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Volumetric, viscometric, spectral studies and viscosity modelling of binary mixtures of esters and alcohols (diethyl succinate, or ethyl octanoate + isobutanol, or isopentanol) at varying temperatures

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ABSTRACT

Density, viscosity and refractive index of four binary mixtures consisting of diethyl succinate or ethyl octanoate + 2-methyl-1-propanol or 3-methyl-1-butanol have been measured at atmospheric pressure and over the temperature range from 288.15 K to 323.15 K. Excess and deviation functions have been calculated from these data and fitted to the Redlich-Kister equation. The values of excess molar volume and deviation functions, with FT-IR study, were further used in the analysis of molecular interactions present in the mixture as well as the temperature influence on them. Molar excess Gibbs free energies of activation of viscous flow were additionally calculated from measured density and viscosity data for better understanding of present molecular interactions. Viscosity modelling was done with two approaches, predictive by group contribution models (UNIFAC-VISCO and ASOG-VISCO), and correlative by one to three-parameter models (Teja-Rice, Grunberg–Nissan, McAlister, Eyring-UNIQUAC and Eyring-NRTL). The obtained results were compared with experimental data and conclusions about applied approaches and models were made.

1. Introduction

This paper is a continuation of the research work whose objective is to measure thermodynamic properties for binary systems involved in wine production processes [1,2]. The main wine constituents are water and ethanol, but other components including esters, alcohols, aldehydes, and acetates, called congeners, are also present [3–7]. For modelling and process simulation in which these mixtures appear, binary data of the properties such as density, viscosity and refractive index over a wide range of temperature, are needed.

Similar to ethyl butyrate, already investigated in our laboratory [1], diethyl succinate and ethyl octanoate have excellent properties for industrial applications. These esters are byproducts of the fermentation of sugar and as such are often present in fermented wines and beers that have aged a long time. They are also present as additives in food or synthetic flavorings and aromas. They are FDA approved as "food additives permitted for direct addition to food for human consumption".

Binary mixtures of wine congeners have been analyzed before [8,9]. Also, several studies of the thermophysical properties of diethyl succinate [10,11], and a lot more of ethyl octanoate [12–16], have been conducted in the recent years. However, property data for the mixtures investigated in this paper are still missing in the literature.

Densities, refractive indices and viscosities for four binary mixtures ofdiethyl succinate or ethyl octanoate with 2-methyl-1-propanol (isobutanol) or 3-methyl-1-butanol (isopentanol), are reported at atmospheric pressure and at eight temperatures ranging from 288.15 K to 323.15 K with temperature step of 5 K. The experimental results from this study have been used to calculate excess molar volumes (V^E), deviation functions ($\Delta\eta$, Δn_D) and molar excess Gibbs free energies of activation of viscous flow (ΔG^{*E}). These properties were correlated with Redlich-Kister equation [17] and used afterwards for analysis of molecular interactions existing in the mixtures. Fourier-transform infrared (FT-IR) spectroscopy studies of pure compounds and mixtures were also performed, to obtain a better insight into major inter- and intramolecular interactions in the studied mixtures, by examining the position and shifts of the band, the band width and changes of band shape.

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Also, in this work, modelling of viscosity of the selected binary mixtures was done using predictive UNIFAC-VISCO [18,19] and ASOG-VISCO [20] models. These models are used as pure predictive considering that the interaction parameters between functional groups present in the investigated systems are already known and taken from the literature [18–20] and our previous works [21,22]. The main advantage of predictive models is the fact that the only data necessary for calculation, if the interaction parameters are known, are the data for pure components. However, having in mind the fact that correlative models often lead to better results, the viscosity data were also correlated by Teja-Rice [23,24], Grunberg-Nissan [25], McAlister [26], Eyring-UNIQUAC [27] and Eyring-NRTL [28] models. This modelling approach requires experimental data for binary systems to calculate interaction parameters (one or more) by applying some optimization technique.

2. Experimental section

Basic informations about the chemicals used in this investigation are given in Table 1. Diethyl succinate ($w = 0.99$) was purchased from Acros Organics, ethyl octanoate from Merck ($w = \geqslant 0.98$) and isobutanol ($w = 0.997$) and isopentanol ($w = 0.99$) from Fisher Chemical.

Experimental data on density, viscosity and refractive index of these chemicals were compared with literature values at 298.15 K (Table 2 [10,11,15,29–33]). The agreement was satisfactory with differences within 0.8 $kg \cdot m^{-3}$ for densities, mostly less than $6 \cdot 10^{-4}$ for refractive indices and up to $9 \cdot 10^{-2}$ mPa·s for viscosities.

Since new density, viscosity and refractive index data are reported only for pure ethyl octanoate (for other pure substances are previously published in our papers [1,2]); all three measured properties for this ester are compared with available literature data [14,15,29,34–47] in the whole temperature range present in the literature, and the comparison is shown on Fig. 1.

Table 1
Sample information.

Chemical name	Source	Initial mass fraction purity	Purification method
Diethyl succinate	Acros Organics	0.99	None
Ethyl octanoate	Merck	⩾0.98	None
2-methyl-1-propanol (isobutanol)	Fisher Chemical	0.997	None
3-methyl-1-butanol (isopentanol)	Fisher Chemical	0.99	None

Densities of the investigated binary mixtures and pure components were measured on Anton Paar DMA 5000 densimeter, viscosities on Stabinger SVM 3000/G2 viscometer, while measurements of refractive indices were conducted on Anton Paar RXA-156 refractometer. Calibration of each apparatus was performed daily using ambient air and Milipore quality water. Mixtures were prepared gravimetrically on a Mettler AG 204 balance. The balance precision is $1 \cdot 10^{-7}$ kg and the standard uncertainty in mole fraction is evaluated as $\pm 1 \cdot 10^{-4}$. The repeatability of density measurements is $5 \cdot 10^{-2}$ $kg \cdot m^{-3}$, while the combined expanded uncertainty, including the influence of sample purities, which is slightly lower for ethyl octanoate, is within ±1.6 $kg \cdot m^{-3}$ with a 0.95 level of confidence. The uncertainty in excess molar volume is less than $\pm 3 \cdot 10^{-7}$ $m^3 \cdot mol^{-1}$. The uncertainties in refractive indices and viscosity data are estimated as $\pm 2.8 \cdot 10^{-3}$ units and ±0.7 %, respectively, while for viscosity and refractive index deviation they are ±0.4 % and $\pm 3.4 \cdot 10^{-3}$ units.

Spectra of pure components and binary mixtures were acquired directly using Attenuated Total-internal Reflection (ATR) accessory (with Zn-Se crystal) and FT-IR Spotlight 400 System (Perkin Elmer, Italy). All the spectroscopic studies were performed at 298.15 K.

Before each acquisition of the new sample spectrum, ATR plate was cleaned with acetone using lens tissues and the background infrared spectrum was collected in order to eliminate unwanted influences on spectra such as water vapor and carbon-dioxide from the atmosphere, as well as potential impurities left on the ATR crystal. The spectra were collected in the range 4000–650 cm^{-1} with 4 cm^{-1} resolution, and each spectrum was averaged across 16 scans in order to minimize noise in spectra. Acquired spectra were baseline corrected using software Spectrum 10 (Perkin Elmer, Italy).

3. Results and discussion

Densities ρ, viscosities η and refractive indices n_D for four binary systems (diethyl succinate + isobutanol, diethyl succinate + isopentanol, ethyl octanoate + isobutanol and ethyl octanoate + isopentanol), measured at eight temperatures $T = (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15$ and $323.15)$ K and $p = 0.1$ MPa are given in Table 3.

Experimental densities of the mixtures ρ and the pure components ρ_i, were used to calculate the excess molar volumes V^E from equation:

$$V^E = \sum_{i=1}^{2} x_i M_i \left[\left(\frac{1}{\rho} \right) - \left(\frac{1}{\rho_i} \right) \right] \quad (1)$$

Table 2
Densities ρ, dynamic viscosities η and refractive indices $n_D$of the pure components studied in this work at 298.15 K and 0.1 MPa.[a]

Component	$10^{-3}\rho$/(kg·m^{-3})		η/(mPa·s)		n_D	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Diethyl succinate	1.03444[b]	1.0353 [10] 1.03553 [11]	2.4914[b]	2.466 [10] 2.393 [11]	1.4173[b]	1.4196 [10] 1.4179 [11]
Ethyl octanoate	0.86228	0.86215 [29] 0.86219 [15]	1.4104	1.411 [29]	1.4155	1.4156 [29] 1.415 [15]
2-methyl-1-propanol	0.79816[c]	0.7978[30] 0.79784 [31]	3.4307[c]	3.333 [30]	1.3937[c]	1.3937 [31]
3-methyl-1-butanol	0.80484[c]	0.8071[30] 0.80446[32]	3.6709[c]	3.738[30] 3.740[33]	1.4047[c]	1.4052[30] 1.4047[32]

[a] Standard uncertainties u for each variables are $u(T) = \pm 0.01$ K; $u_r(p) = \pm 0.05$; $u(x_1) = 0.0001$, and the combined expanded uncertainties U_c are $U_c(\rho) = \pm 1.6$ $kg \cdot m^{-3}$; $U_c(n_D) = \pm 2.8 \times 10^{-3}$ and $U_{c,r}(\eta) = \pm 0.007$, with 0.95 level of confidence ($k \approx 2$).
[b] Previously published data [2].
[c] Previously published data [1].