

# Excess Volumes and Viscosities of Binary Mixtures of Aliphatic Alcohols (C<sub>1</sub>–C<sub>4</sub>) with Nitromethane

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Densities and viscosities were measured for the binary mixtures of methanol, ethanol, propan-1-ol, propan-2-ol, butan-2-ol, and 2-methyl-propan-2-ol with nitromethane at temperatures from 293.15 K to 313.15 K and atmospheric pressure. Densities were determined using a vibrating-tube densimeter. Viscosities were measured with an automatic Ubbelohde capillary viscometer. The estimated uncertainties are less than  $\pm 0.0001 \text{ g}\cdot\text{cm}^{-3}$  for density and  $\pm 0.7\%$  for viscosity. Excess volumes and viscosity deviations as a function of mole fraction average were derived, and the computed results were fitted to the Redlich–Kister equation. Furthermore, McAllister's three-body-interaction model is used to correlate the binary kinematic viscosities.

## 1. Introduction

Nitromethane is an aprotic solvent with high polarity which is used in a variety of applications. Upon mixing with alcohols of varying chain lengths, these mixtures might generate interesting properties due to specific interactions, hydrogen bond effects, and so forth. On the other hand, alcohols are the most well-known solvents with protic and self-associated properties, which are used to study the hydrophobic effects. Thus, accurate knowledge of their thermodynamic mixing properties, such as excess volume, excess enthalpy, and excess Gibbs energy, has great relevance in theoretical and applied areas of research.

In this study we measure the density and viscosity for the binary mixtures of methanol, ethanol, propan-1-ol, propan-2-ol, butan-2-ol, and 2-methyl-propan-2-ol with nitromethane in the temperature interval 293.15 K to 313.15 K over the entire composition range. The experimental results are used to calculate excess molar volumes and viscosity deviations from the mole fraction average. These results are used to qualitatively discuss the nature of interactions that occur in mixing the components. The present paper is, therefore, concerned about the study of the influence of the hydrocarbon chain of the alcohols and the chemical structure of the nitromethane upon the excess volumes and viscosity deviations. The excess volumes and viscosity deviations have been fitted to the Redlich–Kister equation,<sup>1</sup> and the coefficients of the Redlich–Kister equation were determined. An attempt has also been made to correlate the kinematic viscosities with the McAllister equation.<sup>2</sup> To the best of our knowledge, data in the literature were available for the excess volumes of propan-1-ol and propan-2-ol with nitromethane at 288.15 K, 293.15 K, 298.15 K, and 308.15 K and atmospheric pressure.<sup>3</sup>

## 2. Experimental Section

The chemicals used were of analytical grade and obtained from Fisher, Tedia, and Merck. All components were dried over molecular sieves (Aldrich, 0.3 nm). Nitromethane was distilled through a glass column (23-mm i.d. and 470-mm length, Teflon mesh packing) under nitrogen. The other components were used without further purification.

The purity of all chemicals was checked by gas chromatography. In all cases chemicals with a purity greater than 99.6 mass% were used for the experimental investigations. The purity of solvents was further ascertained by measuring their densities, viscosities, and refractive indices at 298.15 K (Table 1), which agreed reasonably with the corresponding literature values.<sup>4</sup> Refractive indices,  $n_D$ , of pure chemicals were measured with a digital refractometer RX-5000 (ATAGO, Tokyo/Japan), with an uncertainty of  $\pm 0.00001$  units.

All dried liquids were boiled to remove dissolved air. Solutions of different composition were prepared by mass in a 50-cm<sup>3</sup> Erlenmeyer flask provided with a joint stopper, using a Mettler AB204 balance with an uncertainty of  $\pm 0.1$  mg. The uncertainty in the mole fraction is  $\pm 5 \times 10^{-5}$ . Densities were measured using a DMA-58 vibrating-tube densimeter (Anton-Paar, Graz/Austria) with a stated uncertainty of  $\pm 0.00002 \text{ g}\cdot\text{cm}^{-3}$ . The temperature in the measuring cell was regulated to  $\pm 0.01$  K. The uncertainty of the density measurements was less than  $\pm 0.0001 \text{ g}\cdot\text{cm}^{-3}$ .

The kinematic viscosities were determined with a commercial capillary viscometer of the Ubbelohde type (SCHOTT-GERÄTE, Hofheim/Germany). The kinematic viscosity ( $\nu$ ) was then calculated from the following relationship

$$\nu \equiv \eta/\rho = k(t - \theta) \quad (1)$$

where  $t$  is the flow time,  $\eta$  is the dynamic viscosity, and  $k$  and  $\theta$  are respectively the viscometer constant and the Hagenbach correction. The constants  $k$  for several viscometers were provided by the manufacturer and were checked with both pure water and benzene. The value  $\theta$ , which is dependent on the flow time and the size of the capillary, was taken from the tables supplied by the manufacturer. The viscometer was kept in a D20KP (LAUDA, Lauda-Königshofen/Germany) thermostat controlled to  $\pm 0.01$  K with a proportional-integral-differential regulator. The accuracy of the flow-time measurement is  $\pm 0.01$  s. Triplicate measurements of flow times were reproducible within  $\pm 0.02\%$ . The uncertainty of the viscosity measurement was less than  $\pm 0.7\%$ .

The densities and viscosities of the binary mixtures formed by methanol, ethanol, propan-1-ol, propan-2-ol, butan-2-ol, and 2-methyl-propan-2-ol with nitromethane

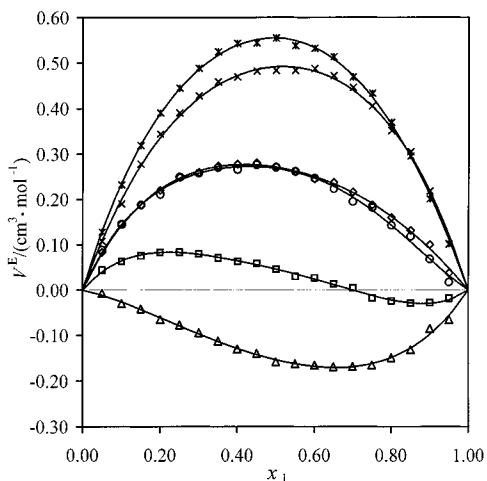
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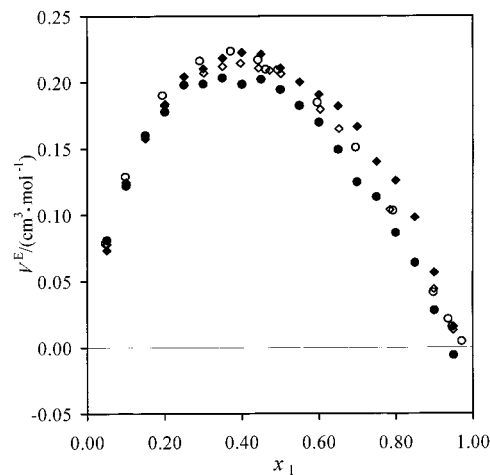
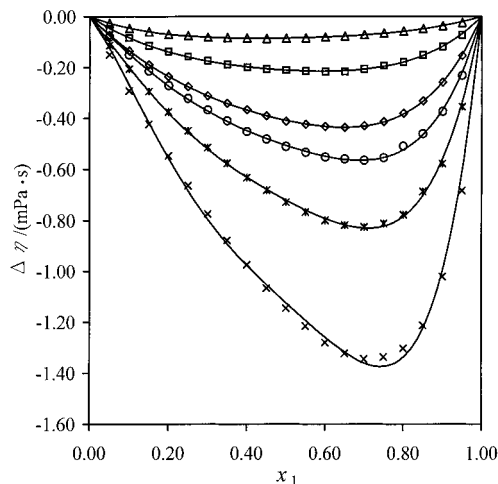
**Table 8. Coefficients of the Redlich–Kister Equation and Standard Deviations for  $V^E$  and  $\Delta\eta$** 

$V^E/\text{unit}$	$T/\text{K}$	$a_0 \times 10^2$	$a_1 \times 10^2$	$a_2 \times 10^2$	$a_3 \times 10^2$	$\sigma$
Methanol (1) + Nitromethane (2)						
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	293.15	-67.287	36.404	-12.453	14.396	0.004
	303.15	-61.360	40.649	-11.243	14.248	0.005
	313.15	-52.932	45.776	-7.022	13.247	0.004
$\Delta\eta/\text{mPa} \cdot \text{s}$	293.15	-36.306	-5.435	-15.527	0.573	0.001
	303.15	-33.595	-4.471	-17.408	-2.727	0.001
	313.15	-30.363	-4.603	-15.056	-2.990	0.001
Ethanol (1) + Nitromethane (2)						
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	293.15	0.671	54.674	8.941	17.884	0.004
	303.15	18.516	40.859	1.718	38.014	0.003
	313.15	40.727	35.117	13.435	37.783	0.003
$\Delta\eta/\text{mPa} \cdot \text{s}$	293.15	-97.693	25.504	-37.795	0.735	0.001
	303.15	-84.247	17.771	-41.377	7.988	0.002
	313.15	-68.319	13.280	-26.699	3.726	0.006
Propan-1-ol (1) + Nitromethane (2)						
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	293.15	85.190	22.734	26.614	33.703	0.005
	303.15	108.420	26.430	32.952	14.181	0.004
	313.15	126.995	35.581	35.618	2.584	0.005
$\Delta\eta/\text{mPa} \cdot \text{s}$	293.15	-209.387	92.828	-112.489	40.102	0.001
	303.15	-163.224	65.926	-83.967	29.952	0.001
	313.15	-126.531	47.629	-59.294	19.858	0.001
Propan-2-ol (1) + Nitromethane (2)						
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	293.15	76.889	30.655	14.774	57.856	0.006
	303.15	107.308	24.564	17.038	43.524	0.006
	313.15	138.876	15.857	25.596	39.859	0.006
$\Delta\eta/\text{mPa} \cdot \text{s}$	293.15	-285.287	156.123	-192.612	131.683	0.010
	303.15	-202.519	102.056	-128.097	78.581	0.006
	313.15	-145.279	66.991	-87.044	51.509	0.005
Butan-2-ol (1) + Nitromethane (2)						
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	293.15	187.976	5.992	24.975	37.682	0.008
	303.15	221.831	4.886	38.827	21.286	0.006
	313.15	255.825	2.886	44.140	12.050	0.004
$\Delta\eta/\text{mPa} \cdot \text{s}$	293.15	-452.198	277.508	-402.529	316.870	0.021
	303.15	-288.034	161.129	-208.707	138.230	0.010
	313.15	-186.063	94.347	-108.134	55.387	0.004
2-Methylpropan-2-ol (1) + Nitromethane (2)						
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	298.15	194.772	-6.467	64.528	-20.074	0.009
	303.15	196.591	-9.328	55.527	-4.738	0.008
	313.15	208.243	-9.585	57.337	-9.874	0.008
$\Delta\eta/\text{mPa} \cdot \text{s}$	298.15	-594.570	428.248	-627.330	515.880	0.041
	303.15	-449.653	279.597	-394.684	352.457	0.028
	313.15	-251.259	148.635	-177.410	117.325	0.008

**Figure 1.** Excess volume variation with mole fraction for alkanol (1) + nitromethane (2) at 303.15 K: ( $\Delta$ ) methanol, ( $\square$ ) ethanol, ( $\diamond$ ) propan-1-ol, ( $\circ$ ) propan-2-ol, ( $*$ ) butan-2-ol, ( $\times$ ) 2-methylpropan-2-ol, (—) Redlich–Kister equation.

mixtures with propan-1-ol and  $0.0133 \text{ cm}^3 \cdot \text{mol}^{-1}$  higher than ours for mixtures with propan-2-ol.

In the present investigation, alcohols are strongly self-associated through hydrogen bonding, with degrees of association depending on such variables as chain length, the position of the OH group, temperature, and dilution by other substances. Nitromethane has a fairly high dipole moment ( $3.56 \times 10^{-30} \text{ C} \cdot \text{m}$ ), but there is little evidence that its molecules are strongly associated in their pure liquid

**Figure 2.** Comparison of our excess volume with literature data at 293.15 K. Propan-1-ol (1) + nitromethane (2): ( $\blacklozenge$ ) present work; ( $\bullet$ ) Cerdeirina et al. Propan-2-ol (1) + nitromethane (2): ( $\bullet$ ) present work; ( $\circ$ ) Cerdeirina et al., 1999.**Figure 3.** Viscosity-deviation variation with mole fraction for alkanol (1) + nitromethane (2) at 303.15 K: ( $\Delta$ ) methanol; ( $\square$ ) ethanol; ( $\diamond$ ) propan-1-ol; ( $\circ$ ) propan-2-ol; ( $*$ ) butan-2-ol; ( $\times$ ) 2-methylpropan-2-ol; (—) Redlich–Kister equation.

state.<sup>5</sup> Although a theoretical study on nitromethane indicates that C–H...O hydrogen bonding can occur in liquid nitromethane,<sup>6</sup> it can be expected that this interaction would be weaker, probably negligible, than that in alkanols. Some authors<sup>7–9</sup> explain both composition and temperature dependence of excess volumes of alkanol + polar mixtures as a balance between positive contributions (hydrogen bond rupture and dispersive interactions between unlike molecules) and negative contributions (dipole–dipole interactions and geometrical fitting between components). In addition, the dilution of dipoles affects  $V^E$  considerably and Marsh showed the evidence of this effect for nitromethane + and nitroethane + each of several nonpolar liquids.<sup>10</sup>

The values of the deviations in viscosity calculated from eq 3 are presented in Figure 3. There is a clear trend in  $\Delta\eta$  values for all of the mixtures. The  $\Delta\eta$  values, which generally decrease with increasing size of the alcohol molecules, are negative. According to McAllister, the three-body-interaction model for the kinematic viscosity of liquid mixtures is defined as

**Table 9. Parameters of McAllister's Three-Body-Interaction Model and Standard Deviations for Kinematic Viscosities of Alkanol (1) + Nitromethane (2) Mixtures**

<i>T</i> /K	$\nu_{12}$	$\nu_{21}$	$\sigma/10^{-6}$ $\text{m}^2\cdot\text{s}^{-1}$	$\nu_{12}$	$\nu_{21}$	$\sigma/10^{-6}$ $\text{m}^2\cdot\text{s}^{-1}$
	methanol			propan-2-ol		
293.15	0.529 94	0.472 08	0.004	0.869 37	0.638 98	0.032
303.15	0.468 34	0.419 24	0.005	0.736 47	0.539 49	0.023
313.15	0.417 02	0.378 90	0.004	0.623 31	0.490 52	0.016
	ethanol			butan-2-ol		
293.15	0.757 60	0.530 44	0.008	1.069 31	0.753 55	0.078
303.15	0.644 31	0.461 88	0.010	0.881 35	0.621 07	0.046
313.15	0.558 00	0.422 33	0.006	0.741 01	0.542 17	0.028
	propan-1-ol			2-methyl-propan-2-ol		
293.15	1.095 51	0.643 40	0.024	0.902 69 <sup>a</sup>	0.822 32 <sup>a</sup>	0.100 <sup>a</sup>
303.15	0.906 45	0.551 74	0.018	0.847 24	0.649 51	0.070
313.15	0.755 46	0.498 25	0.011	0.748 75	0.557 71	0.035

<sup>a</sup> For temperature at 298.15 K.

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln(x_1 + x_2 M_2/M_1) + 3x_1^2 x_2 \ln [(2 + M_2/M_1)/3] + 3x_1 x_2^2 \ln [(1 + 2M_2/M_1)/3] + x_2^3 \ln(M_2/M_1) \quad (6)$$

where  $\nu_{12}$  and  $\nu_{21}$  are the model parameters,  $\nu$  is the kinematic viscosity of the mixture, and  $x_1$ ,  $\nu_1$ ,  $M_1$ ,  $x_2$ ,  $\nu_2$ , and  $M_2$  are the mole fractions, kinematic viscosities, and molecular weights of pure components 1 and 2, respectively. Kinematic viscosities of the present study were fitted to the McAllister equation. Table 9 records the calculated results, which include McAllister's parameters and standard deviations. It is observed that McAllister's model correlates the mixture kinematic viscosity to a significant degree of accuracy for all of the systems, as evidenced by small standard deviations.

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