ClCOOH < CH_3COOH$.

The Middle Asia State University,
Laboratory of Physical Chemistry,
Tashkent.

Received
August 1, 1945.