PARTIAL MOLAL VOLUMES IN THE SYSTEMS METHANOL-WATER AND NITROMETHANE-WATER AT 30°C

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INTRODUCTION

Hydrate formation and the phase relations in systems containing water and water-insoluble-methane derivatives have been under investigation in the Physical Chemistry Laboratories of the University of Oklahoma (Blankenship 1946, Sampson and Blankenship 1948). As a result it became of interest to investigate the changes in partial molal volumes in the water-rich region of complete miscibility. Of the various water-insoluble-methane derivatives known to form hydrates, nitromethane is the most soluble. For this reason it was chosen for study.

There was further interest attached to the water-nitromethane system. Wright, Murray-Rust, and Hartley (1931) reported that the viscosity behavior in this system is unique. The viscosity of water is increased by the addition of the less viscous nitromethane and the viscosity of nitromethane is decreased when more viscous water is added.

The partial molal volume of methanol in water solutions was determined by the method of graphical intercepts. In the nitromethane-water system, extrapolation to the intercept on the nitromethane axis is uncertain because of the narrow range of miscibility. For this reason the method based on a plot of the apparent molal volume of nitromethane against log n_2, where n_2 is the number of moles of nitromethane, was employed (Lewis and Randall 1923).

EXPERIMENTAL

To obtain densities, a 25-ml Gay-Lussac pyknometer was used. Temperature was controlled in a thermostatted bath set at 30° C by use of a conductance-cell thermometer, graduated to 0.1° C and readable to 0.05° C. The temperature did not vary more than 0.02° C as shown by a Philadelphia differential thermometer, which was graduated to 0.01° C. Solutions were mixed by weight using an analytical balance. The methanol was Baker's c. p. anhydrous and was used without further purification.

The densities found for methanol-water solutions at 30° are shown in Fig. 1. The literature contains data for 0°, 10°, and 20° C; these data have been plotted (Anonymous 1928) for comparison. Since our data at 30° C supplement these earlier values and appear to be consistent with them, we believe that the technique was satisfactory. The choice of 30° as a working temperature was influenced by convenience in thermostatting.

The nitromethane used was Eastman Kodak (impure) and was purified according to the method of Wright, Murray-Rust, and Hartley (1931), i. e., distillation through a two-foot column, refluxing with a stream of dry air for two hours, and a second distillation. These authors reported that nitromethane was soluble in water to the extent of ten percent by weight at 25° C and that water was soluble in nitromethane only to the extent of two percent by weight at 25° C. It was found that between eleven and twelve percent nitromethane is soluble in water at 30° C. Therefore, only a small range could be studied.

RESULTS

When the specific volume of methanol solution was plotted against weight percentage a smooth curve was obtained as shown in Fig. 2. The tangent at 50 percent methanol was found to have an intercept at 1.224 (which, when multiplied by the molecular weight of methanol, gave the value 39.22 for the partial molal volume). The tangent for the range from 0.0 to 10.0 percent methanol was approximately constant so that the partial molal volumes of

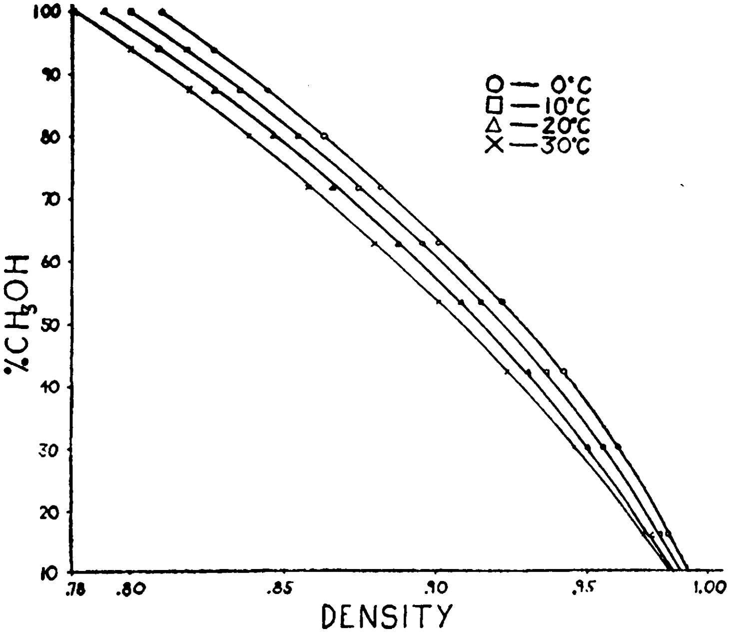

FIGURE 1

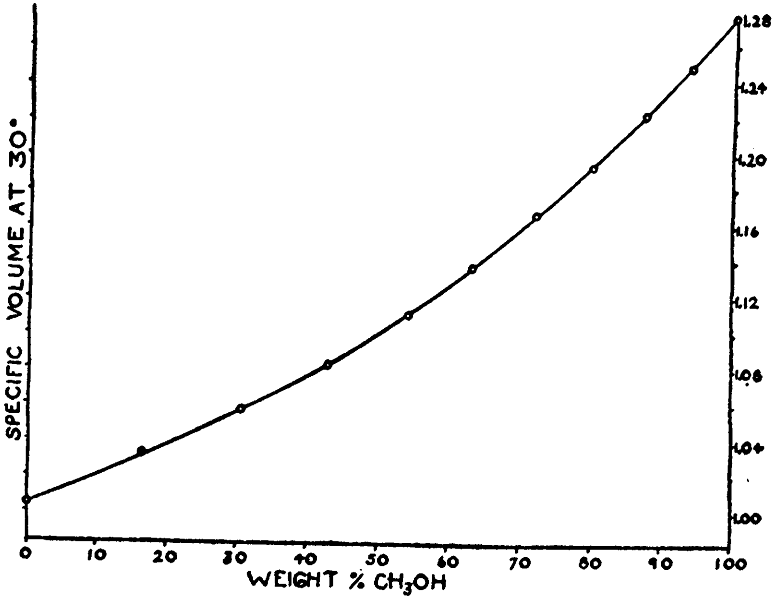

FIGURE 2

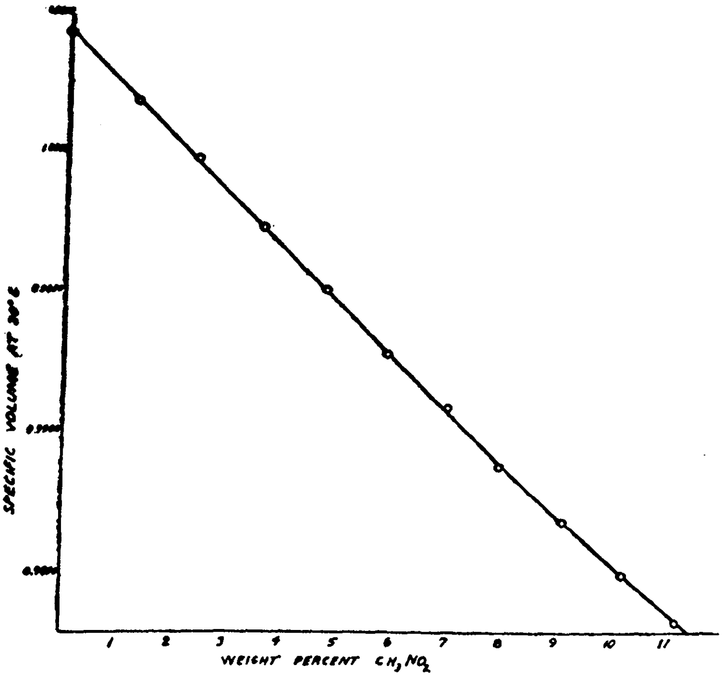

FIGURE 3

both water and methanol were constant throughout this concentration range. Other values are given in Table I.

TABLE I

Wt. % CH_3OH	Tangent intercept H_2O (ml/g)	Tangent intercept CH_3OH(ml/g)	Partial molal volume H_2O(ml)	Partial molal volume CH_3OH(ml)
20	1.002	1.180	18.036	37.81
50	0.978	1.224	17.62	39.22
80	0.900	1.264	16.22	40.50

When the specific volumes of the nitromethane-water system were plotted against weight percent as in Fig. 2 the curve was best represented by two straight lines of slightly different slope. The tangents thus lay on these lines and the intercepts multiplied by the molecular weight gave the partial molal volumes, which were constant on either side of the discontinuity at 8.5 percent. However, extrapolation to the nitromethane axis involved a magnification of any error by more than tenfold. For this reason average values for specific volume were taken from the curve in Fig. 3, and the values of the apparent molal volume calculated therefrom were plotted against the log n_2 as shown in Fig. 4. Tangents to the curve in Fig. 4 were drawn and the value of the slopes added to the ordinates at which the tangents were drawn. The resulting values for the partial molal volumes were plotted against mole percentage of nitromethane as shown in Fig. 5. The curve obtained has two horizontal portions reflecting the fact that the partial molal volume is constant over two ranges with a break between the two. The rounding off of the curve is due to limitations of the graphical method. The value for the partial molal volume of nitromethane calculated from the specific-volume—

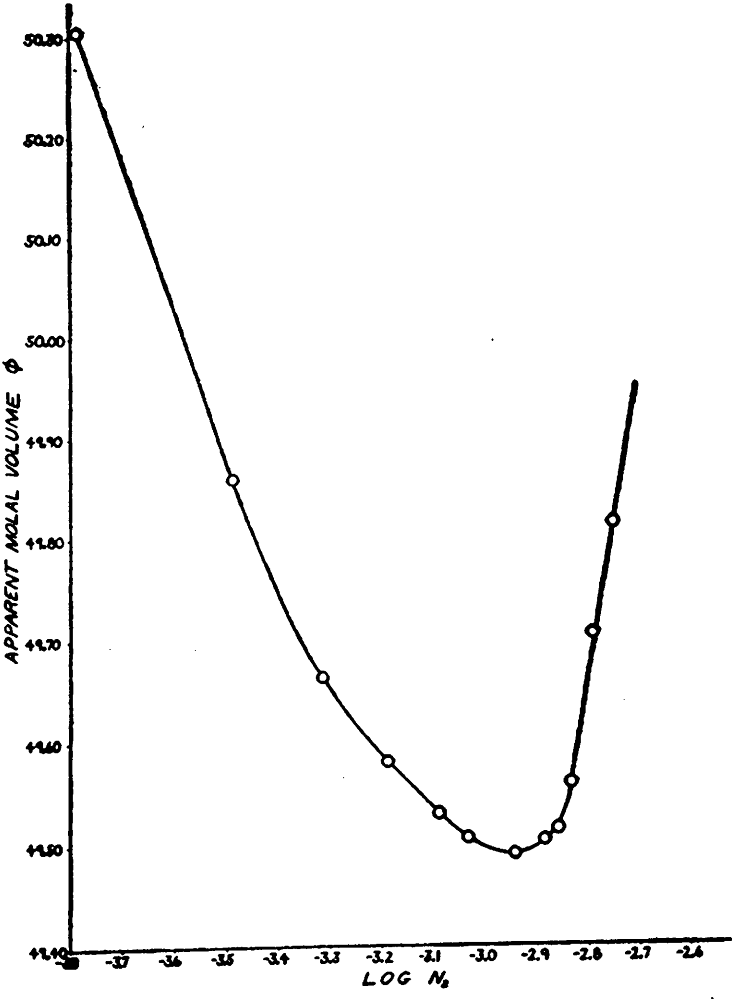

FIGURE 4

weight-percentage curve is shown on the water axis and corresponds to the lower of the two flat portions of the curve in Fig. 5.

SUMMARY

The partial molal volumes for both methanol and water in their solutions at 30° C have been obtained.

The partial molal volume of nitromethane in water at 30° has been obtained for the range 0.0 to 11 percent by weight of nitromethane. This corresponds to a range of 0.0 to 3.6 mole percent. From 0.0- to 2.0-mole percent of nitromethane, the partial molal volume is 49.33 ± 0.03 ml. From 2.0-mole percent on to the limit of miscibility, the value is 51.0 ± 0.1 ml.

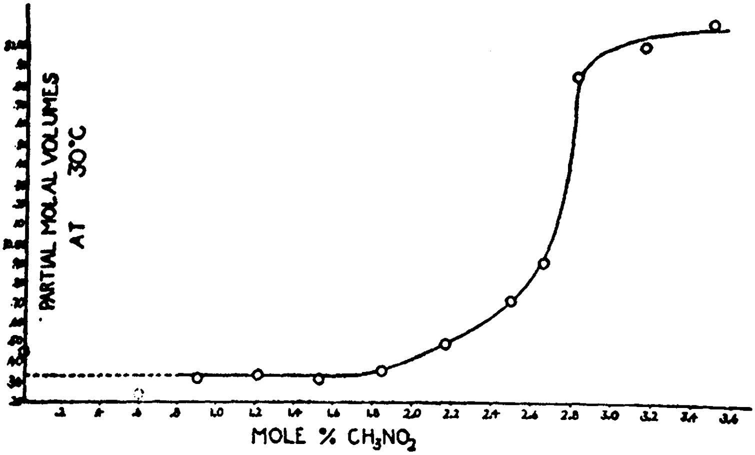

FIGURE 5

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