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Excess molar volumes of diisopropylamine + (C_1–C_5) alkan-1-ols: Application of the ERAS model and cubic EOS

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ABSTRACT

Densities of the binary mixtures consist of methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol with diisopropylamine were measured at temperatures (293.15, 298.15, 303.15 and 313.15) K and atmospheric pressure. Data were used to calculate the excess molar volumes. All the excess molar volumes are large and negative over the whole range of mole fraction, indicating strong interactions between unlike molecules. The ERAS-model has been applied for describing the binary excess molar volumes. The ERAS parameters confirm that the strong interactions between unlike molecules are encountered in mixtures. Also the Peng–Robinson–Stryjek–Vera (PRSV) equation of state has been used to predict the binary excess molar volumes.

1. Introduction

Excess thermodynamic functions and deviations of non-thermodynamic ones of binary liquid mixtures are fundamental for understanding of the interactions between molecules in these types of mixtures, particularly when polar components are involved. These functions have also been used as a qualitative and quantitative guide to predict the extent of complex formation in this kind of mixtures [1–3].

Mixtures containing associating components such as alkanols and/or amines are highly non-ideal systems. Due to the formation of hydrogen bonds between the unlike species and disruptive of hydrogen bonding between like species, large negative heats as well as volumetric effects are observed upon mixing.

The Extended Real Associated Solution (ERAS) model developed by Heintz [4] has been successfully applied in order to calculate molecular interaction parameters from binary excess molar volumes data. Intending to establish a comparison with this model, Peng–Robinson–Stryjek–Vera (PRSV) cubic equations of state (CEOS) were applied [5,6] in combination with simple mixing rules. The results obtained with the EOS show lower deviations and reduced complexity in parameter determination. Although EOS are quite valuable tools for correlation and/or prediction purposes, in practice they are not most useful for learning fluid properties at a microscopic level [7]. Hence, the ERAS-models were used to correlate the excess molar volume of binary mixtures; to obtain meaningful results, a global optimization procedure (simulated annealing method) was applied, and thus the parameters and contributions evaluated were analyzed in terms of intermolecular forces. The necessary data for the calculations with PRSV EOS are the critical properties, fitting parameters, and the Pitzer's acentric factor of the pure substances [8] which can be estimated in the lack of experimental information.

The main purpose of the preceding papers of this series [9,10] was to provide a set of thermodynamic data for the analysis and characterization of molecular interactions in binary liquid mixtures containing alkanols. In continuation with these investigations the present paper reports the excess molar volumes, for methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol with diisopropylamine at temperatures (293.15, 298.15, 303.15 and 313.15) K, with the aim of analyzing the influence of temperature and chain length of alkanols upon the excess molar volumes.

2. Experimental

2.1. Materials

Diisopropylamine, methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol, were purchased from Merck with mass fraction higher than 99%, and used without further purifications. The experimental densities of the pure materials are presented at 303.15 K in Table 1 along with the corresponding literature values [11–13].

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Table 1
Densities ρ of the pure components at 303.15 K and comparing by literature values.

Compound	ρ (g cm^{-3})	
	This work	Lit
Diisopropylamine	0.71023	0.70998[a]
Methanol	0.78224	0.782286[b]
Ethanol	0.78130	0.78089[c]
1-Propanol	0.79505	0.795469[b]
1-Butanol	0.80203	0.80194[c]
1-Pentanol	0.80707	0.807593[b]

[a] [11].
[b] [12].
[c] [13].

2.2. Apparatus and procedure

The densities of the pure compounds and mixtures were measured by an Anton Parr DMA 4500, provided with automatic viscosity correction. The accuracy of the density measurements is $\pm 1 \times 10^{-5}$ g cm^{-3}. The apparatus was calibrated once a day with dry air and bidistillated water. The temperature in the cell was regulated to ±0.01 K with a solid state thermostat. The mixtures were prepared by weighing known masses of pure liquids in airtight, narrow-mouth ground stoppered bottles taking due precautions to minimize evaporation losses. All of the mass measurements were performed on an electronic balance (model: Mettler AE 163, Switzerland) accurate to 0.01 mg. The error in the mole fraction was estimated to be $\pm 1 \times 10^{-4}$.

3. Results and discussion

The excess molar volumes of the solutions of molar composition x measured at temperatures (293.15, 298.15, 303.15 and 313.15) K are calculated from the densities of the pure liquids and their mixtures according to the following equation:

$$V_m^E = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (1)$$

where ρ is the density of the mixture, ρ_i is the density of pure component i, x_i is the mole fraction, M_i is the molar mass of component i, and N stands for the number of components in the mixture.

The corresponding V_m^E values of binary mixtures of diisopropylamine (1) + alkanols (2) plotted against mole fraction of diisopropylamine at 298.15 K are presented in Fig. 1. The uncertainty for excess molar volume is $\pm 1 \times 10^{-3}$ cm^{-3} mol^{-1}. The values of densities for binary mixtures, at different temperatures are reported in Table 2. Each set of results was fitted using a Redlich–Kister polynomial [14], which for binary mixtures is

$$Y^E = x_1(1 - x_1)\sum_{k=0}^{N} A_k(1 - 2x_1)^k \quad (2)$$

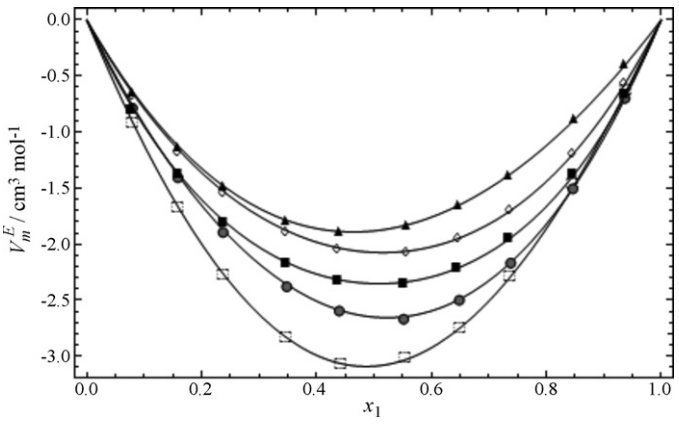

Fig. 1. Excess molar volumes V_m^E vs. mole fraction of diisopropylamine for binary mixtures of diisopropylamine with (□) methanol, (●) ethanol, (■) 1-propanol, (◊) 1-butanol, (◄) 1-pentanol at 298.15 K. The solid curves were calculated from coefficients of Eq. (2) given in Table 3.

Table 2
Densities, ρ, and excess molar volumes, V_m^E, for diisopropylamine (1) + alkanols (2) mixtures at different temperatures.

x_1	ρ (g cm^{-3})	V_m^E (cm^3 mol^{-1})
Diisopropylamine (1) + methanol (2)		
T (K) = 293.15		
0.0000	0.79172	
0.0808	0.78998	−0.910
0.1599	0.78675	−1.664
0.2399	0.78233	−2.276
0.3477	0.77490	−2.829
0.4444	0.76744	−3.068
0.5563	0.75792	−3.014
0.6507	0.74984	−2.736
0.7388	0.74220	−2.273
0.8482	0.73294	−1.465
0.9400	0.72556	−0.628
1.0000	0.72089	
T (K) = 298.15		
0.0000	0.78735	
0.0808	0.78535	−0.924
0.1599	0.78166	−1.67
0.2399	0.77702	−2.283
0.3477	0.76938	−2.834
0.4444	0.76176	−3.066
0.5563	0.75229	−3.022
0.6507	0.74422	−2.747
0.7388	0.73662	−2.286
0.8482	0.72737	−1.473
0.9400	0.71998	−0.627
1.0000	0.71535	
T (K) = 303.15		
0.0000	0.78224	
0.0808	0.77968	−0.902
0.1599	0.77601	−1.655
0.2399	0.77120	−2.258
0.3477	0.76360	−2.811
0.4444	0.75606	−3.046
0.5563	0.74680	−3.019
0.6507	0.73878	−2.741
0.7388	0.73130	−2.288
0.8482	0.72219	−1.484
0.9400	0.71487	−0.638
1.0000	0.71023	
T (K) = 313.15		
0.0000	0.77273	
0.0808	0.76872	−0.850
0.1599	0.76423	−1.565
0.2399	0.75893	−2.135
0.3477	0.75116	−2.668
0.4444	0.74411	−2.944
0.5563	0.73546	−2.978
0.6507	0.72796	−2.761
0.7388	0.72089	−2.361
0.8482	0.71205	−1.589
0.9400	0.70462	−0.707
1.0000	0.69971	
Diisopropylamine (1) + ethanol (2)		
T (K) = 293.15		
0.0000	0.79217	
0.0808	0.78865	−0.736
0.1601	0.78461	−1.355
0.2386	0.77998	−1.845
0.3497	0.77263	−2.330
0.4411	0.76601	−2.536
0.5532	0.7574	−2.549
0.6500	0.74949	−2.321