Phase Equilibrium in the System Water–Ethanol–Hydrazine Monochloride at 25° and 15° C.

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THE HALIDES of hydrazine containing one equivalent of acid per mole of hydrazine have the ability to salt out aliphatic alcohols from water, forming a binodal curve, the extent of which increases with increasing temperature. This fact becomes evident in the purification of these salts by recrystallization from aqueous alcoholic solutions. Data are reported here for hydrazine monochloride with ethanol as the alcohol at two temperatures.

EXPERIMENTAL

Hydrazine monochloride was prepared by the reaction of hydrazine with reagent grade hydrochloric acid to a neutral methyl orange end point, followed by recrystallization from 80% methanol. Analysis: calculated for N_2H_5Cl: Cl, 51.74%; found: Cl, 51.65, 51.66%.

The ethanol was reagent grade $n^{25}_D = 1.3592$. Conductivity water was used, being maintained in a reservoir protected from CO_2 by soda-lime.

Solubility data were determined by rotation of samples in a constant temperature bath until equilibrium was reached (sometimes 5 days), as determined by analysis of repetitive samples. Samples were drawn, weighed, and analyzed for chloride content with standard silver nitrate, using dichlorofluorescein as indicator.

Table I. Solubility and Tie-Line Data

Solubility Data at 25° C., Wt. %[a]			Solubility Data at 15° C., Wt. %[a]		
N_2H_5Cl	Water	Ethanol	N_2H_5Cl	Water	Ethanol
64.4	35.6	0.0	56.8	43.2	0.0
61.6	36.5	1.9	54.1	43.5	2.3
58.6	37.3	4.1	50.0	45.0	5.0
1.2	9.9	88.9	47.2	44.9	7.9
0.6	4.9	94.5	45.5	43.4	11.1
0.32	0.0	99.68	0.8	9.9	89.3
			0.4	5.0	94.6
			0.24	0.0	99.76
Binodal Curve			Binodal Curve		
1.8	11.4	86.8	3.0	17.2	79.8
3.7	18.6	77.7	9.5	31.7	58.8
4.6	20.0	75.4	11.2	34.1	54.7
9.0	28.8	62.2	14.5	25.6	67.9
10.3	31.6	58.1	16.7	38.7	44.6
17.7	38.8	43.5	20.6	41.2	38.2
22.0	41.5	36.5	22.8	42.3	34.9
28.7	44.7	26.6	26.9	44.0	29.1
51.2	41.5	36.5	33.1	46.3	20.6
45.3	45.1	9.6	37.3	45.6	17.1
57.7	37.4	4.9	44.3	43.9	11.8
Tie-Line Data, Wt. %			Tie-Line Data, Wt. %		
N_2H_5Cl in water layer	N_2H_5Cl in ethanol layer		N_2H_5Cl in water layer	N_2H_5Cl in ethanol layer	
41.0	14.7		38.6	23.0	
46.9	8.3		40.5	18.9	
51.1	7.5				

[a] Solid phase present.

Many years of experience in this laboratory using recrystallization from aqueous alcohol as the best method of preparing pure hydrazine monochloride seemed to justify the assumption, made in this work, that no compound formation occurs in this system, and that the solid phase in every case is the anhydrous salt.

For the determination of the binodal curves, mixtures containing a known amount of water and salt were titrated in a constant temperature bath with ethanol to a cloudy end point. The method of Frankforter and Frary (*3*) of adding a very small amount of the alcohol-soluble dye, Spirit Blue, permitted a much sharper determination of the end point of this titration than was possible by visual observation without the dye. The amount added was so small that it could reasonably have no effect on the solubility. The two ends of the binodal curve were obtained by analysis of the two liquid layers in the nonvariant three-phase system with solid salt present. The tie lines were determined by analysis of both layers for chloride in two-liquid layer systems of known total composition.

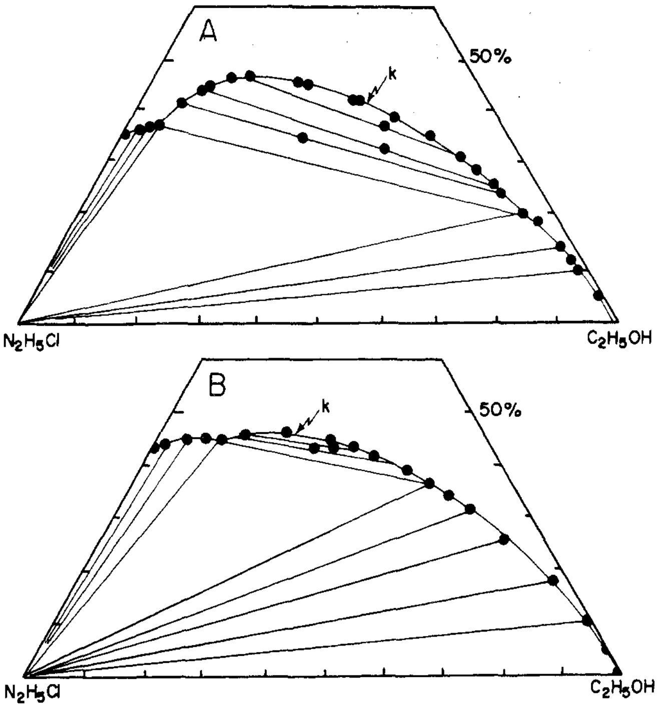

Figure 1. Isotherms of the system N_2H_5Cl-C_2H_5OH-H_2O
A. At 25° C., *B*. At 15° C., *k* = plait point

All values on the solubility curves are the average of three to six determinations with an average deviation of 0.14%. The method of locating the binodal curve rendered exact duplication difficult, but many points were determined which are not shown in the graphs or tables and all fell on a smooth curve. The plait point was estimated at each temperature using Heric's (*4*) modification of the Bachman equation (*1*). The method was demonstrated to apply to systems of alcohols and salts for which data already exist in the literature (*2*). The points plotted for the equation at 15° showed a slight curvature, so the location of the plait point at this temperature is subject to more uncertainty than at 25°.

RESULTS

The results are given in Table I and shown graphically in Figure 1. The binodal area at 15° C. is considerably smaller than at 25° C., indicating the probability of a lower critical point at which the binodal area disappears. The total area under the two curves is strikingly similar, the only major difference being a slight reduction in the over-all solubility of the salt in water at the lower temperature.

LITERATURE CITED

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Solid Hydrates of Some Halomethanes

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A NUMBER of nonpolar gases and volatile liquids which are relatively inert form solid hydrates that are stable over a range of temperature extending in some cases to well above 0° C. Such hydrates have a fairly uniform and reproducible composition and are clathrate compounds, with the volatile component included in interstices in a water framework, which bears some resemblance to the structure of ice. Hydrates of this type have been found to form, for example, at temperatures well above the freezing point of water in pipelines carrying natural gas.

In this work phase equilibria, composition, and crystal structure of hydrates formed by some fluoromethanes have been studied. Halogenated methanes are commonly used as refrigerants, and therefore a problem of hydrate formation in refrigeration systems arises. Furthermore, it has been proposed that cyclic formation and decomposition of gas hydrates may be a means of purification of saline water. Aside from the practical significance of these materials, there is probably a relation between the simple gas hydrates and more complex hydrates which occur in biological systems. The relations between properties of the hydrate former and the structure and stability of the resulting hydrate deserve further exploration.

The materials were obtained from commercial sources as Freons; they are also commercially available as Genetrons. Hydrates prepared were those of Freon 11, trichlorofluoromethane; Freon 12, dichlorodifluoromethane; Freon 13B1, bromotrifluoromethane; and Freon 22, chlorodifluoromethane. Some properties of each of these halomethanes are given in Table I, along with the composition of each hydrate as calculated from phase equilibrium data in the manner described below. Previously available information on the hydrates of these materials includes mention of the existence of hydrates of trichlorofluoromethane and of dichlorodifluoromethane by von Stackelberg (*13*), and some phase data at temperatures above 0° C. for the hydrates of trichlorofluoromethane, dichlorodifluoromethane, and chlorodifluoromethane by Chinworth and Katz (*2*).

EXPERIMENTAL PROCEDURE FOR PHASE STUDIES

Several batches of each Freon investigated were employed in making the hydrates. The purity of each batch was checked by vapor pressure measurements, and, when the need was indicated by the results, the material was fractionated through a vacuum-jacketed, low-temperature column.

The samples of hydrate were prepared in a cylindrical metal chamber, about 6 inches long by ½ inch i.d., or, with Freon 11, which has a low vapor pressure, in a similar vessel of glass. The sample chamber was connected to a manifold, to which were attached the container of Freon, a pressure gage, and a vacuum connection. Depending on the vapor pressures of the particular Freon and hydrate, gages of range 100 or 200 p.s.i., graduated in 1-pound increments, were used. For pressures below atmospheric, a mercury manometer was used.

The chamber was immersed in an agitated water bath, which was cooled by refrigeration coils; the temperature was regulated to within 0.1° C. by a thermostat. The temperature was measured with mercury thermometers, graduated in tenths, one with a range from -2° to 50° C., and another from -38° to 2° C. The thermometers were calibrated against thermometers from the National Bureau of Standards.

In forming the hydrate, a quantity of demineralized water was placed in the chamber, which was connected to the manifold and immersed in the water bath. The chamber was then evacuated and the appropriate Freon was allowed to condense into it. Each of the Freons was more dense than water and settled to the bottom of the chamber. The pressure of the system now corresponded very closely to the vapor pressure of the liquid Freon at the working temperature. Hydrate formation, which usually did not occur spontaneously, was initiated by allowing some of the liquid Freon to evaporate, either by opening the valve to the atmosphere or by applying suction. Thus hydrate was formed as the bubbles of gas rose through the aqueous layer. The pressure of the system then decreased, after which release of vapor was repeated, sometimes several times, followed by a period of equilibration, until a constant and reproducible pressure was obtained. If the pressure was lowered still further by release of vapor, a portion

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