PHYSICO-CHEMICAL INVESTIGATION OF SYSTEMS CONTAINING DIOXANE

VIII. THE SYSTEM SULFURIC ACID - DIOXANE

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In our previous papers we described the results of investigations of dioxane solutions of aluminum bromide [1], sulfur trioxide [2], pyrosulfuric acid [3], phosphorous acid [4], and hydrogen chloride [5, 6]. In the present paper we consider the system sulfuric acid - dioxane.

A. E. Favorsky [7] had already established that on reaction of sulfuric acid with dioxane the dioxanate of sulfuric acid is formed. A. E. Favorsky isolated this compound and determined its composition and melting point. As far as we know, however, the fusion diagram of the system dioxane - sulfuric acid has never been studied. The starting substances in the present investigation were dioxane with m.p. 10.7° and sulfuric acid with m.p. 10.6°.

Thermal analysis of the system sulfuric acid - dioxane. As we see from the diagram, the fusion curve descends to 69 mol-% H_2SO_4. Its further plotting had to be abandoned due to the considerable experimental difficulties associated with rising viscosity and change of color to brown. The diagram clearly indicates the existence of only one compound of dicxane with sulfuric acid, corresponding to the composition $H_2SO_4 \cdot C_4H_8O_2$. A compound of the same composition was established by an entirely different method by A. E. Favorsky [7]. The melting point of this compound on our fusion diagram is 100-101°. Favorsky reports a melting point of 101° for his compound. We also established a eutectic point on the diagram corresponding to 14 mol-% sulfuric acid with a crystallization temperature of approximately 5°.

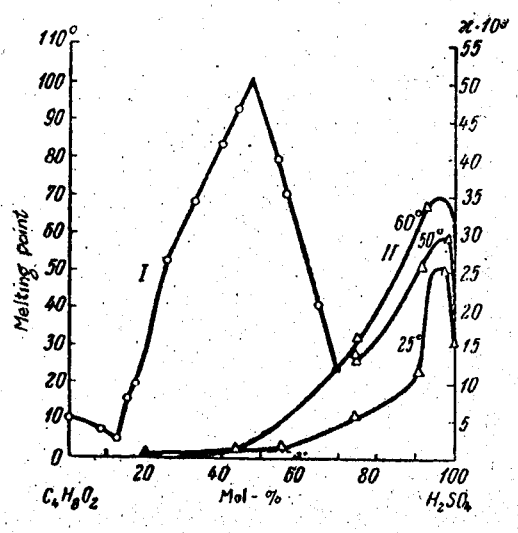

Diagram. System sulfuric acid - dioxane.
I) Melting point, II) specific electrical conductivity.

Electrical conductivity of the system sulfuric acid - dioxane. Measurements were made with addition of dioxane to pure sulfuric acid as well as of sulfuric acid to dioxane. Due to the circumstance that over a wide concentration interval at room temperature the system dioxane - sulfuric acid is in the solid state, it was necessary to deviate rather widely from the previously selected temperature conditions. The sulfuric acid at 25° had the specific electrical conductivity $\varkappa = 1.64 \cdot 10^{-2}$. According to the measurements of M. Usanovich [8, 9] the specific electrical conductivity of the acid at 25° is $1.17 \cdot 10^{-2}$ *. We see from the diagram that sulfuric acid in dioxane at low and even quite high concentrations has a relatively low specific electrical conductivity with a maximum shifted toward the sulfuric acid, i.e. into the region of dilute solution of the compound $H_2SO_4 \cdot C_4H_8O_2$ in sulfuric acid.

Our results for the electrical conductivity of

* With variations between $0.9 \cdot 10^{-2}$ and $1.5 \cdot 10^{-2}$;

solutions of sulfuric acid in dioxane, converted to equivalent electrical conductivity, are given in Table 1.

Table 1
Equivalent Electrical Conductivity (λ) of Solutions of Sulfuric Acid in Dioxane

Temperature	Concentration (g-equiv./liter)	λ
60°	36.20	3.74
25	36.20	1.422
25	28.02	0.796
20	2.48	0.0238

TABLE 2
Cryoscopic Investigation of the System Sulfuric Acid-Dioxane. (Dioxane sample G = 6.629 g)

Weight of sulfuric acid (g) in g	Δt	$M=4.83\frac{1000\,g}{\Delta t \cdot G}$
0.7394	4.20	135
0.9943	6.20	118

We see from the data of Table 1 that within the sulfuric acid concentration range of 36 to 2.48 g-equiv./l, the values of λ are between 3.74 and 0.0238, the values falling steeply with dilution. At a concentration of 1.1 g-equiv./l the value of λ is of the order of only 10^{-3}. Consequently, sulfuric acid in dioxane is a weaker electrolyte than acetic acid in water, since at a concentration in water of 1 g-equiv./l, the λ of acetic acid = 1.32.

Cryoscopy of sulfuric acid in dioxane. Measurement of the electrical conductivity of dilute solutions of sulfuric acid in dioxane does not give grounds for classifying it either as a strong or weak electrolyte. This conclusion was checked by cryoscopic measurements of solutions of sulfuric acid in dioxane, results of which appear in Table 2.

These data show that cryoscopy likewise does not indicate the existence of simple ions of sulfuric acid.

SUMMARY

1. One point corresponding to the complex compound $H_2SO_4 \cdot C_4H_8O_2$ with m.p. approx. 100° was found from the fusion diagram of the system dioxane-sulfuric acid.

2. The specific electrical conductivity of this system is insignificant at low concentrations of sulfuric acid, and it rises with increasing relative amount of sulfuric acid. The curve of composition versus κ of this system has a maximum which is very strongly displaced in the direction of sulfuric acid and falls steeply on transition to pure sulfuric acid.

3. The molecular weight of sulfuric acid in dioxane determined by the cryoscopic method is higher than that theoretically expected.

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* T.p. = C. B. Translation pagination.