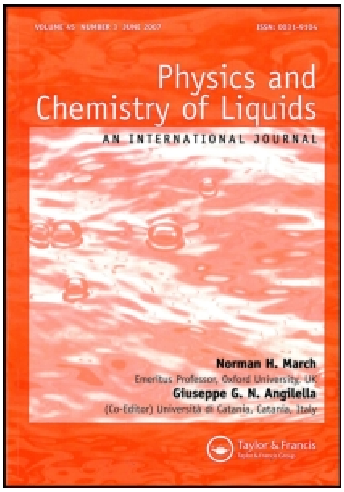

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Thermodynamic Properties of Nonelectrolyte Solutions: Part 1. Excess Molar Volumes of Binary Mixtures Containing Chlorobenzene

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To cite this Article Teng, I. Lih and Acree Jr., William E.(1992) 'Thermodynamic Properties of Nonelectrolyte Solutions: Part 1. Excess Molar Volumes of Binary Mixtures Containing Chlorobenzene', Physics and Chemistry of Liquids, 25: 1, 1 — 5

To link to this Article: DOI: 10.1080/00319109208027281
URL: http://dx.doi.org/10.1080/00319109208027281

Phys. Chem. Liq., 1992, Vol. 25, pp. 1–5
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THERMODYNAMIC PROPERTIES OF NONELECTROLYTE SOLUTIONS: PART 1. EXCESS MOLAR VOLUMES OF BINARY MIXTURES CONTAINING CHLOROBENZENE

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(Received 7 January 1991)

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

KEY WORDS: Lone pairs, aromatic π-electrons, binary mixtures, excess volumes

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]

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

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

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

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

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 Eqns. 1 and 2 $\Delta_r V_{AB}^0$ refers to the standard

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molar volume 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 (ˆ) 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 Eqns. 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 cyclohexane + chlorobenzene, *n*-heptane + chlorobenzene, *n*-octane + chlorobenzene, 2,2,4-trimethylpentane + chlorobenzene and 1,1-oxybisbutane + chlorobenzene mixtures at 298.15 K.

EXPERIMENTAL

Chlorobenzene (Aldrich HPLC, 99.9+%), *n*-heptane (Aldrich HPLC, 99.9+%), cyclohexane (Aldrich HPLC, 99+%), *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 a 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 chlorobenzene 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		
$v_{AB}^{(0)} = -2.3023$	$v_{AB}^{(1)} = -0.26072$	$v_{AB}^{(2)} = -0.09734$	
$v_{AB}^{(3)} = 0.11831$	Dev.[a] = 0.004		
Chlorobenzene (A) + *n*-Heptane (B)			
0.1455	−0.068	0.6841	−0.261
0.2709	−0.140	0.7672	−0.218
0.3856	−0.204	0.8462	−0.177
0.4875	−0.252	0.9245	−0.096
0.5891	−0.271		
$v_{AB}^{(0)} = -1.01658$	$v_{AB}^{(1)} = -0.51992$	$v_{AB}^{(2)} = 0.17223$	
$v_{AB}^{(3)} = -0.07147$	Dev.[a] = 0.004		
Chlorobenzene (A) + 2,2,4-Trimethylpentane (B)			
0.1632	−0.147	0.7108	−0.323
0.2983	−0.226	0.7910	−0.285
0.4174	−0.303	0.8621	−0.236
0.5243	−0.341	0.9309	−0.119
0.6217	−0.344		
$v_{AB}^{(0)} = -1.31354$	$v_{AB}^{(1)} = -0.65927$	$v_{AB}^{(2)} = -0.22488$	
$v_{AB}^{(3)} = 0.30419$	Dev.[a] = 0.005		
Chlorobenzene (A) + Cyclohexane (B)			
0.1123	0.186	0.6169	0.273
0.2139	0.283	0.7052	0.208
0.3105	0.321	0.8036	0.148
0.4108	0.340	0.9054	0.063
0.5150	0.315		
$v_{AB}^{(0)} = 1.27670$	$v_{AB}^{(1)} = -0.59665$	$v_{AB}^{(2)} = 0.06735$	
$v_{AB}^{(3)} = -0.18396$	Dev.[a] = 0.003		
Chlorobenzene (A) + *n*-Octane (B)			
0.1595	0.006	0.7082	−0.083
0.2920	−0.008	0.7879	−0.083
0.4130	−0.031	0.8630	−0.068
0.5119	−0.055	0.9340	−0.043
0.6127	−0.072		
$v_{AB}^{(0)} = -0.20126$	$v_{AB}^{(1)} = -0.42557$	$v_{AB}^{(2)} = -0.11372$	
$v_{AB}^{(3)} = -0.04820$	Dev.[a] = 0.001		

[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

$$\bar{V}^E_m = x_a x_B \sum_{i=0}^{n} v^{(i)}_{AB}(x_A - x_B)^I \tag{3}$$

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 $\bar{V}^E_m$ 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 $\bar{V}^E_m$, purity of substances is not a crucial factor if the contaminant is non-reactive. In the simple case of a mixture of compounds *A* and *B*, obeying a one-parameter equation of the $\bar{V}^E_m = x_A x_B v_{AB}$ type, the effect of a single impurity (component *C*) contaminating component *A* can be evaluated through:

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

where P_A is the degree of purity (in mole fraction) of component *A*, and v_{ij} is the parameter for mathematically describing $\bar{V}^E_{mij}$. Generally, an impurity is chemically very similar to the contaminated solvent. *i.e.*, $v_{AB} \approx v_{BC}$ and $v_{AC} < v_{AB}$, so that the systematic error in $\bar{V}^E_m$ is less than $(1 - P_A)$, or less than $\pm 1\%$ in the present study.

Examination of Table 1 reveals that the binary chlorobenzene + *n*-heptane system exhibits negative excess volumes, whereas mixtures containing *n*-octane cosolvent show both positive and negative $\bar{V}^E_m$ values depending upon mixture composition. Mixtures containing even larger *n*-alkanes are expected to exhibit positive $\bar{V}^E_m$ values over the entire mole fraction range. Negative excess molar volumes for the chlorobenzene + 1,1-oxybisbutane system likely result from weak dipole-induced dipole interactions between the lone electron pairs on the oxygen atom and the polarizable aromatic π-cloud. Presence of the electron withdrawing chlorine substituent would tend to deplete the aromatic ring electron density and thus help to stabilize a weak chlorobenzene-oxybisbutane specific interaction. A positive excess molar volume would be expected in the case of chlorobenzene + cyclohexane mixtures. The molecular shapes of the two molecules facilitate packing in the neat liquid. Chlorobenzene is a planar molecule and cyclohexane exists predominantly in the "chair" conformation. Dissimilarity in molecular shapes results in a "void" volume ($\bar{V}^E_m > 0$) when the two components are mixed.

Acknowledgements

Research supported in part by the National Science Foundation (Grant No. CTS-8922485).

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