

PHYSICOCHEMICAL STUDY OF AQUEOUS DIOXAN SOLUTIONS

IX. AQUEOUS DIOXAN SOLUTIONS OF SULFURIC ACID

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The properties of solutions of hydrogen chloride in dioxan [1], and in aqueous dioxan mixtures [2] and also sulfuric acid solutions in dioxan [3], were described earlier. In the present work the electrical conductivity of sulfuric acid in aqueous dioxan mixtures is studied.

It has been shown [3], that sulfuric acid solutions in dioxan, not only at low, but even at considerable concentrations (~ 10 mole %) are very bad conductors of electricity. Even for sulfuric acid concentrations of 2.48 N, the equivalent electrical conductivity of sulfuric acid solutions in dioxan is equal to $0.0238 \Omega^{-1}$. For

aqueous solutions of 2 N concentration, the equivalent electrical conductivity of sulfuric acid reaches about $220 \Omega^{-1}$, i.e., approximately 10,000 times as much.

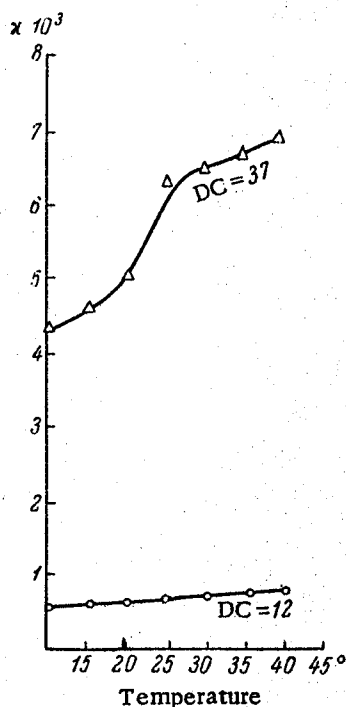
At the same time, sulfuric acid in dioxan, as in water, forms a complex compound — the crystalline dioxanate [3, 4]. It was of interest to study the behavior of sulfuric acid in mixed aqueous dioxan solvent for varying ratios of dioxan to water.

For this purpose, 0.1 N and 0.01 N solutions of sulfuric acid were prepared in aqueous dioxan mixtures having electrical constants equal to 12 and 37. If we add to these the well studied solutions of sulfuric acid in water and also solutions of sulfuric acid in dioxan [3], we obtain a series of solutions of sulfuric acid in media with the following dielectric constants: 2.28, 12, 37 and 81.

Aqueous dioxan solutions of sulfuric acid were prepared in graduated jars with ground-glass stoppers. They were both transparent and colorless like aqueous solutions of sulfuric acid and kept well. The results of the specific and equivalent electrical conductivity measurements for sulfuric acid in aqueous dioxan mixtures are given in Table 1.

As seen from the data in Table 1, at different concentrations and temperatures, specific electrical conductivity of aqueous dioxan solutions of sulfuric acid increases with increasing content of water in the system.

The specific electrical conductivity of solutions increases with increasing temperature, as may be concluded from Fig. 1. The curve for DC = 12 in the temperature range studied is represented by an ascending straight line; for DC = 37 the increase is more pronounced and not so even.



Dependence of specific electrical conductivity of 0.1 N solutions of sulfuric acid in aqueous dioxan on temperature.

TABLE 1

Specific Electrical Conductivity of Aqueous Dioxan Solutions of Sulfuric Acid.

DC	H ₂ SO ₄ concentration (N)	$\kappa \cdot 10^8$						
		45°	40°	35°	30°	25°	20°	15°
12	0.1	0.7431	0.7311	0.7014	0.6671	0.6328	0.5982	0.5609
12	0.01	0.1108	0.1060	0.09811	0.09609	0.09156	0.08396	0.07816
37	0.1	6.901	6.639	6.561	6.393	5.184	4.618	4.412
37	0.01	0.7027	0.6311	0.5801	0.5373	0.4875	0.4267	0.3941

TABLE 2

Equivalent Electrical Conductivity of Aqueous Dioxan Solutions of Sulfuric Acid.

DC	Dilution	λ						
		45°	40°	35°	30°	25°	20°	15°
12	10	7.431	7.311	7.014	6.671	6.328	5.982	5.609
12	100	11.08	10.60	9.811	9.609	9.156	8.396	7.816
37	10	69.01	66.39	65.61	63.93	51.84	46.18	44.1
37	100	70.27	63.11	58.01	53.73	48.75	42.67	39.41

The results are no less interesting on comparing the values for the equivalent electrical conductivities of these solutions.

As seen from the data in Table 2, an increase in the relative water content is accompanied by an increase in equivalent electrical conductivity of aqueous dioxan solutions of sulfuric acid.

SUMMARY

1. Specific and equivalent electrical conductivity of solutions of sulfuric acid in aqueous dioxan mixtures with high dielectric constants 37 and 12, have been determined. The studies were carried out at the temperature range 15 to 45°, for each 5°.
2. It has been established that for different concentrations and the same temperature, the electrical conductivity of solutions is higher, the greater the amount of water contained in the aqueous dioxan solvent.
3. Electrical conductivity of the solutions increases with increasing temperature.

LITERATURE CITED

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STUDY OF ADDITION OF HYDROGEN TO VINYL ACETATE BY MEANS OF A PHOSPHORIC ACID CATALYST USING CARBON-14

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In connection with results obtained in our earlier work [1], relating to a study of secondary catalytic reactions of hydrogen by using isotopic methods, the necessity arose to elucidate the mechanism of the addition of hydrogen to the vinyl acetate of different substituents. The most direct way would be the use of isotopes of hydrogen, however, in view of the great scarcity of hydrogen, it is difficult to carry out such an investigation without a replacement of hydrogen. We tried to overcome this difficulty by using radioactive carbon C^{14} in a study of the exchange between hydrocarbons.

An advantage of work with C^{14} , apart from the absence of isotope exchange, is the relatively simple method with a high sensitivity of radioactive analysis, which permits detection of even minute amounts of hydrogen. In this work the results are given of a study, with the aid of C^{14} , of addition of hydrogen to vinyl acetate and to other esters, ethyl, n-butyl and t-butyl.

The reaction was carried out in a continuous apparatus, all of which is described in detail in our previous work [2]. Hydrogen was made up in a synthesizer and fed slowly through a glass tube packed with a previously dried and packed containing catalyst. A phosphoric acid catalyst was heated to 150°C. After passing through the catalyst, the products were fed into a trap held at 0°C and then analyzed by chemical and physical methods. On using a heated hydrogenation tube our results showed that, depending without change on the hydrogenation medium, only hydrogenation of the double bond in the polymer can be produced. This, in the case of esters of allyl and ethyl and vinyl and n-butyl, being expected by Equations (a) and (b):



In such a reaction of hydrogen, redistribution of isotopes does not proceed between the reaction components. In Equation (a) a mixture of radioactive ethane, where all the atoms of hydrogen in methane, ethane and ethyl, is converted into ethane while retaining its radioactivity, and radioactive ethane is hydrogenated by hydrogen obtained from ethane and ethyl respectively, so as to give the general case, specific radioactivity in the reaction mixture and on the basis of the radioactivity of the reaction product, the degree of approximation of the system to equilibrium, in which the C^{14} atoms of ethane and ethyl, in the same, may be determined. In Equation (b) radioactive ethane is hydrogenated by hydrogen, and after transferring to methane, redistribution of isotopes between ethane and ethyl, n-butane and n-butyl, etc., is accompanied by a change in the isotopic composition of ethane and ethyl, in the presence of isotopic exchange reactions.

Proper use of isotopes of C^{14} between two hydrocarbons permits us to assume that the isotopic exchange of carbon is connected with a transfer of hydrogen. Transfer of hydrogen from one hydrocarbon to the expense of transfer of atoms of another, is not fully fragmentary in character, but is a process, the portion that is distributed of hydrogen between the hydrocarbons is different in respect of isotopic atoms in the reaction mixture. T. p. = C. B. Translation pagination.

1. In the case of isotopic exchange, the isotopic composition of the hydrocarbons and the rate of isotopic exchange of carbon.