



## Excess molar volumes of 1,3-propanediol + (C<sub>1</sub>–C<sub>5</sub>) alkan-1-ols: application of a cubic equation of state

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**Abstract:** The densities of binary mixtures consisting of methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol with 1,3-propanediol were measured at the temperatures 293.15, 298.15, 303.15 and 313.15 K and at atmospheric pressure. Measurements were made over the full range of compositions and for the pure compounds using a vibrating tube densimeter. Excess molar volumes were obtained from these experimental results and were fitted to a Redlich–Kister type expansion. The results were interpreted in terms of molecular interactions and structural factors of the alcohols. It was observed that an increase in the carbon chain length of the alcohol led to lower interactions on mixing. The Peng–Robinson–Stryjek–Vera (PRSV) Equation of state was used to correlate the binary excess molar volumes.

**Keywords:** excess molar volumes; 1-alkanols; 1,3 propanediol; cubic EOS.

### INTRODUCTION

Volumetric properties of mixtures are of interest from both theoretical and engineering points of view. These properties depend not only on solute–solute and solvent–solvent interactions, but also on the interstitial accommodations of unlike molecules arising from differences in molar volume and free volume of the solution components.<sup>1</sup>

Some useful information can be derived from density data, such as excess molar volumes and partial molar volumes. In addition, densities for mixtures at different temperatures are required for engineering design and for the succeeding operations.

The Peng–Robinson–Stryjek–Vera (PRSV) cubic equations of state (CEOS) were applied to predict the binary excess molar volumes<sup>2,3</sup> in combination with simple mixing rules. Although EOS are quite valuable tools for correlation and/or predictive purposes, in practice they are not the most useful for determining fluid

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properties at a microscopic level.<sup>4</sup> The necessary data for calculations with the PRSV EOS are the critical properties, fitting parameters and the Pitzer acentric factor of the pure substances,<sup>5</sup> which can be estimated in the lack of experimental information.

In continuation of prior investigations,<sup>6–8</sup> the present paper reports the excess molar volumes of methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol with 1,3-propanediol over the entire composition interval at temperatures ranging from 293.15 to 313.15 K, with the aim of analyzing the influence of temperature and chain length of the alkanols on the excess molar volumes.

#### EXPERIMENTAL

1,3-Propanediol, 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 densities of the pure compounds and mixtures were measured by an Anton Parr DMA 4500 instrument, provided with automatic viscosity correction. The uncertainty of the density measurements was estimated to be better than  $\pm 1 \times 10^{-5}$  g cm<sup>-3</sup>. The apparatus was calibrated daily with dry air and bidistilled water. The temperature in the cell was regulated to  $\pm 0.01$  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 uncertainty in the mole fraction was estimated to be  $\pm 1 \times 10^{-4}$ .

#### RESULTS AND DISCUSSION

The experimental densities of the pure materials are presented at various temperatures in Table I-S of the Supplementary material, along with corresponding literature values.<sup>9–12</sup>

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

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

where  $\rho$  is the density of the mixture,  $\rho_i$  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 1,3-propanediol (1) + alkanols (2) plotted against the mole fraction of 1,3-propanediol at 298.15 K are presented in Fig. 1. The excess molar volumes of 1,3-propanediol with methanol at 298.15 K are compared literature values<sup>13</sup> in Fig. 2. The discrepancy between experimental data and the literature values may be due to the viscosity correction

on the density measurements in the vibrating tube density meter. The employed instrument has an automatic viscosity correction. The values of densities and excess molar volumes for binary mixtures, at different temperatures are reported in Table II-S in the Supplementary material. Each set of results was fitted using a Redlich–Kister polynomial,<sup>14</sup> which for binary mixtures is:

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

where  $Y^E \equiv V_m^E$  and  $x_1$  is the mole fraction of 1,3-propanediol.  $A_k$  is an adjustable parameter obtained by the least-squares method and  $k$  is the degree of the polynomials. In each case, the optimum number of coefficients was ascertained from an examination of the variation of standard deviation  $\sigma$ . The values of the parameter  $A_k$  together with the standard deviation  $\sigma$  are presented in Table I.

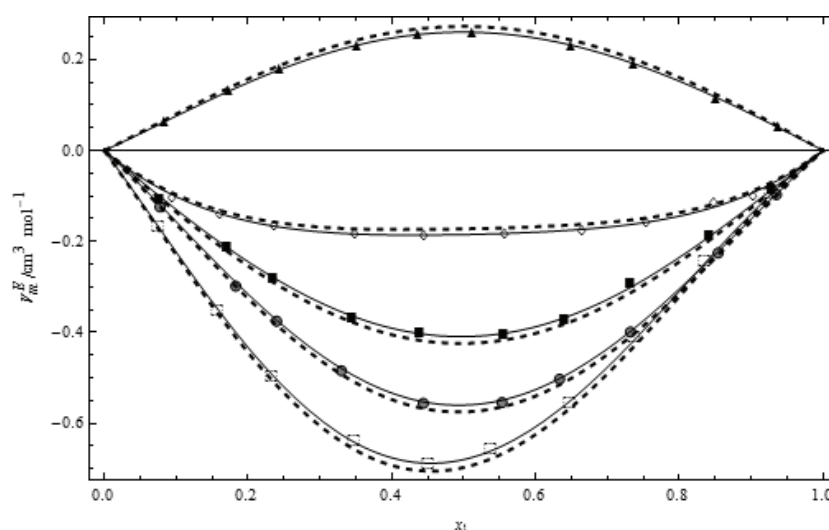


Fig. 1. Excess molar volumes,  $V_m^E$ , vs. mole fraction of 1,3-propanediol for binary mixtures of 1,3-propanediol with ( ) methanol, (●) ethanol, (■) 1-propanol, (◇) 1-butanol, (◄) 1-pentanol at 298.15 K. (—) Redlich–Kister Equation, (---) PRSV CEOS. The numerical data for this Figure as well as for all systems at all the studied temperatures are given in Table II-S of the Supplementary Material to this paper.

Over the whole composition range, the values of  $V_m^E$  for the binary mixtures of methanol, ethanol, 1-propanol and 1-butanol with 1,3-propanediol are negative but the values of  $V_m^E$  for the 1-pentanol + 1,3-propanediol mixtures are positive. It is obvious from Fig. 1 that the  $V_m^E$  values generally increase with increasing size of the alcohol molecules.

The magnitude and sign of  $V_m^E$  are the consequence of interactions occurring in the mixture at different temperatures. It is known that pure alkanols can form

either ring- or chain-like complexes,<sup>15</sup> and while the fraction of ring complexes increases with the number of  $-\text{CH}_2$  groups in the alkanols, the degree of association decreases. The associated rings break down to chains with increasing temperature, which is then followed by a total break down of the associated species.<sup>16</sup>

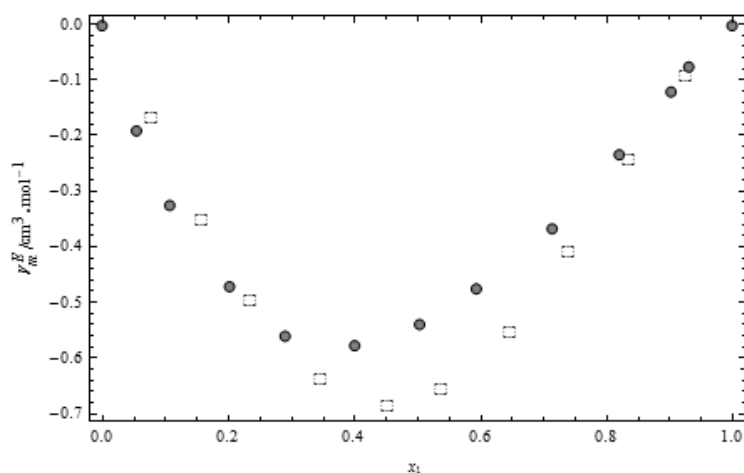


Fig. 2. Excess molar volumes,  $V_m^E$ , vs. mole fraction of 1,3-propanediol with methanol at 298.15 K; this work – □, Ref. 13 – ●.

TABLE I. Coefficients  $A_j$  and standard deviations,  $\sigma$ , for 1,3-propanediol (1) + alkanols (2) at various temperatures

$T / \text{K}$	$A_0$	$A_1$	$A_2$	$\sigma$
1,3-propanediol + methanol				
293.15	-2.896	-0.610	1.043	0.008
298.15	-2.721	-0.639	1.111	0.005
303.15	-2.508	-0.517	0.751	0.006
313.15	-2.344	-0.467	0.703	0.005
1,3-propanediol + ethanol				
293.15	-2.307	-0.061	0.635	0.005
298.15	-2.236	-0.065	0.829	0.002
303.15	-2.072	0.033	0.860	0.004
313.15	-1.874	0.0292	0.778	0.005
1,3-propanediol + 1-propanol				
293.15	-1.706	-0.047	0.223	0.004
298.15	-1.632	-0.041	0.380	0.004
303.15	-1.521	-0.040	0.581	0.002
313.15	-1.379	0.019	0.529	0.003
1,3-propanediol + 1-butanol				
293.15	-0.767	-0.041	-0.728	0.003
298.15	-0.742	-0.059	-0.549	0.005
303.15	-0.712	-0.052	-0.387	0.003
313.15	-0.693	-0.036	-0.200	0.002

TABLE I. Continued

$T / \text{K}$	$A_0$	$A_1$	$A_2$	$\sigma$
1,3-propanediol + 1-pentanol				
293.15	0.979	-0.085	-0.479	0.003
298.15	1.047	-0.019	-0.277	0.002
303.15	1.143	0.040	0.042	0.002
313.15	1.234	0.071	0.476	0.001

The observed negative  $V_m^E$  values for the methanol, ethanol, 1-propanol and 1-butanol with 1,3-propanediol mixtures are due to the formation of hydrogen bonding between unlike molecules, resulting in a decrease in the volume of the mixture. Another negative contribution to  $V_m^E$  comes from structural contributions that arise from the geometrical fitting of one component into the other components.<sup>17</sup> The positive  $V_m^E$  values for 1-pentanol + 1,3-propanediol system indicate a loose packing of the molecules in the mixtures, *i.e.*, dilatation occurs. Most likely, in this case, the different molecular sizes and shapes of 1,3-propanediol and 1-pentanol and steric hindrance between them, play important roles. Simultaneously, it seems that the disruption of hydrogen-bonded structures upon mixing should also be taken into account. The excess molar volumes increased with increasing temperature for all of the studied systems over the whole composition range. This can be expected since hydrogen bonds are more easily broken at higher temperatures.  $V_m^E$  at equimolar concentrations of 1,3-propanediol increases from methanol up to 1-pentanol, as the length of the alkanol chain increases.

#### PRSV CEOS

The general two-parameter CEOS has the form:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+ub)(v+wb)} \quad (3)$$

where the EOS-dependent constants  $u$  and  $w$  for the Peng–Robinson–Stryjek–Vera Equation applied herein are:  $u = 1 - \sqrt{2}$  and  $w = 1 + \sqrt{2}$ . For the pure substance, the energy  $a_i$  and co-volume  $b_i$  parameters of van der Waals are determined by the following set of equations:

$$a_i(T) = 0.457235 \frac{(RT_{ci})^2}{P_{ci}} [1 + m_i(1 - T_{ri}^{0.5})]^2 \quad (4)$$

$$b_i = 0.07779 \frac{RT_{ci}}{P_{ci}} \quad (5)$$

$$m_i = k_{0i} + k_{1i}(1 + T_{ri}^{0.5})(0.7 - T_{ri}) \quad (6)$$

$$k_{0i} = 0.378893 + 1.4897153\alpha_1 - 0.1713848\alpha_1^2 + 0.0196554\alpha_1^3 \quad (7)$$

where  $R$  is the gas constant,  $T_{ci}$  and  $P_{ci}$  are the critical temperature and pressure of component  $i$ , respectively,  $T_{ri}$  stands for the reduced temperature ( $T/T_{ci}$ ),  $\omega$  is the acentric factor, and  $k_{1i}$  represents the adjustable parameter of the pure substance.

For the mixtures, the van der Waals mixing rules in the PRSV CEOS can be presented as:<sup>18,19</sup>

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} [1 - k_{ij} + l_{ij}(x_i - x_j)] \quad k_{ij} = k_{ji} = 0 \text{ and } l_{ij} \neq l_{ji} \quad (8)$$

$$b = \sum_i \sum_j x_i x_j (1 - m_{ij}) \left( \frac{b_i + b_j}{2} \right) \quad m_{ii} = 0 \quad (9)$$

where  $k_{ij}$ ,  $l_{ij}$  and  $m_{ij}$  are fitting parameters of the binary interaction and can be determined by simultaneously adjusting the theoretical expression of the PRSV EOS to the experimental  $V_m^E$ . The necessary data, such as critical properties and the Pitzer acentric factor, of the pure substances for the calculations with the PRSV CEOS were taken from the literature.<sup>20</sup> The PRSV CEOS parameters of the pure compound ( $k_{1i}$ ) are given in Table II. The binary coefficients for Eqs. (8) and (9) are listed in Table III together with the standard deviations,  $\sigma$ . From the results of Fig. 2 and Table II, it must be emphasized that the equations of state offer good agreement with the experimental data of the binary excess molar volumes.

TABLE II. Adjustable parameter of PRSV CEOS for the pure substances

Component	$k_{1i}$
1,3-Propanediol	0.242
Methanol	0.325
Ethanol	0.410
1-Propanol	0.321
1-Butanol	0.256
1-Pentanol	0.434

TABLE III. Adjustable PRSV CEOS parameters and the standard deviations for the  $V_m^E$  of the binary mixtures at 298.15 K

System	$m_{12}$	$k_{12}$	$l_{12}$	$l_{21}$	$\sigma$
1,3-Propanediol + methanol	-0.1875	-0.1034	0.0154	0.3135	0.0124
1,3-Propanediol + ethanol	-0.0231	-0.1740	0.0027	0.1865	0.0080
1,3-Propanediol + 1-propanol	-0.2132	-0.0225	0.1325	0.0328	0.0091
1,3-Propanediol + 1-butanol	-0.0170	-0.1454	0.1643	0.1231	0.0087
1,3-Propanediol + 1-pentanol	0.0230	0.2734	0.0413	0.1408	0.0082

## CONCLUSIONS

The experimental data of the excess molar volumes of methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol with 1,3-propanediol were measured over

the entire composition ranges and at several temperatures. These data were used to compute the excess molar volumes of the systems, and a Redlich–Kister type equation was used for fitting each set of data. Moreover, the obtained results showed that the excess molar volume for the system 1-pentanol + 1,3-propanediol were positive, while for the other studied systems, they were found to be negative. Furthermore, it was observed that the values of the excess molar volumes were temperature dependent. The behavior of the excess molar volumes of these systems can be explained as a balance between the positive contributions due to hydrogen bond rupture and dispersive interactions between unlike molecules, and negative contributions due to packing effects. The PRSV CEOS is a quite valuable tool for the correlation of the excess molar volumes of the investigated systems.

#### SUPPLEMENTARY MATERIAL

Densities of the pure components and excess molar volumes for 1,3 propanediol (1) + alkanols (2) mixtures at various temperatures are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

#### ИЗВОД

#### ДОПУНСКА МОЛАРНА ЗАПРЕМИНА СМЕША 1,3-ПРОПАНДИОЛ + (C<sub>1</sub>–C<sub>5</sub>) 1-АЛКОХОЛИ: ПРИМЕНА КУБНИХ ЈЕДНАЧИНА СТАЊА

МОХАММАД АЛМАСИ и ЛАДАН ХОСРАВИ

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Густине бинарних смеша метанола, етанола, 1-пропанола, 1-бутанола и 1-пентанола са 1,3-пропандиолом измерене су на температурама 293,15, 298,15, 303,15 и 313,15 К и на атмосферском притиску. Мерења су извршена коришћењем вибрационог густинометра у читавом концентрационом опсегу и за све чисте компоненте. На основу експерименталних мерења одређене су допунске моларне запремине које су корелисане једначином Redlich–Kister-а. Добијени резултати су објашњени на основу молекулских интеракција и структурних карактеристика алкохола. Запажа се да повећање броја угљеникових атома алкохола води ка смањењу интеракција у смеси. За корелисање допунских моларних запремина бинарних смеша коришћена је Peng–Robinson–Stryjek–Vera (PRSV) једначина стања.

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