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## Hydrazine-Water System: The Water-Rich Eutectic

Abstract. The melting point and composition of the water-rich eutectic of hydrazine and water have been determined by differential thermal analysis as  $193^{\circ} \pm 0.5^{\circ}$ K and  $27 \pm 1$  mole percent hydrazine, respectively.

The solid system, hydrazine-water, exhibits a monohydrate N<sub>2</sub>H<sub>4</sub> · H<sub>2</sub>O and two eutectic compositions. The monohydrate and the hydrazine-rich eutectic are easy to identify since crystallization in these composition ranges proceeds without difficulty. Their melting points have been reported as -51.7°C and  $-54^{\circ}$ C, respectively, and the eutectic composition as 69 percent of hydrazine by weight (55.6 mole percent) (1, 2). Mohr and Audrieth (1) did not report values for the water-rich eutectic because of the strong tendency of these solutions to become supercooled. Mohr and Audrieth's diagram, however, clearly showed the existence of the waterrich eutectic. Hill and Sumner (2) determined a series of liquidus points as functions of composition and, by extrapolation, arrived at -90°C for the melting point and 40.5 percent (27.7 mole percent) of hydrazine by weight as the probable temperature and composition of the water-rich eutectic.

We have crystallized a eutectic containing  $27 \pm 1$  mole percent of hydrazine melting at  $-80^{\circ} \pm 0.5^{\circ}$ C. Differential thermal analysis of other waterrich samples has confirmed this value. Crystallizable low-temperature glasses are characterized by a fairly reproducible temperature of spontaneous crystallization during warm-up. Mixtures of otherwise crystallizable compounds may

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have ranges of composition within which crystallization does not occur. In these cases the interpolated values of the spontaneous crystallization temperature overlap and eventually exceed the interpolated values of the melting points. However, we found that crystallization appeared to be possible at all compositions with this system if it was properly conditioned. Conditions that would induce crystallization were then investigated. A well-known, though not well-understood, behavior of some of these systems is their capacity to crystallize after appropriate cooling, warming, and cooling again (3). Suspecting that our system might behave in this way, we applied this technique and succeeded in obtaining a well-crystallized eutectic containing 27 mole percent of hydrazine. Crystallization was always induced after a second cooling from a temperature between the spontaneous crystallization (extrapolated from other compositions) and the eutectic melting point temperatures, but it never occurred during the warming up period of samples cooled from temperatures above the eutectic's melting point. The apparatus used consisted of a copper-constantan thermocouple assembly permitting the recording of the temperature difference between the sample and a reference body as a function of the reference body temperature.

The two samples were cooled and warmed up in a copper block that furnished a controlled homogeneous temperature. The samples were cooled by immersion in liquid nitrogen. The samples were warmed up at rates of the order of 3°K per minute between 77° and 200°K and lower near room temperature. The sample tubes were sealed test tubes with an inner, thin-walled capillary that housed the thermocouples and was filled with benzene to assure good thermal contact. The reference junction for measuring the reference body temperature was kept in liquid nitrogen. Benzene was used as the reference body since it does not exhibit any transformation at temperatures between that of liquid nitrogen and its melting point (5.51°C). The samples were prepared by weighing distilled water and hydrazine of reagent quality. The temperature difference was plotted against the reference temperature by means of an X-Y recorder having a sensitivity of 0.1 mv/in. (0.25 mv/cm) and 0.5 mv/in. (1.3 mv/cm) in the  $Y(T_s-T_R)$  and  $X(T_R)$  axes, respectively. Figure 1 shows the warm-up curve of a water-rich sample of 24.8 percent of hydrazine by weight (15.6 mole percent). The four stages represent (i) glass transformation, characterized by a change in specific heat; (ii) spontaneous crystallization, char-



Fig. 1. Differential thermal analysis warm-up recording of a 15.6 mole percent of hydrazine solution in water showing (i) the glass transformation at  $133 \,^{\circ}$ K, (ii) the spontaneous crystallization occurring at  $170 \,^{\circ}$ K, (iii) the solidus point at  $193 \,^{\circ}$ K, and (iv) the liquidus point at  $240 \,^{\circ}$ K.

acterized by a heat release; (iii) melting point of the eutectic, characterized by heat absorption at constant temperature; and (iv) melting point of the last solid fraction (liquidus point), above which there is a single, liquid phase. The figures obtained for the other points of the thermal diagram correspond in general with those quoted by previous investigators (1, 2).

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## Light Scattering by Liquids at 6937 Angstroms

Abstract. We report Rayleigh ratios at 6937 angstroms for nine organic liquids. The Rayleigh ratios of benzene, carbon tetrachloride, and normal octane are exactly those predicted from published data for ratios at shorter wavelengths and from the inverse fourth power of wavelength dependence of scattering.

We report what we believe to be the first measurements of Rayleigh scattering made by using red light. Past studies of Rayleigh scattering have been limited to relatively short wavelengths -that is, to the intense emission lines of mercury at 4358 and 5461 Å. Only a few measurements have been made at 3663, 4047, and 5791 Å. Masers provide both the means (intense, collimated sources) and the necessity for extending light-scattering studies to longer wavelengths. Use of light as a carrier in transmission will probably be limited ultimately by scattering at surfaces and by transmission media.

In the course of extending our studies of light scattering to longer wavelengths, we have measured Rayleigh ratios at 90° with vertically polarized light for nine organic liquids at 6937 Å by means of a pulsed, ruby maser. The Rayleigh ratio, an experimentally accessible measure of Rayleigh scattering, is given by

$$R(\theta) = i(\theta)r^{\theta}/I_{0}, \qquad (1)$$

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where  $R(\theta)$  is the Rayleigh ratio at angle  $\theta$  from an incident light beam of intensity  $I_0$  and  $i(\theta)$  is the intensity of light scattered at angle  $\theta$  and detected at a distance r from the center of the scattering (1, 2).

For these measurements we built a ratio photometer similar to those described in the literature (3), except that a pulsed, ruby maser served as a light source. No collimating system was necessary, photomultiplier tubes of the multi-alkali type (RCA 7265) detected scattered light and a portion of the incident beam, and a dual trace oscilloscope (with camera) measured photomultiplier currents as voltage drops across load resistors in the anode circuits of the photomultiplier tubes. The excellent collimation of the beam from the ruby maser (half a degree or less divergence), and our efforts to reduce stray reflections, edge scatter from slits, and surface scattering from the scattering cell and attenuators minimized background interference but did not eliminate the necessity for making a background correction  $(i/i_0)_{bkgd}$ . This correction must be subtracted from the apparent scattering,  $(i/i_0)_{solv}$ , of the light-scattering cell and the contained liquid to obtain the net scattering of the liquid alone  $[(i/i_0)_{solv} - (i/i_0)_{bkgd}]$ . We determined this background correction by making ten measurements of the apparent scattering from a rectangular prism of high quality, optical crown glass of the same square cross section as our light-scattering cells. High-quality glass does scatter light; therefore, if all of the apparent scattering from the glass is ascribed to stray reflections and surface scattering, an overestimate of the background correction should be obtained. However, we consider this overestimate to be very small, if not negligible, at 6937 Å. When another sample of the same glass was observed at 4358 Å without background scattering being taken into consideration (4), the amount of scatter was small compared to that from organic liquids. The scattering caused by glass and organic liquids may be expected to vary approximately as the inverse fourth power of wavelength, while stray reflections and surface scatter decrease but little with increasing wavelength. The background correction is about equal to the net scattering from normal octane, the liquid which caused the least scattering among those we measured. We calibrated our photometer by making three measurements of the apparent scatterings from each of six dilute solutions of a poly-



Fig. 1. Test of the dependence of scattering by carbon tetrachloride, normal octane, benzene, toluene, and carbon disulfide, on the inverse fourth power of wavelength (temperature  $25^{\circ}$ C).

styrene of known molecular weight in toluene, and by subtracting from each of them the mean of 52 measurements of the apparent scattering from an identical cell containing toluene. We calculated the excess turbidity (for solution minus solvent) due to the dissolved polymer (5). From these and our observed values for apparent scattering from the solutions minus the mean of the measurements of apparent scatterings from toluene, we calculated our calibration constant with an uncertainty of about 4.1 percent, as determined by standard deviations of the means of apparent scatterings, molecular weights of the polymer, and other parameters of Debye's equation for molecular weight and excess turbidity of a dissolved polymer (5).

Measured scattering ratios, background correction, and Rayleigh ratios at 90° for vertically polarized light,  $R_{\rm v}(90^{\circ})$ , are given in Table 1. In the case of toluene, where a large number of measurements were made, the principal contribution to the standard deviation of the Rayleigh ratio (which corresponds to 4.6 percent of the ratio) is from the standard deviation of the mean of the calibration measurements and calculated excess turbidities. In the cases of the other solvents we made too few measurements of apparent scattering to ascribe errors to sources other than our measurements of apparent scattering. Two sets of measurements of the Rayleigh ratio of normal octane, made on successive days, give what we believe is a maximum estimate of the uncertainty in our measurements. These are the smallest Rayleigh ratios observed. For these the background correction is slightly greater than the net scattering ratios from normal octane. Small changes in the system, such as

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