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Excess Volumes of 1,4-Dioxane + Ethane-1,2-diol at 298.15 K

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Excess molar volumes of the 1,4-dioxane + ethane-1,2-diol liquid mixture were measured at 298 K using a dilution dilatometer. The observed composition dependence does not confirm the W-shaped form as suggested by some other data published in the literature.

Introduction

The W-shaped concentration dependencies of excess molar volumes of binary liquid mixtures are unusual (Hnědkovský et al., 1990). Excess molar volumes calculated from the density data for the 1,4-dioxane + ethane-1,2-diol mixture in the temperature interval 288.15–353.15 K (with 5 K increments for nine mixtures) recently published by Corradini et al. (1993) indicate that this mixture might be an example of the mixture which shows this rare composition dependence. There are at least two more density measurements published in the literature for this system by Schkodin et al. (1980) and Wang (1940). Excess volumes calculated from the densities of Wang (1940) at 288.15 and 303.15 K are negative and exhibit a nearly symmetrical composition dependence, and this is in contradiction to the values by Corradini et al. (1993). Schkodin et al. (1980) measured densities of the mixture in the temperature interval from 278.15 to 318.15 K but did not report densities for the pure components. Excess volumes calculated from their mixture data using pure component densities taken from the literature are scattered and, due to the absence of original pure component densities, are not reliable for a comparison. This discrepancy has prompted us to measure the excess volumes using a precise dilatometric technique with the aim to determine whether the composition dependence is W-shaped.

Experimental Section

1,4-Dioxane ($C_4H_8O_2$, R.P.H., Poland) was refluxed with concentrated hydrochloric acid for 4 h and then with metallic sodium and traces of diphenyl ketone until the color turned blue (this shows absence of water). The amount of 1,4-dioxane needed for the measurement was rectified and degassed by boiling for a short time immediately before the measurements. Ethane-1,2-diol ($C_2H_6O_2$, Lachema, Pure) was dried with anhydrous sodium sulfate, distilled under reduced pressure, and stored over molecular sieves (4A). An oil vacuum pump was used to degas the sample (at about 333 K) prior to measurements. The densities of pure liquids measured at 298.15 K using the bicapillary pycnometer agreed well with the literature data: 1.027 98 ± 0.000 05 $g{\cdot}cm^{-3}$ for 1,4-dioxane (Riddick et al., 1986, 1.027 97 $g{\cdot}cm^{-3}$), 1.109 51 ± 0.000 05 $g{\cdot}cm^{-3}$ for ethane-1,2-diol (Riddick et al., 1986, 1.1100 $g{\cdot}cm^{-3}$). Excess volumes were measured using the tilting dilution dilatometer (Cibulka and Holub, 1981) immersed in a water-bath thermostat adjusted to 298.15 ± 0.02 K and with a temperature stability of ±1 mK. The uncertainty in the excess volume was estimated to be about ±0.002 $cm^3{\cdot}mol^{-1}$. The density of the mixture containing 47.53 mol % of 1,4-dioxane was measured by means of a vibrating-tube densitometer (Anton Paar DMA 45 calibrated with air and redistilled water) to verify the excess volumes obtained from the dilatometric measurements. The densities of pure dioxane and ethane-1,2-diol determined by the vibrating-tube densitometer were 1.0280 ± 0.0002 and 1.1098 ± 0.0002 $g{\cdot}cm^{-3}$, respectively. These values were used to calculate the excess volume of this mixture (see Table 1).

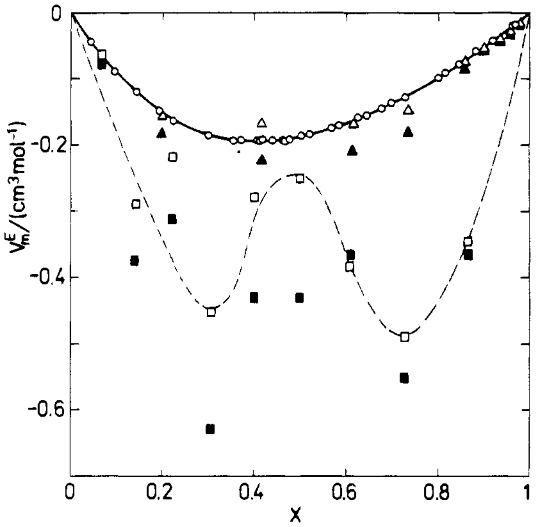

Figure 1. Plot of the excess molar volume for (*x*)1,4-dioxane + (1 − *x*)ethane-1,2-diol: (○) this work, 298.15 K; (△) Wang (1940), 288.15 K; (▲) Wang (1940), 303.15 K; (□) Corradini et al. (1993), 298.15 K; and (■) Corradini et al. (1993), 343.15 K.

Results and Discussion

The measured excess volumes are presented in Table 1 and plotted in Figure 1 along with selected values from the literature. The equation

$$V_m^E/(cm^3{\cdot}mol^{-1}) = x(1-x)[A_0 + A_1(1-2x) + A_2(1-2x)^2 + A_4(1-2x)^4]$$

with $A_0 = -0.7448 \pm 0.0013$, $A_1 = -0.2868 \pm 0.0029$, $A_2 = -0.1445 \pm 0.0167$, $A_4 = 0.127 \pm 0.029$ was fitted to the experimental values with a standard deviation $\sigma(V_m^E) = 0.0010$ $cm^3{\cdot}mol^{-1}$. The observed composition dependence

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Table 1. Experimental Excess Molar Volumes, V_m^E of the $xC_4H_8O_2 + (1 - x)C_2H_6O_2$ Mixture at 298.15 K

x	V_m^E ($cm^3 \cdot mol^{-1}$)	x	V_m^E ($cm^3 \cdot mol^{-1}$)	x	V_m^E ($cm^3 \cdot mol^{-1}$)	x	V_m^E ($cm^3 \cdot mol^{-1}$)
0.0437	−0.0444	0.4041	−0.1931	0.5188	−0.1829	0.8010	−0.0990
0.0962	−0.0886	0.4071	−0.1941	0.5683	−0.1735	0.8129	−0.0911
0.1432	−0.1205	0.4178	−0.1923	0.5841	−0.1699	0.8432	−0.0773
0.1928	−0.1482	0.4380	−0.1935	0.6267	−0.1581	0.8816	−0.0578
0.2230	−0.1626	0.4572	−0.1909	0.6439	−0.1547	0.9170	−0.0422
0.2994	−0.1853	0.4645	−0.1927	0.6774	−0.1440	0.9606	−0.0180
0.3520	−0.1927	0.4753	−0.1898[a]	0.6990	−0.1368	0.9664	−0.0182
0.3691	−0.1925	0.5013	−0.1852	0.7278	−0.1269		

[a] Measured by Anton Paar DMA 45 vibrating-tube densitometer. The density of this mixture was 1.0650 ± 0.0002 $g \cdot cm^{-3}$, the corresponding uncertainty in excess volume is about ± 0.015 $cm^3 \cdot mol^{-1}$.

at 298.15 K shown in Figure 1 is similar to the results of Wang (1940), i.e., a nearly symmetrical curve slightly skewed toward lower mole fractions of 1,4-dioxane. It is difficult to explain the large deviations in excess volumes of Corradini et al. (1993) from the present results or those of Wang (1940). The densities of Corradini et al. (1993) were presented as smoothed, probably over the temperature range for each of nine mixtures measured. The excess volume for each temperature follow the same pattern (in Figure 1 the values of Corradini et al. (1993) for two temperatures are shown), and therefore it is likely that large deviations of excess volumes might be due to large uncertainties in the composition of the mixtures. The sensitivity of excess volume to composition uncertainty (dV_m^E/dx), at 298.15 K lies between −6.3 $cm^3 \cdot mol^{-1}$ (as $x \rightarrow 0$) and +4.4 $cm^3 \cdot mol^{-1}$ (as $x \rightarrow 1$). A difference in excess volume of 0.2 $cm^3 \cdot mol^{-1}$ (an average difference between our results and the data of Corradini et al. (1993)) could be explained by an error of 0.04 in mole fraction.

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