Thermal Analysis of Systems of Hydrazine With Propyl Alcohol, Isopropyl Alcohol, and Allyl Alcohol

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INVESTIGATION of the systems hydrazine-methanol and hydrazine-ethyl alcohol by the method of thermal analysis showed that compound formation occurred in both systems (*1*). The phase diagram of the hydrazine-methanol system indicated formation of three addition compounds, $N_2H_4 \cdot CH_3OH$, $N_2H_4 \cdot 2CH_3OH$, and $N_2H_4 \cdot CH_3OH$, melting at −47.3°, −57.8°, and −69.5° C., respectively. The melting point of the 1 to 1 compound was incongruent. Hydrazine and ethyl alcohol exhibited less interaction; only one addition compound, $N_2H_4 \cdot 2C_2H_5OH$, melting at −31.2° C., was formed. The work described in the present report is a continuation of this study of systems of hydrazine with alcohols. The systems investigated were hydrazine with propyl alcohol, isopropyl alcohol, and allyl alcohol. Thermal analysis techniques were used and phase diagrams were constructed from the data thus obtained.

EXPERIMENTAL PROCEDURE

Materials. Anhydrous hydrazine was prepared as reported previously (*1*). Propyl alcohol (Eastman Kodak Co.) was dried first with magnesium sulfate and then was further dried by distillation over magnesium activated with iodine. The distilled material was fractionated through a 4-foot column packed with ⅛-inch glass helices and middle fractions were collected at a reflux ratio of 10 to 1. The purity was checked by determination of density and refractive index; values for the purified product were d_4^{20} 0.8040 and n_D^{20} 1.3860. Isopropyl alcohol (Baker and Adamson Co.) was refluxed with aluminum amalgam for 4 hours. It was then fractionated through the 4-foot column at a reflux ratio of 10 to 1, and middle fractions were collected. The purified material had a freezing point of −87.4° C., d_4^{20} 0.7852 and n_D^{20} 1.3771. Allyl alcohol (Fisher Scientific Co.) was fractionated through an 18-inch vacuum-jacketed column packed with ⅛-inch glass helices. The constant-boiling middle fractions were then distilled from freshly ignited potassium carbonate to ensure a throughly dry product. The density was d_4^{20} 0.8536.

After the materials were purified, all subsequent operations were carried out in a desiccator box in an atmosphere of dry nitrogen.

Apparatus and Melting Point Determinations. Freezing and melting points of the pure compounds and mixtures were determined in a cell similar to the one described previously (*1*). The temperature in the cell was measured with a calibrated copper-constantan thermocuple inserted into a well, which contained propyl alcohol as a thermal conducting medium. Thermocouple potentials during melting and freezing point determinations were read from recording potentiometers. For work on the systems hydrazine-propyl alcohol and hydrazine-isopropyl alcohol, an Elektronik recording potentiometer (Brown Co.) with a 1-μv. chart scale was used. In the study of the system hydrazine-allyl alcohol a Type G Speedomax recorder (Leeds and Northrup) in combination with a low-level direct current amplifier was employed. The amplifier made it possible to vary the scale on the Speedomax from 50 to 2000 μv. In most of the work the potentials were read to 1 μv. A portable precision potentiometer (Leeds and Northrup) was used as a zero point suppressor with both recorders.

The mixtures of hydrazine and the alcohols were prepared by direct weighing in the cell. The procedure for filling the cell was described previously (*1*). Attempts to determine freezing points from cooling curves gave widely scattered results because of the excessive supercooling which took place. Therefore, thermal analysis data were obtained from warming curves. In this procedure the mixture was frozen with constant stirring and approximate freezing point was noted. The cell assembly was then placed in a warming bath which was 5° to 10° C. above the freezing point, and the temperature was allowed to rise. A warming rate of 0.1° to 0.2° C. per minute was obtained. Stirring was continued during warming until the mixture was completely melted. This procedure gave reproducible warming curves from which points on and below the liquidus line could be determined.

RESULTS AND DISCUSSION

The phase diagram for the system hydrazine-propyl alcohol plotted from melting point composition data is shown in Figure 1. The system resembles the hydrazine-ethyl alcohol system in exhibiting one fairly weak addition compound, $N_2H_4 \cdot 2C_3H_7OH$. This compound melts at

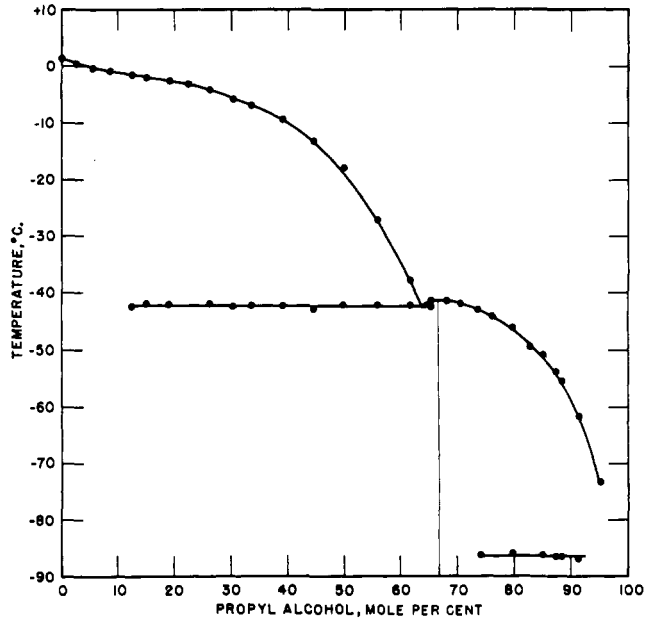

Figure 1. Melting point–composition diagram for the system hydrazine–propyl alcohol

−41.3° C.; the eutectic between hydrazine and the compound melts at −42.4° C. Attempts to freeze mixtures containing more than 94.9 mole % of propyl alcohol were unsuccessful. Glasses were formed in this region and melting points, therefore, could not be obtained. Similar results were obtained with pure material. Although a freezing point of −127° C. is given in the literature for propyl alcohol (*3*), present work indicates points on a eutectic line at about −86.5° C. This indicates that the

freezing point is probably higher than this latter figure.

The system hydrazine–allyl alcohol also forms a 1 to 2 addition compound as shown in the phase diagram (Figure 2). This compound, which melts at −68° C., is a weak addition compound as indicated by the comparatively flat maximum. The eutectic mixture of hydrazine and this compound contains 62 mole % of allyl alcohol and solidifies at -69° C. At concentrations of more than 90 mole % of allyl alcohol, glasses were formed when the mixtures were cooled. Such mixtures did not crystallize after standing for long periods at low temperatures, and efforts to obtain data in this region of the phase diagram were finally abandoned. Similarly, no freezing point could be obtained for pure alcohol. At allyl alcohol concentrations slightly below 90 mole %, breaks in the cooling curve indicated a eutectic between the 1 to 2 addition compound and allyl alcohol which froze at approximately −130° C.

The melting point–composition diagram for the system isopropyl alcohol–hydrazine (Figure 3) is more complex than of hydrazine with either propyl or allyl alcohol. In order to understand better the nature of the hydrazine–isopropyl alcohol system, a considerable number of points were determined under the liquidus curve. The horizontal lines from the two inflection points of the liquidus and from the eutectic approach the hydrazine side of the diagram. The behavior on warming frozen mixtures containing about 50 to 80 mole % of isopropyl alcohol were also observed visually, using clear Dewar flasks as containers for the warming baths. In the temperature range between the eutectic (−90° C.) and the lower inflection (−75° C.) such mixtures contained a white, crystalline solid phase and liquid. When the temperature of the lower inflection was reached, the white crystals disappeared and were replaced by liquid and a translucent solid phase. This solid phase was present in the liquid until the temperature of the upper inflection point (−66° C.) was reached. On the basis of the shape of the phase diagram alone, two possible interpretations are polymorphism of hydrazine, and formation of an incongruently melting compound (upper inflection) having an "inverse fusion" point (lower inflection). Although not reported previously,

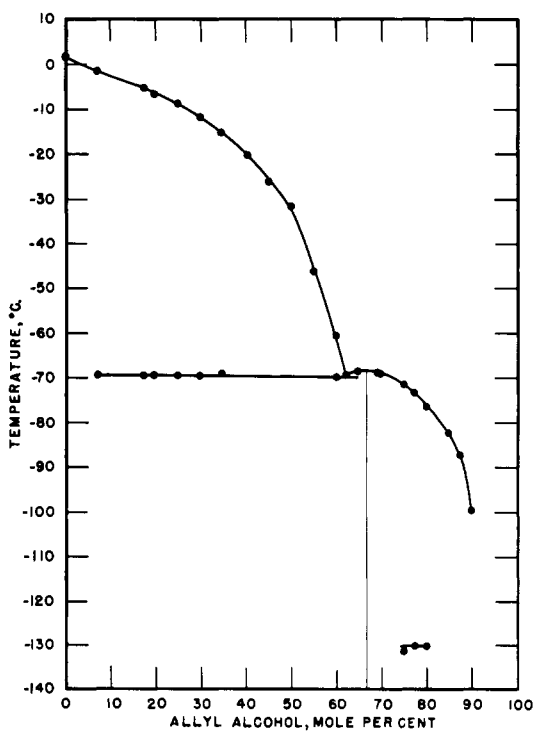

Figure 2. Melting point–composition diagram for the system hydrazine–allyl alcohol

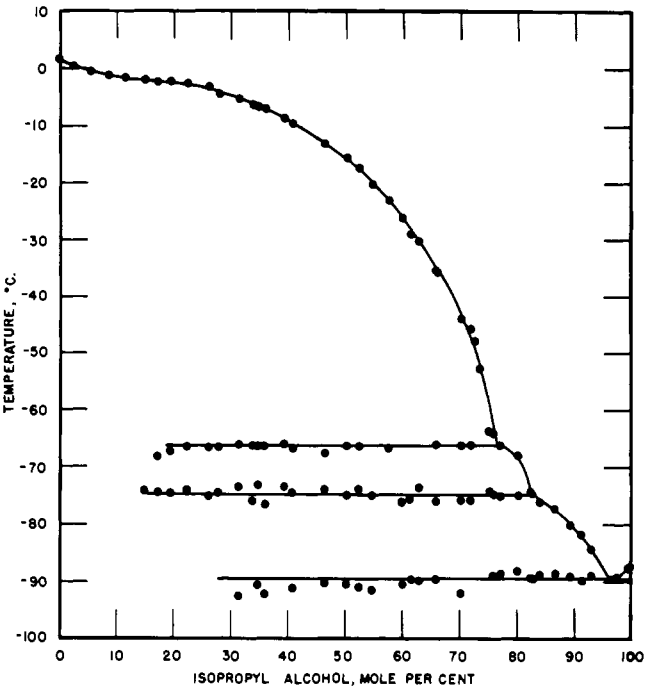

Figure 3. Melting point–composition diagram for the system hydrazine–isopropyl alcohol

polymorphism of hydrazine appears to be the better tentative explanation for inflections in the liquidus curve of this system. This is borne out by the presence of liquid phase over the temperature range −75° to −66° C. in mixtures containing less than 66.6 mole % of isopropyl alcohol. If a compound having an inverse fusion point were formed, only solid phase would be present in this region of the temperature-composition diagram. A number of attempts were made to identify, by isolation and analysis, the solid phases present in the midportion of the system. The technique employed was that used in the study of the hydrazine-methanol system (*1*). Because of the extremely high viscosity of the mixtures at low temperatures, however, the solid phases could not be satisfactorily separated from the liquid.

Of the binary systems containing hydrazine previously investigated, only two have liquidus curves extending as low as −66° C. in the absence of compound formation. One is the system hydrazine–allyl alcohol described in this report, and the other is the system hydrazine-ammonia studied by Friedrichs (*2*). In the former system no transition was observed at −66° C. This can probably be attributed to the proximity of the transition to the eutectic and the fact that warming curves were determined immediately after crystallization was complete. If the frozen mixture had been maintained below −66° C. for a relatively long period, the transition point might have been detected. In the case of the system hydrazine-ammonia, a replot of the data of Friedrichs shows a slight discontinuity in the liquidus curve in the neighborhood of −73° C. This inflection, although not pronounced, tends to corroborate the transition found at −75° C. in the present investigation.

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