SOME TERNARY SYSTEMS OF WATER – DIOXAN – ELECTROLYTE

Yu.B. Klemenik

A mixture of water and dioxan is one of the most widely used mixed solvents in physicochemical investigations. So, naturally, this binary system has been investigated from many points of view – melting point, vapor pressure, density, surface tension, viscosity, refractive index, heat of mixing [1-3]. The diagrams of density, viscosity and heat of mixing provide evidence of the existence in the system of a chemical compound which, apparently, is a hydrate unstable to heat. But the absence of any indication of this compound from the diagrams of other properties has induced some investigators to doubt the existence of a definite compound between water and dioxan [4, 5].

A number of investigators have successfully developed the idea of using a ternary system, with separation of phases, to elucidate the chemical nature of the binary systems of which the ternary is composed.

Separation of phases in the ternary system water-dioxan-electrolyte (where the electrolyte is HCl, NaCl, LiCl, $LiNO_3$, KCl, etc.) has been noted in the literature [4, 6]. The present paper is an attempt to use some of these systems to elucidate the character of the interaction between the components of the binary system water–dioxan.

EXPERIMENTAL

Dioxan was dried over anhydrous calcium chloride, distilled, cooled to 6-7°, and further dried by distillation from metallic sodium; the fraction distilling in the range 101.1-101.2° was collected. The product had m.p. 11.6°. All the other substances used were of chemically pure grade. Hydrogen chloride was obtained by heating sodium chloride with sulfuric acid and dried by passing it through 95% sulfuric acid.

With regard to the component binary systems of the water–dioxan –hydrogen chloride ternary system, it is known that hydrogen chloride is very soluble in water and also in dioxan [7], that water and dioxan are miscible in all proportions, but that hydrogen chloride causes separation into two liquid phases.

The principal difficulty in the determination of the solubility of hydrogen chloride in mixtures of water and dioxan was that it was impossible to pass a stream of hydrogen chloride over the surface of the liquid without producing a change in the composition of the latter, due to evaporation. For this reason, the hydrogen chloride (shown to be free from air) was only passed through the saturation flask until all the air originally present in the flask had collected in a eudiometer tube over water. At the end of this saturation period, in order to remove any residual air, a further volume of hydrogen chloride equal to three times the volume of the free space over the saturated solution was passed through the flask. The pressure of hydrogen chloride in the apparatus was controlled using a manometer. The content of hydrogen chloride in weighed samples of the saturated solution was determined, after dilution, by titration with alkali to the end point of methyl orange. The solubility of hydrogen chloride was measured three times for each water–dioxan mixture. The differences between separate determinations did not excede 0.3%.

Mean values obtained for the solubility of hydrogen chloride in water–dioxan mixtures at atmospheric pressure (25°) are shown in Table 1.

Solubility isotherms, derived from these data, are shown in Figure 1. It is clear that separation into two liquid phases does not occur with any of the solutions saturated with hydrochloric acid. The region of separation is of the closed loop type. The boundaries of this region were determined by titration of a mixture within this

region until two layers no longer existed. Solutions, corresponding to points lying to the left of the line joining dioxan to the point d, were prepared by mixing dioxan, water and hydrogen chloride in different proportions. The right hand boundary was then determined by titration of two phase mixtures with solutions of hydrogen chloride in dioxan. Similarly, the left hand boundary was determined by titration with mixtures of water and dioxan. The composition of the initial mixture and the quantity of solution added were checked by weighing (calculating from the specific gravities of the solutions used). The composition of each solution corresponding to a point on the boundary isotherm, was determined three times. The differences between separate determinations did not excede 0.3%. Table 2 gives the mean values of the compositions of these solutions.

TABLE 1

The $H_2O-C_4H_8O_2-HCl$ System

Composition of solutions saturated with hydrogen chloride (mole %).		
H_2O	$C_4H_8O_2$	HCl
74.3	0	25.7
55.6	14.3	30.1
42.5	23.0	34.5
30.2	31.0	38.8
22.2	37.8	40.0
11.3	47.2	41.5
0	56.0	44.0

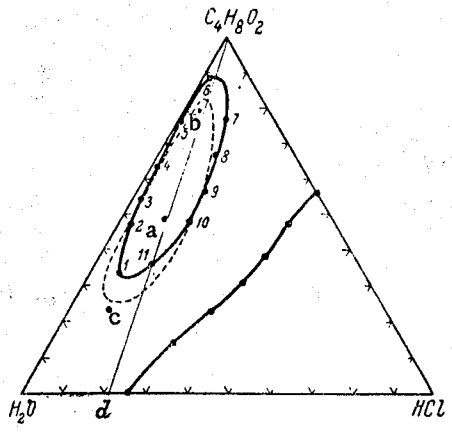

Fig. 1. Solubility diagram for the system water–dioxan–hydrogen chloride Explained in the text.

The boundary isotherm drawn from this data is shown in Fig. 1 (the number of the solution corresponds to the number of the point on the isotherm). In the upper part of the two phase region it is the lower layer that gradually diminishes on movement outwards, and vanishes as the boundary is crossed. In the lower part of the region it is the upper layer that diminishes and finally disappears. At points 3 and 9 separation occurs instantly into two layers of nearly equal volume for a small change in composition, corresponding to passage through the boundary isotherm.

TABLE 2

The $H_2O-C_4H_8O_2-HCl$ System

No. of Solution	Composition of solution corresponding to the boundary of the heterogeneous region (mole %)		
	H_2O	$C_4H_8O_2$	HCl
1	59.6	33.5	6.9
2	49.8	46.6	3.6
3	44.0	53.6	2.4
4	35.0	63.4	1.6
5	23.1	76.0	0.9
6	10.5	87.7	1.8
7	12.0	76.4	11.6
8	18.9	66.9	14.2
9	27.0	56.6	16.4
10	35.1	47.8	17.1
11	50.5	35.6	13.9

Analysis showed that the main component of the upper layer was dioxan. At the point a (molecular composition $H_2O : C_4H_8O_2 : HCl = 40.4 : 49.0 : 10.6$) the upper layer at 25° occupied 40% of the total volume. The relative concentrations of hydrogen chloride (determined by analysis) in the upper and lower layers were 1:13.4. The melting point of the upper layer was 9.4°. At the point b (molecular composition $H_2O : C_4H_8O_2 : HCl = 17.6 : 78.6 : 3.8$) the upper layer at 25° occupied 90% of the total volume. The relative concentrations of hydrogen chloride in the upper and lower layers were 1:19.7. The melting point of the upper layer was 9.12°. These results confirm that the separation of the system into two layers has the character of a salting out of dioxan by hydrogen chloride.

On heating any of the two phase mixtures, the upper layer increased in volume at the expense of the lower layer.* Thus, heating a mixture corresponding to the point b caused a diminution of the lower layer. The latter vanished at 127°. With a mixture corresponding to a the upper layer already occupied the greater part of the volume at 100°. With a solution corresponding to 1 (a critical point at 25°) warming caused an upper layer to appear, occupying 28% of the

* All experiments above room temperature were done in sealed tubes by the variable temperature method.

volume at 130°.* At the point c (molecular composition $H_2O : C_4H_8O_2 : HCl = 67.3 : 23.3 : 9.4$) an upper layer began to form at 140°. Upon a rise in temperature the boundary isotherm was displaced in the direction of greater water content. The position of the isotherm at 100° is shown in Fig. 1 by a dotted line.

It was not possible to draw the boundary of the two phase region sufficiently accurately at much higher temperatures, nor to find the upper ternary critical point. On heating the mixture corresponding to a, the lower layer diminished and vanished at approximately 200°. On heating above 200° and subsequently cooling, the previous distribution of layers was not restored, and, often, separation into two layers did not occur. Repeated heating—not above 160-170° gave completely reproducible separation into layers.

A similar dependence of separation into two layers on temperature was found for the ternary systems water—dioxan—lithium chloride and water—dioxan—potassium chloride. Thus, with a mixture of composition $H_2O : C_4H_8O_2 : LiCl = 70.5 : 26.6 : 2.9$, the upper layer was 9.1% of the total volume at 25° and 47% at 95°. A ternary mixture of the composition $H_2O : C_4H_8O_2 : KCl = 69.6 : 28.8 : 1.6$ was homogeneous at normal temperature. Separation, with formation of an upper layer, only occurred at 70°. With these solutions, the melting point of the upper layer, separated at the higher temperature, was never less than 7°. Clearly, the main component of the upper layer was dioxan.**

With regard to the ternary system water—dioxan—sulfuric acid, it is known that the components are completely miscible in the binary systems water—dioxan and water—sulfuric acid; in the system dioxan — sulfuric acid a fairly stable complex $C_4H_8O_2 \cdot H_2SO_4$ is formed, with a melting point of 101° [8]. The boundary of the heterogeneous region (crystalline complex of dioxan with sulfuric acid and its saturated solution) was determined for this system, at 25°, by the titration method. The composition of the solution, corresponding to the point nearest to the H_{20} vertex, was found by adding water to a mixture of dioxan and sulfuric acid. The compositions of the solutions, corresponding to the other points on the boundary, were found by adding dioxan to aqueous solutions of sulfuric acid. Some difficulty was experienced in these determinations because the crystalline complex dissolved very slowly in nearly saturated solutions (concentrated solutions of the complex were highly viscous). For this reason, the solutions were heated gently — not above 35°, and then cooled and seeded with the crystalline complex. The composition of each solution, corresponding to a point on the boundary of the heterogeneous region, was determined three times. Differences between separate determinations did not excede 0.4% (for the composition by weight of dioxan in the mixture). Table 3 gives the results obtained. The heterogeneous region is shown graphically in Fig. 2.

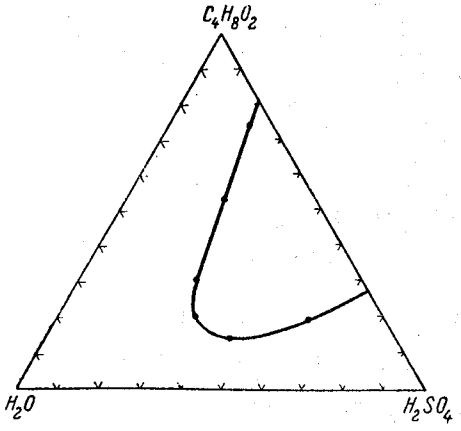

Fig. 2. Solubility diagram for the system water—dioxan—sulfuric acid

Addition of sulfuric acid to water—dioxan mixtures of various compositions (mixtures were taken with molecular ratios of water to dioxan 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2 and 9:1) did not produce separation. With a rise in temperature the boundary of the heterogeneous region contracted. Its limit lay at the midpoint of the dioxan—sulfuric acid side at a temperature of 101° (the melting point of the pure complex).

A noteworthy feature of the above data on ternary systems is the dependence of separation into two phases on temperature. In the absence of a definite chemical compound between water and dioxan, it would be expected that the salting out effect would decrease with a rise in temperature. But, in fact, the reverse happens. With a rise in temperature the upper layer of dioxan increases. A similar type of dependence on temperature has been described in the literature for phase separation in the system water—dioxan—lithium nitrate [4]. In the water—dioxan—hydrogen chloride system, for points lying below the separation isotherm at 25° (in the direction of the H_2O vertex), separation of phases only begins at elevated temperatures.

* Graduated tubes were used to determine the relative volumes of the upper and lower layers at higher temperatures.

** The systems containing potassium and lithium chlorides were only of interest in connection with the dependence on temperature of the relative volumes of the upper and lower layers. The two phase regions were not investigated systematically.

TABLE 3

The $H_2O - C_4H_8O_2 - H_2SO_4$ System

Composition of solutions corresponding to the boundary of the heterogeneous region (mole%).

H_2O	$C_4H_8O_2$	H_2SO_4
5.8	73.8	20.4
22.6	52.9	24.5
40.2	30.7	29.1
46.4	20.2	33.4
41.1	14.0	44.9
18.0	19.7	62.3

There is a universal rule enunciated by V. F. Alekseev, according to which the existence in a system of a lower critical point of phase separation is evidence of the formation of a thermally unstable compound, in most cases a hydrate [9]. The complexity of the processes, controlling phase separation in the ternary systems investigated, makes it difficult to identify the components whose interaction is responsible for the variation with temperature of phase separation in these systems. But the fact that the nature of this variation is the same for all the systems investigated, although the third components – KCl, LiCl, $LiNO_3$ and HCl – differ markedly in their solubilities in water and especially in dioxan, strongly suggests that the water–dioxan system is the controlling factor.

In the system water–dioxan–hydrogen chloride, as the temperature rises, a considerable part of the separation isotherm approaches close to the water–dioxan side. This shift of the separation isotherm is characteristic of ternary systems containing a binary system with a considerable tendency to separation [10]. In this case, it clearly provides evidence of an appreciable tendency to separation -in the water–dioxan system, which may be attributed to increased thermal dissociation of dioxan hydrate with increasing temperature. Phase separation in the water–dioxan–sulfuric acid system may be explained by the powerful interaction between dioxan and sulfuric acid (formation of a complex).

The author wishes to thank O. A. Osipov and Ya. F. Mezhenny for their valuable advice.

SUMMARY

1. An investigation has been made of the ternary systems water–dioxan–hydrogen chloride and water–dioxan–sulfuric acid, and a few points have been determined for the ternary systems water–dioxan–lithium chloride and water–dioxan–potassium chloride.

2. It was found that the region of phase separation in the system water–dioxan–hydrogen chloride has the form of a closed loop, which vanishes at an upper ternary critical point. The phase diagram of the system water–dioxan–sulfuric acid at normal temperature is composed of a large area of homogeneous solutions, with a heterogeneous region adjacent to the dioxan–sulfuric acid side.

3. The nature of the variation of phase separation with temperature for the systems investigated indicates the existence in the water–dioxan system of a thermally unstable compound.

LITERATURE CITED

[1] F. Hovorka, R. Chaefer, D. Dreisbach, J. Am. Chem. Soc., 58, 2264 (1936).

[2] A. Jeddes, J. Am. Chem. Soc., 55, 4832 (1933).

[3] N. N. Feodosev, O. A. Osipov and G. K. Morozova, J. Gen. Chem., 24, 1540 (1954). *

[4] M. A. Klochko, and I. G. Grigorev, Bull. Acad. Sci., USSR., Sect. Phys. Chem. Anal. 21, 318 (1952).

[5] Ya. F. Mezhenny, Physicochemical Investigation of Dioxan and Dioxan–Water Solutions, Thesis, Kiev (1954).

[6] J. Scatchard, M. A. Benedict, J. Am. Chem. Soc., 58, 837 (1936).

[7] Ya. F. Mezhenny, J. Gen. Chem., 24, 1945 (1954).*

[8] A. E. Favorsky, J. Russ. Phys. Chem. Soc., 38, 741 (1906).

[9] V. F. Alekseev, J. Russ. Phys. Chem. Soc., 17, 99 (1885).

* Original Russian pagination. See C. B. translation.

[10] R. V. Mertalin and V. F. Ust-Kachkintsev, J. Gen. Chem. 5, 771 (1935).

Rostov-on-Don State University. Received March 7, 1956.