EXCESS MOLAR VOLUMES OF MIXING OF SOLUTIONS OF NITROMETHANE AND CARBON TETRACHLORIDE

JOHN F. WETTAW AND BORIS MUSULIN
Department of Chemistry,
Southern Illinois University,
Carbondale, Illinois 62901

ABSTRACT.—The direct measurement, by means of weight and density measurements, of the excess molar volume of mixing in solutions of nitromethane and carbon tetrachloride at 35°C. is described. The data confirm the quadratic nature of deviations from ideality for these solutions.

Gunter *et al.* (1967) have reported values of excess molar volumes of mixing of binary solutions of CH_3NO_2 and CCl_4 which were derived from measured densities assuming that the molar volumes of mixing of ideal solutions were additive. Although the reported values are consistent in functional form and magnitude with those reported by Brown and Smith (1955), they appear to be of lesser quality. The purpose of this investigation is to ascertain if directly measured values, from a simple experiment, are of better quality than derived values.

EXPERIMENTAL

Fisher Spectrograde nitromethane and carbon tetrachloride were used without further purification. Temperature, specific gravity, and weight measurements were made as described in Gunter *et al.* (1967). A temperature of 35°C. was used in this work. Two sets of pipets, one for CH_3NO_2 and one for CCl_4, each containing a 25-ml, a 10-ml, and a 5-ml pipet, were calibrated by weight techniques. Of the seven physically independent permutations that can be made by mixing a pipetful from each set, four were used to make the sample solutions whose weights were determined directly. The solution densities were measured directly and the solution volumes calculated from these densities and weights. The densities of the pure components used in calibration were taken from Gunter *et al.* (1967). The excess molar volumes of mixing were obtained by differences of the measured volumes.

RESULTS AND DISCUSSION

All measured and calculated values are given in Table 1. The mole fraction values for each solution are at least one magnitude more reliable than those given by Gunter *et al.* (1967). In calculations, the mole fraction was used, as reported, with four significant figures.

The measured solution densities are compared to values calculated from the density-mole fraction function derived by Musulin (1971).

TABLE 1.—Densities and Molar Volumes of Mixing of Nitromethane-Carbon Tetrachloride Solutions

Mole Fraction (CH_3NO_2)	Density (g/ml)	Calculated Density[a] (g/ml)	Molar Volume of Mixing (ml/mole)	Calculated Molar Volume of Mixing[a] (ml/mole)	Additive Molar Volume of Mixing (ml/mole)
0.4174	1.43137	1.43479	0.2064	0.1990	0.2404
0.6414	1.33347	1.33201	0.2088	0.1925	0.2465
0.8178	1.23861	1.23410	0.1078	0.1189	0.1652
0.8989	1.18568	1.18408	0.06250	0.07192	0.04940

a. Musulin (1971)

The maximum difference is 0.0045 g/ml. i.e. 0.36%. Excluding pure experimental error, two reasons may be given for the variation. First, Musulin derived the function using lesser quality mole fraction data, e. g. the 0.8989 mole fraction CH_3NO_2 solution of the present work would have been reported as 0.900 mole fraction CH_3NO_2 in the earlier work. Second, the temperature variation (inherent in the Musulin function) which was allowable with lesser quality mole fraction data becomes a controlling factor in the present investigation. Nevertheless, it is clear that the present densities are in good agreement with the earlier work.

The measured excess molar volumes of mixing are compared to values calculated from the excess molar volume of mixing-mole fraction function derived by Musulin (1971) and to values calculated assuming additivity of molar volumes for ideal solutions as was done by Gunter *et al.* (1967). The measured values are in good agreement with those calculated by the Musulin function. The deviations were about 0.01 ml. As before, these variations could be attributed to mole fraction and temperature measurements. The increased magnitude of the variation could be attributed to the fact that excess molar volume of mixing is a difference quantity. Comparison to the values obtained from the additivity assumption indicates that values obtained by that assumption are overstated in the middle of the mole fraction range. The existence of this error introduces another error in the function derived by Musulin and establishes the final reason for the greater deviations from calculated values with excess molar volumes of mixing compared to the deviations with densities.

These new, accurate measurements confirm the quadratic form and the magnitude of the deviation from ideality of solutions of CH_3NO_2 and CCl_4. The weight techniques presented in this work provide a meaningful way to obtain better quality data than that obtained by Gunter *et al.* (1967) and is an appropriate compromise if the vapor density equipment is not available. Finally, the present results emphasize the necessity of utilizing an excess type equation for the excess molar volumes of mixing for CH_3-NO_2-CCl_4 solutions as opposed to utilization of a simple additive assumption.

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