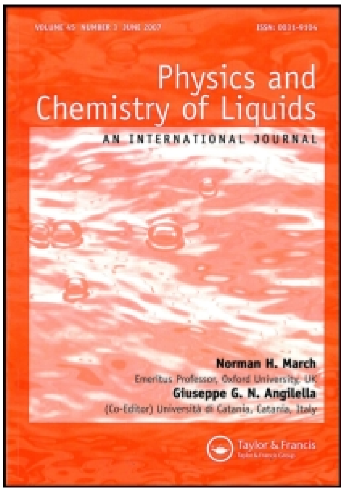

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THERMODYNAMIC PROPERTIES OF NONELECTROLYTE SOLUTIONS: PART 2. EXCESS MOLAR VOLUMES OF BINARY MIXTURES CONTAINING 1,1-OXYBISBUTANE

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Excess molar volumes of binary 1,1-oxybisbutane + *n*-heptane, 1,1-oxybisbutane + cyclohexane, 1,1-oxybisbutane + *n*-octane, 1,1-oxybisbutane + chlorobenzene and 1,1-oxybisbutane + 2,2,4-trimethylpentane mixtures have been measured at 298.15 K. For the first three systems, $\bar{V}_m^E$ is positive throughout the entire concentration range. $\bar{V}_m^E$ is negative for binary mixtures containing 1,1-oxybisbutane with chlorobenzene and 2,2,4-trimethylpentane.

KEY WORDS: Binary systems, molar volumes, vibrating-tube densimeter.

INTRODUCTION

As part of a continuing study on the thermochemical behavior of nonelectrolyte solutions, we have previously derived expressions for predicting excess molar volumes of both noncomplexing[1,2]

$$\bar{V}_m^E = (x_A + x_B)(f_A + f_B)(\bar{V}_{mAB}^E)^* + (x_A + x_C)(f_A + f_C)(\bar{V}_{mAC}^E)^* \\ + (x_B + x_C)(f_B + f_C)(\bar{V}_{mBC}^E)^* \tag{1}$$

and complexing systems containing a single AB molecular complex[3,4]

$$A_1 + B_1 \rightleftharpoons AB \qquad K_{AB}^x = \hat{x}_{AB}/(\hat{x}_{A_1}\hat{x}_{B_1})$$

$$\bar{V}_m^E = \frac{\hat{x}_{A_1}\hat{x}_{B_1}K_{AB}^x\Delta_r V_{AB}^0}{1 + K_{AB}^x\hat{x}_{A_1}\hat{x}_{B_1}} + (x_A\Gamma_A + x_B\Gamma_B + x_C\Gamma_C)f_Af_BB_{A_1B_1} \\ + (x_A + x_C)(f_A + f_C)(\bar{V}_{mAC}^E)^* + (x_B + x_C)(f_B + f_C)(\bar{V}_{mBC}^E) \tag{2}$$

from measured binary $(\bar{V}_{mij}^E)^*$ data, which are determined at mole fraction compositions $x_i^* = 1 - x_j^* = x_i/(x_i + x_j)$. In Eqs. 1 and 2 $\Delta_r V_{AB}^0$ refers to the standard

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molar colume change for AB complex formation, $B_{A_1B_1}$ denotes a volumetric binary interaction parameter for the AB sub-binary system, and f_i is the weighted mole fraction composition of component i, *i.e.*, $f_i = x_i\Gamma_i/(\sum x_j\Gamma_j)$. The caret ($\wedge$) indicates that the compositions refer to the associated solution, rather than the stoichiometric concentrations. The weighting factors (Γ_i) are used in describing the probability that two molecules interact in solution, and represent a rough measure of the skew of the binary excess property from a symmetric curve with an extremum at the equimolar composition. Several methods[1,5] have been suggested for the evaluation of these weighting factors from the thermodynamic properties of binary mixtures.

Past studies have documented that predictive expressions, such as Eqs. 1 and 2 and others[1,6–9], provide very reasonable estimates of $\bar{V}_m^E$ (and also $\bar{H}_m^E$ for a large number of ternary systems. Application of these equations is limited; however, to systems for which one knows *a priori* the volumetric (enthalpic in the case of $\bar{H}_M^E$) behavior of all contributing subbinary systems. To expand the available data base, we report in this communication the excess volumes of binary 1,1-oxybisbutane + chlorobenzene, 1,1-oxybisbutane + *n*-heptane, 1,1-oxybisbutane + *n*-octane, 1,1-oxybisbutane + 2,2,4-trimethylpentane and 1,1,-oxybisbutane + cyclohexane mixtures at 298.15 K.

EXPERIMENTAL

Chlorobenzene (Aldrich HPLC, 99.9 + %), *n*-heptane (Aldrich HPLC, 99 + %), cyclohexane (Aldrich HPLC, 99.9 + %). *n*-octane (Aldrich, 99 + % anhydrous), 2,2,4-trimethylpentane (Aldrich HPLC, 99.7 + %) and 1,1,-oxybisbutane (Aldrich, 99 + % anhydrous) were stored over molecular sieves to remove trace amounts of water. Gas chromatographic analysis showed solvent purities to be 99.8% (or better), which is well within the manufacturer's stated claims. Binary solvent mixtures were prepared by weight so that concentrations could be calculated to 0.0001 mole fraction.

Densities were measured with an Anton PAAR DMA 55 calculating precision density meter thermostated with a Neslab closed-loop refrigerating constant temperature bath. The reproducibility of the programmable circulating thermostat was better than 0.005 K while fluctuations in the bath temperature were within 0.003 K during the actual time required for each series of measurements. Samples were pre-equilibrated in the temperature bath for over 30 minutes and then introduced into the vibrating densimeter tube *via* a glass syringe. One of the pure solvents was run between each binary mixture, and the measured density for the pure liquid was used in $\bar{V}^E$ calculations for the preceding binary mixture. This procedure was found to correct for slow drifts in the vibrating-tube frequency and improve the reproducibility of the $\bar{V}^E$ measurements. Picker *et al.*[10] describe the mechanical design and precision of vibrating-tube densimeters, as well as the calculational methods, in greater detail.

Table 1 Excess molar volumes of several binary mixtures containing 1,1-oxybisbutane at 298.15 K.

x_A	$\bar{V}_m^E(cm^3\ mol^{-1})$	x_A	$\bar{V}_m^E(cm^3\ mol^{-1})$
Chlorobenzene (*A*) + 1,1-Oxybisbutane (*B*)			
0.1693	−0.309	0.7115	−0.492
0.3029	−0.473	0.7924	−0.409
0.4232	−0.559	0.8649	−0.291
0.5306	−0.571	0.9333	−0.156
0.6280	−0.548		
$v_{AB}^{(0)} = -2.30203$	$v_{AB}^{(1)} = -0.26072$	$v_{AB}^{(2)} = -0.09734$	
$v_{AB}^{(3)} = 0.11831$	Dev.[a] = 0.004		
1,1-Oxybisbutane (*A*) + *n*-Heptane (*B*)			
0.0939	0.025	0.5656	0.074
0.1831	0.050	0.6669	0.062
0.2755	0.064	0.7714	0.048
0.3661	0.073	0.8812	0.029
0.4646	0.075		
$v_{AB}^{(0)} = 0.30429$	$v_{AB}^{(1)} = -0.03153$	$v_{AB}^{(2)} = -0.02514$	
Dev.[a] = 0.002			
1,1-Oxybisbutane (*A*) + 2,2,4-Trimethylpentane (*B*)			
0.1030	−0.030	0.5942	−0.090
0.2014	−0.056	0.6876	−0.088
0.3008	−0.073	0.7911	−0.070
0.3961	−0.086	0.8931	−0.035
0.4912	−0.090		
$v_{AB}^{(0)} = -0.37576$	$v_{AB}^{(1)} = -0.04467$	$v_{AB}^{(2)} = 0.02816$	
Dev.[a] = 0.003			
1,1-Oxybisbutane (*A*) + Cyclohexane (*B*)			
0.0713	0.154	0.4876	0.393
0.1429	0.262	0.5890	0.356
0.2193	0.339	0.7119	0.275
0.2991	0.384	0.8435	0.170
0.3886	0.409		
$v_{AB}^{(0)} = 1.55357$	$v_{AB}^{(1)} = -0.60628$	$v_{AB}^{(2)} = 0.31873$	
Dev[a] = 0.002			
1,1-Oxybisbutane (*A*) + *n*-Octane (*B*)			
0.1080	0.074	0.5930	0.129
0.1965	0.099	0.6906	0.110
0.2925	0.121	0.7914	0.074
0.3867	0.137	0.8865	0.045
0.4882	0.139		
$v_{AB}^{(0)} = 0.53922$	$v_{AB}^{(1)} = -0.16770$	$v_{AB}^{(2)} = 0.07888$	
Dev.[a] = 0.004			

[a] Dev. $= (1/N) \sum_{i=1}^{N} |(\bar{V}_m^E)_i^{calc} - (\bar{V}_m^E)_i^{exp}|$.

RESULTS AND DISCUSSION

Experimental excess molar volumes of the five binary systems are tabulated in Table 1, along with the coefficients and average absolute deviations (Dev.) for

$$\bar{V}_m^E = x_A x_B \sum_{i=0}^{n} v_{AB}^{(i)}(x_A - x_B)^i \tag{3}$$

which is the Redlich–Kister representation. Measurements at each composition were performed in triplicate to insure that the $\bar{V}^E$ data was correct and reproducible. Based upon replicate determinations, we believe that the experimental uncertainty is on the order of ±0.01 (or less) for the larger $\bar{V}_m^E$ values.

Chemical impurities could conceivably result in a systematic error which would not be detected in the replicated measurements. As argued by Lepori *et al.*[11] in an investigation on sources of errors in $\bar{V}_m^E$, purity of substances is not a crucial factor if the contaminant is non-reactive. In the simple case of a mixture of components A and B, obeying an one-parameter equation of the $\bar{V}_m^E = x_A x_B v_{AB}$ type, the effect of a single impurity (component C) contaminating component A can be evaluated through:

$$\delta \bar{V}_m^E / \bar{V}_m^E = (1 - P_A)(v_{BC} - v_{AC} P_A - v_{AB})/v_{AB} \tag{4}$$

where P_A is the degree of purity (in mole fraction) of component A, and v_{ij} is the parameter for mathematically describing $\bar{V}_{mij}^E$. Generally, an impurity is chemically very similar to the contaminated solvent, *i.e.*, $v_{AB} \approx v_{AC}$ and $v_{AC} < v_{AB}$, so that the systematic error in $\bar{V}_m^E$ is less than $(1 - P_A)$, or less than ±1% in the present study. A further indication of the experimental error can be gained by comparing our experimental $\bar{V}_m^E$ data for 1,1-oxybisbutane (A) + cyclohexane (B) system to published values found in the chemical literature. Excess molar volumes back-calculated with Redlich–Kister parameterization reported by Berti *et al.*[12]

$$\bar{V}_m^E = x_A x_B[1.5373 - 0.6231(x_A - x_B) + 0.2605(x_A - x_B)^2 - 0.0724(x_A - x_B)^3] \tag{5}$$

differ from the values listed in Table 1 by an average deviation of less than 0.007 $cm^3 mol^{-1}$.

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