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Ultrasonic speeds, refractive indices, and densities of dimethoxymethane + aliphatic alcohols (C_1–C_4) at (298.15 and 303.15) K with COSMO-RS and ERAS analyses

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ABSTRACT

The ultrasonic speeds, refractive indices, and densities of binary mixtures dimethoxymethane + aliphatic alcohols (C_1–C_4) were determined. The excess quantities for the binary mixtures are fitted to the Redlich–Kister polynomials. The observed excess molar volumes are rationalized in terms of the intermolecular force and geometry contributions of the constituent molecules. The intermolecular forces are discussed using accepted theories and the more recent conductor-like screening model (COSMO). The extended real associating solution (ERAS) model is also utilized in the analysis of excess molar volumes. The σ-profile of dimethoxymethane and alcohols are computed with COSMO-RS and interpreted to be not supportive of earlier interpretations of hydrogen bonds in the energetics. Sign changes in excess molar volume and excess isentropic compressibility are discussed and rationalized in detail quantitatively. Sellmeier's equation is used to quantitatively rationalize the measured refractive indices and a consistency with regard to sign and sign changes of the other measured excess quantities can be deduced.

1. Introduction

1.1. Properties of dimethoxymethane

Dimethoxymethane (DMM) (methylal, 2,4-dioxapentane, or formaldehyde dimethyl acetal), is one of the simplest molecules exhibiting the stereoelectronic Edward–Lemieux or anomeric effect, that causes the *synclinal* (or *gauche*) conformation to be more stable than the usually anticipated *antiperiplanar* (or *anti*) conformation [1,2] and is used to model carbohydrates that commonly exhibit such effects [3,4]. Due to environmental concerns, DMM has long been considered a potential oxygenate candidate in diesel fuel additives because of its high oxygen number per molecule [5,6] and its lower boiling point and autoignition temperature that are usually necessary for clean combustion [7,8].

1.2. Survey of the literature and objective of the present work

Several investigations of binary mixtures containing DMM have been conducted with hydrocarbons, ethers and alcohols as the second component, confined however to investigations of vapor–liquid equilibria and excess enthalpies of dimethoxymethane + hydrocarbons [9–11], + ethers and alcohols [12], + water + methanol [13] and densities, viscosities, refractive indices and excess molar enthalpies of dimethoxymethane + poly(ethylene glycol) 200 and 400 [14] but not with a series of alcohols. Therefore this work complements previous studies by presenting data on the densities, refractive indices, and ultrasonic speeds of the binary mixtures of DMM with aliphatic alcohols (C_1 to C_4) at two temperatures 298.15 K and 303.15 K so that the first temperature derivative may be determined.

1.3. The COSMO theory

COSMO analysis [15] is included in this work due to its success in predicting certain thermodynamical properties from electronic structures [16]. In COSMO-RS, a refinement of COSMO theory, a gas-phase optimized molecule X is embedded in a cavity in a conductor-like universe. The surface of the cavity is divided up into segments-i of surface area S_i with induced charge density σ_i. The induced charges on the surface segments-i are described by a surface potential matrix, Φ^X that is obtained from the distribution of charge on the molecule X, i.e. $\Phi_i^X = \int_V \rho(\mathbf{r}) d\mathbf{r} / \|\mathbf{t}_i - \mathbf{r}\|$, and a Coulomb interaction matrix, $\mathbf{A}$ between the surface segments defined as $A_{ij} = \|\mathbf{t}_i - \mathbf{t}_j\|^{-1}$ for $i \neq j$ and $A_{ij} = -3.8 S_i$ for $i = j$, where $\rho(\mathbf{r})$ is the charge distribution function

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and $\mathbf{t}_i$ is the coordinate of the center of each surface segment. The surface charge densities are obtained as

$$\boldsymbol{\sigma} = -f(\varepsilon)\mathbf{S}^{-1}\mathbf{A}^{-1}\boldsymbol{\Phi}^{X}, \quad (1)$$

where $f(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 0.5)$ is the scaling factor chosen for the medium [16,17]. The scaling factor in COSMO-RS has enabled the efficient computation of surface charge densities that are used to predict other thermodynamic properties of solvated systems. Among other simplifications made in COSMO-RS is to treat the van der Waals attraction as a sum of individual molecular interaction energies of surface segments as the molecule is brought from the vacuum to a conductor-like cavity. Similarly, hydrogen bonding is assumed to operate if the charge density σ_i exceeds certain threshold values. These simplifications make the computational cost of COSMO-RS to be lower than many competing theories and although COSMO-RS is still limited to several thermodynamic properties, a center piece of COSMO-RS—the σ-profile of the molecules—can nonetheless be useful in qualitative rationalizing several experimentally derived quantities, as demonstrated here.

2. Experimental

2.1. Materials

The details of the materials used are shown in Table 1. Each component was distilled and stored with 0.3 nm molecular sieves for at least 24 h before use. The purity was confirmed with gas chromatography (Shimadzu GC-2010, Japan). The densities, refractive indices and ultrasonic speeds of the pure components were compared to the literature values as shown in Table 2.

2.2. Methods

Four binary mixtures were investigated: (1) dimethoxymethane + methanol, (2) dimethoxymethane + ethanol, (3) dimethoxymethane + propan-1-ol, and (4) dimethoxymethane + butan-1-ol at two temperatures 298.15 K and 303.15 K. The binary mixtures were prepared gravimetrically using an electronic balance (Shimadzu AY220, Japan, ± 0.0001 g) over the entire composition range. The expanded uncertainties at $\alpha = 95\%$ in the mole fraction were estimated to be $U(x_1) = 0.0001$ in all cases.

Ultrasonic speeds, u in the pure components and the binary mixtures were determined using a single-crystal variable-path multi-frequency ultrasonic interferometer (Mittal M-81 H, India, ± 0.0001 MHz) operated at 2.0004 MHz and thermostated with a refrigerated digital temperature controller (Polyscience, USA, ± 0.01 K). The expanded uncertainties at $\alpha = 95\%$ of the measurement were $U(u) = 0.8\ \mathrm{m\cdot s^{-1}}$.

Refractive indices, n_D of the pure components and the binary mixtures were measured with Abbe refractometer (Atago NAR-1 T Liquid, Japan, ±0.0002) thermostated with a refrigerated digital temperature controller (Polyscience, USA, ±0.01 K). The refractometer was calibrated with doubly distilled water [23] and 2,2,4-trimethylpentane [24] at both temperatures. All measurements are performed at wavelengths of the sodium D-lines with expanded uncertainties at $\alpha = 95\%$ of $U(n_D) = 0.0002$.

Densities, ρ were measured with a single capillary pycnometer having a bulb capacity about 9 cm^3 and capillary volume to length ratio of about 0.06 cm^2. The pycnometer containing the test liquid was thermostated in a water bath (Julabo EH, Germany, digital controlled increment of ± 0.1 K) and the temperature was monitored independently with a mercury thermometer with accuracy ± 0.02 K. The pycnometer was calibrated with doubly distilled water [25] and 2,2,4-trimethylpentane [24] at both temperatures and the expanded uncertainties at $\alpha = 95\ \%$ was $U(\rho) = 0.0002\ \mathrm{g\cdot cm^{-3}}$.

In all the measurements, the uncertainties introduced in the temperature control are within the estimated expanded uncertainties. We note that there are two independent temperature controls leading to slightly different estimates of uncertainties. All measurements are made at atmospheric pressure: on average $P = 100.9$ kPa, with standard uncertainty $u_c(P) = 0.3$ kPa.

2.3. $\boldsymbol{\sigma}$-profiles

The σ-profiles of DMM, MeOH, EtOH, PrOH and BuOH were calculated based on DFT theory using ADF COSMO-RS (version 2010.01) software with a GGA-BP functional and TZP basis set.

3. Results and discussion

The experimental ultrasonic speeds, u, refractive indices, n_D, and densities, ρ, of the binary mixtures (1) DMM + MeOH, (2) DMM + EtOH, (3) DMM + PrOH, and (4) DMM + BuOH are shown in Table 3. The σ-profiles of DMM and each alcohol (C_1–C_4) are shown in Fig. 1.

3.1. Data processing

The molar volume for each mixture is calculated according to

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho}, \quad (2)$$

where x_i is the mole fraction of component-i, M_i is the molar mass of component-i, and ρ is the experimental density of the mixture. The excess molar volume, V_m^E for each mixture is calculated according to

$$V_m^E = V_m - \left(x_1 V_{m,1}^{*} + x_2 V_{m,2}^{*}\right), \quad (3)$$

where $V_{m,i}^{*}$ is the molar volume and x_i is the mole fraction of the pure component-i for $i = 1, 2$ [14,26].

The V_m^E is analyzed using the extended real association solution (ERAS) model, initially described by Heintz [27]. The V_m^E is thought to be composed of two additive contributions [28]: a physical contribution from non-polar van der Waals interaction and free volume effects on mixing, and a chemical contribution from hydrogen bonding, i.e.

$$V_m^E = V_{phys}^E + V_{chem}^E, \quad (4)$$

Table 1
Details of the chemicals used.

Component	CASRN	Source (purity)	Purity (GC)
Methanol (MeOH)	67-56-1	R&M Chemicals, UK (> 99.5 % A.R.)	> 99 %
Ethanol (EtOH)	64-17-5	Merck, US (> 99 % absolute, A.R.)	> 99 %
Propan-1-ol (PrOH)	71-23-8	R&M Chemicals, UK (> 99.5 % A.R.)	> 99 %
Butan-1-ol (BuOH)	71-36-3	R&M Chemicals, UK (> 99.5 % A.R.)	> 99 %
Dimethoxymethane (DMM)	109-87-5	Acros Organics, Belgium (> 99 % A.R.)	> 99 %