



Temperature dependence and chain length effect on density and viscosity of binary mixtures of nitrobenzene and 2-alcohols



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ABSTRACT

Densities and viscosities of binary nonelectrolyte systems including nitrobenzene + 2-propanol, 2-butanol and 2-pentanol at temperatures 293.15 to 323.15 K and normal atmospheric pressure were measured using an Anton-Paar SVM 3000 Stabinger viscometer. Excess molar volumes V_m^E and viscosity deviations $\Delta\eta$ were calculated and correlated by the Redlich–Kister equation to estimate the standard uncertainty. These values are negative over the full range of composition for all studied mixtures. Free volume theory coupled with the Peng–Robinson equation of state was used to correlate liquid viscosities of pure compounds and binary mixtures. The agreement between measured viscosity data and values calculated from this model is within experimental uncertainties.

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1. Introduction

From the experimental viewpoint, excess and deviation functions are powerful tools for analyzing structural and physicochemical properties of mixtures. Among them, the excess molar volume has been of much interest for the practical purpose of determining composition from the density measurements. Excess molar volumes can also provide information on possible interactions between components of a binary mixture, such as molecular associations and dipole–dipole and induced dipole–dipole interactions [1]. The interest in studying thermodynamic properties of mixtures containing nitrobenzene is due to their toxicity and hazardous effects to human health and also because of widespread industrial use [2]. This study of the density and viscosity of binary mixtures formed by nitrobenzene with selected 2-alkanols continues our recent systematic studies of the thermodynamic and transport properties of binary mixtures [3,4]. A literature survey reveals that some thermodynamic and transport properties of binary mixtures containing nitrobenzene have been studied [5].

Our approach is to correlate the viscosity of the binary mixtures with the free volume theory which relates the viscosity to the probability of occurrence of an empty neighboring site into which a molecule can jump. This probability is exponentially related to the free volume of the liquids. In this study, the free-volume theory (FVT) has been coupled with the Peng–Robinson equation of state to the correlation of viscosities of pure compounds and binary mixtures. Applicability of this

model to the mixtures examined in this work has not yet been verified in the literature.

The importance of free-volume theories for the calculation of viscosities owes to the following facts: (i) their equations are simple and involve only few parameters; (ii) the parameters have, almost always, a physical meaning; (iii) they can be used over wide ranges of temperature and pressure; (iv) the theories are based on statistical mechanics, therefore, giving them a theoretical background and, (v) they may easily be extended to multicomponent systems [6].

2. Experimental

2.1. Materials

All pure materials were obtained from Merck with mass purity >99% and were used as purchased without further purification. Measured densities and viscosities at $T = 298.15$ K are presented in Table 1 along with the data from the literature [7,8]. The largest percentage deviation of our data from the literature data is 0.04% for density and 1.17% for viscosity.

2.2. Methods

Density and viscosity measurements were performed with a fully automated SVM 3000 Anton-Paar Stabinger viscometer. The viscometer is based on a modified Couette principle with a rapidly rotating outer tube and an inner measuring bob which rotates more slowly. The uncertainty is $1 \times 10^{-4} \text{ g} \cdot \text{cm}^{-3}$ for density measurements and 1% for viscosity measurements. Three to five sets of readings for the flow times were taken for each sample. The mixtures were prepared just

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Table 1
Densities, and viscosities η , of pure components at $T = 298.15$ K and $P = 0.1$ mPa.

Chemical name	$\rho/(\text{g}\cdot\text{cm}^{-3})$		$\eta/(\text{mPa}\cdot\text{s})$	
	Exptl.	Lit.	Exptl.	Lit.
Nitrobenzene	1.1978	1.1973 ^a	1.9092	1.9118 ^b
2-Propanol	0.7811	0.7810 ^a	2.0827	2.105 ^b
2-Butanol	0.8027	0.80270 ^a	3.0417	3.114 ^b
2-Pentanol	0.8053	0.80524 ^a	3.2776	3.316 ^b

^a Ref. [7].

^b Ref. [8].

before their use by mass on an electronic balance (Mettler AE 163, Switzerland) accurate to 0.01 mg and kept in airtight stoppered glass bottles to avoid evaporation. The maximum estimated uncertainty in the mole fractions is 1×10^{-4} .

3. Results and discussions

3.1. Densities and excess molar volumes

From the experimental data, excess molar volumes V_m^E at different temperatures were calculated using

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

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 density data as a function of mole fraction for nitrobenzene + 2-propanol, 2-butanol, and 2-pentanol mixtures at various temperatures are reported in Table 2. The densities of the binary mixtures decrease with increasing temperature and increase with increasing carbon chain length. Excess molar volumes of binary mixtures of nitrobenzene + 2-alkanols as a function of mole fraction at $T = 298.15$ K are plotted in Fig. 1. The V_m^E values were correlated with a Redlich–Kister type equation [9]

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

where x_1 is the mole fraction of nitrobenzene and A_k is an adjustable coefficient. Standard deviations were obtained by the equation

$$\sigma = \left[\sum (V_{\text{exp}}^E - V_{\text{cal}}^E)^2 / (n-p) \right]^{1/2} \quad (3)$$

where V_{exp}^E and V_{cal}^E are the experimental and calculated data, respectively. Adjustable parameters of the Redlich–Kister equation and standard deviation values are presented in Table 3.

The excess molar volumes are negative for all studied mixtures and increase with the number of carbon atoms of the alcohols. This behavior arises from the specific interactions between the nitrobenzene and 2-alkanol molecules through dipole–dipole interactions, forming complexes through hydrogen bonds. With the higher chain length of 2-alkanols, the structural contributions arising from the geometrical fitting of one component into the other are negligible because of steric hindrance of carbon chain length. Therefore, mixtures containing higher 2-alkanols have less negative V_m^E values. On the other hand, in all cases the number of cross-associated hydrogen bonds decreases with temperature which leads to less negative values of V_m^E .

3.2. Dynamic viscosities

The measured viscosities are reported in Table 2. The viscosities for binary mixtures increase with chain length and decrease with temperature. The viscosity deviation can be calculated as

$$\Delta\eta = \eta - x_1\eta_1 - x_2\eta_2 \quad (4)$$

where η is the mixture viscosity and η_1 and η_2 are the viscosities of pure components. Values of viscosity deviations were correlated by the Redlich–Kister equation and adjustable coefficients are reported in Table 3. The viscosity deviations for the mixtures of nitrobenzene with 2-alkanol at $T = 298.15$ K are shown in Fig. 2. This figure indicates that the viscosity deviations are negative for all three binary mixtures and become more negative with increasing chain length of the alcohols. This behavior indicates that specific interactions between nitrobenzene and 2-alkanols decrease with the carbon chain length.

3.3. Free volume theory

In the free volume theory [10,11], the viscosity is expressed as the sum of two terms

$$\eta = \eta_0 + \Delta\eta^{\text{res}} \quad (5)$$

η_0 is the viscosity in the dilute gas limit, while the residual viscosity $\Delta\eta^{\text{res}}$ describes deviations from the dilute gas. For η_0 the form proposed by Chung et al. [12]

$$\eta_0 = 40.785 \frac{\sqrt{M_W T}}{v_c^{2/3} \Omega^*} F_c \quad (6)$$

was used. M_W is Molecular weight and v_c is critical volume. The reduced collision integral Ω^* is calculated by

$$\Omega^* = \frac{1.16145}{T^*} + \frac{0.52478}{\exp(0.77320 T^*)} + \frac{2.16178}{\exp(2.43787 T^*)} - 6.435 \cdot 10^{-4} T^* \sin(18.0323 T^{*-0.76830} - 7.27371) \quad (7)$$

$$\text{where } T^* = \frac{1.2593 T}{T_c} \quad (8)$$

and F_c is given by

$$F_c = 1 - 0.275\omega + 0.059035\mu_r^4 + \chi \quad (9)$$

where ω is the acentric factor and χ is a correction for the influence of hydrogen bonds that can be calculated [13] by

$$\chi = 0.0682 + 0.276659 \left(\frac{17N_{\text{OH}}}{M_W} \right) \quad (10)$$

where N_{OH} is the number of OH groups in the alcohol. The dimensionless dipole moment term [13] μ_r is expressed as

$$\mu_r = 131.3 \frac{\mu}{(v_c T_c)^{1/2}} \quad (11)$$

where μ is the dipole moment in Debye. The residual viscosity is described by a generalized dumbbell model

$$\Delta\eta^{\text{res}} = 10^{-14} \rho N_a \zeta L^2 \quad (12)$$

where ρ is the density, ζ is the friction coefficient, N_a is Avogadro's number and L^2 is an average quadratic length related to the size of the molecule. On the other hand, the viscosity depends on free spaces

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