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Thermophysical study of the binary mixtures of *N*,*N*-dimethylacetamide with 1-propanol and 1-butanol

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ABSTRACT

Several thermophysical properties such as densities, ρ, speeds of sound, u, refractive indices, n_D, and kinematic viscosities, ν, have been measured for the binary mixtures of *N*,*N*-Dimethylacetamide with 1-propanol and 1-butanol over the entire range of composition, at the temperatures (283.15, 298.15 and 313.15) K and at atmospheric pressure $p = 0.1$ MPa. From these experimental data, excess molar volumes, V^E, excess isentropic compressibilities, κ_S^E, refractive index deviations, Δn_D, and viscosity deviations, $\Delta\eta$, were calculated. Then, correlated with the Redlich-Kister equation and the corresponding parameters were drived. The results obtained, were discussed in terms of structural effects and specific molecular interactions, and the influence of the alkanol chain length was also considered.

1. Introduction

Alkanols are interesting versatile solvents, used in chemical and technological processes; they are inexpensive and easily available at high purity. These polar liquids are self-associated through hydrogen bonding, creating multimers of different degrees [1,2], this association is disturbed when they are mixed with another solvent.

So, when amide and alkanols are mixing different intermolecular interactions take place, resulting in non-ideal behaviour. Hence, the measurement of thermophysical properties such as density, speed of sound, refractive index, and viscosity allows the calculation of excess and deviation properties. Further, it's easier to explore the sign and the magnitude of these properties, in order to understand the specific interactions occurring between the molecules. The major goal of our research is to provide thermophysical data and to relate them with molecular size, shape and charge distribution of the mixed compounds.

An extensive survey of the literature has shown that, few studies were available concerning the thermophysical properties for these binary mixtures. Density and viscosity measurements were reported for these mixtures at $T = 303.15$ K [3]. Another density measurements and calculated excess molar volumes were given only at $T = 298.15$ K by two authors [4,5], and finally the refractive indices and their deviations at $T = 298.15$ K [5] were reported too. On the other hand, there is more data available regarding the excess enthalpies for these kind of systems at temperatures 298.15 K [4,6,7] and 313.15 K [8], and phase equilibrium for the 1-propanol and *N*,*N*-dimethylacetamide mixture (solid-liquid equilibrium [9] and vapour-liquid equilibrium [10]). An earlier study was undertaken [11], to gain thermophysical information about the *N*,*N*-dimethylacetamide when it is mixed with methanol or ethanol. We continue this study, reporting the experimental density, speed of sound, refractive index and viscosity for the binary mixtures of *N*,*N*-dimethylacetamide with 1-propanol and 1-butanol at temperatures (283.15, 298.15 and 313.15) K and at atmospheric pressure, $p = 0.1$ MPa. The excess molar volume, excess isentropic compressibility, the refractive index deviation and viscosity deviation were also calculated and correlated. The behaviour of these properties with composition helps to understand the effect of temperature, and how raising chain length of alcohols can influence the sign and magnitude of such properties.

2. Experimental

2.1. Materials

Table 1 reports for the chemicals used in this work the provenance, the mass purity checked by gas chromatography and the water content measured by an automatic titrator Crison KF 1S-2B.

The experimental density, speed of sound, refractive index and kinematic viscosity values, of the pure components at work temperatures and at $p = 0.1$ MPa are collected in Table 2 along with isobaric expansibility values, calculated from our density measurements, and molar heat capacity values taken from literature [12–13]. For comparison, some values found in the literature [14–31] are also included in this Table.

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Table 1
Provenance and purity of the liquid compounds.

Chemical name	Source	Purity/mass fraction	Analysis method	Water content/ppm
N,*N*-dimethylacetamide	Sigma-Aldrich	0.999	GC	295
1-propanol	Sigma-Aldrich	0.998	GC	195
1-butanol	Sigma-Aldrich	0.999	GC	175

2.2. Methods

The binary mixtures were prepared by weighing appropriate volumes of pure liquids on an electronic balance Sartorius semimicro balance CP225-D within $\pm 1 \cdot 10^{-5}$ g, the uncertainty in the mole fraction was estimated to be 0.0005. To ensure the homogeneity of samples, they were well mixed, and were kept in airtight stopper glass vials, in order to minimize evaporation losses.

The density, ρ, and the speed of sound, u, of the sample were measured simultaneously by an Anton Paar DSA 5000 densimeter and sound analyzer at 3 MHz. This device automatically corrects the influence of viscosity on density values. The temperature in the cell was maintained stable to ± 0.005 K. The uncertainties of ρ and u measurements are 0.1 $kg \cdot m^{-3}$ and 0.5 $m \cdot s^{-1}$, respectively.

The refractive index at 589.3 nm sodium wavelength, n_D, of the sample was measured by an automatic refractometer Abbemat-HP DR. Kernchen, with an uncertainty of 10^{-5}. During the measurement, the sample temperature is controlled by a Peltier device with a stability of ± 0.002 K.

Finally we measured the kinematic viscosity, ν, using an Ubbelohde capillary viscometer. The viscosimeter filled with the sample liquid was kept in a transparent bath, where temperature is maintained stable within ± 0.01 K, using a Schoot-Geräte CT 1150/2 thermostat. To determine the flow time, an automatic measuring unit Schoot-Geräte AVS-440 was employed, the corresponding kinetic energy correction was applied to measured time. Once density and kinematic viscosity are known, the dynamic viscosity η, can be calculated using: $\eta = \rho \cdot \upsilon$. The uncertainties of both kinematic and dynamic viscosity determinations were estimated to be 0.005 $mm^2 \cdot s^{-1}$ and 0.005 mPa·s respectively. All details of calibration of these devices can be found in previous papers [32,33].

3. Results and discussion

Experimental values of density, speed of sound, refractive index, and kinematic viscosity and calculated values of isentropic compressibility, dynamic viscosity, excess molar volume, excess isentropic compressibility, refractive index deviation, and viscosity deviation for the binary systems of *N*,*N*-dimethylacetamide with 1-propanol and 1-butanol are collected in Table S1 in the Supplementary material.

3.1. Excess molar volume

The excess molar volume ($\pm 10^{-9}$ $m^3 \cdot mol^{-1}$) was calculated from experimental densities of the pure liquids and their mixtures using the following equation:

$$V^E = \sum_i x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \quad (1)$$

where ρ is the density of the mixture and x_i, M_i, and ρ_i are, the mole fraction, the molar mass and density of component *i*, respectively.

Table 2
Thermophysical properties of the pure compounds at $p = 0.1$ MPa and at work temperatures and comparison of densities, speeds of sound, refractive indices, and dynamic viscosities with literature data at $T = 298.15$ K.[a]

T/K	ρ/kg·m^{-3}		u/m·s^{-1}		C_p/J·mol^{-1}·K^{-1}	α_p/kK^{-1}	n_D		η/mPa·s	
	Exptl.	Lit.	Exptl.	Lit.			Exptl.	Lit.	Exptl.	Lit.
N,*N*-dimethylacetamide										
283.15	950.13		1516.80		170.70[e]	0.9719	1.442726		1.1683	
298.15	936.29	936.34[b] 936.28[c]	1453.68	1455.91[b] 1455.37[d]	172.69[e]	0.9863	1.435794	1.4356[f] 1.4359[g]	0.9299	0.920[f] 0.937[h]
313.15	922.43		1393.35		175.46[e]	1.0011	1.429006		0.7644	
1-propanol										
283.15	811.74		1258.06		136.29[l]	0.9936	1.389271		2.8407	
298.15	799.77	799.66[i] 799.62[j]	1206.17	1206[i] 1205.93[k]	144.18[l]	1.0085	1.383104	1.3832[m] 1.38309[n]	1.9491	1.947[o] 1.9503[p]
313.15	787.54		1155.36		153.09[l]	1.0241	1.376864		1.3892	
1-butanol										
283.15	817.20		1291.66		167.94[l]	0.9394	1.403162		3.8636	
298.15	806.09	805.93[k] 806.06[q]	1240.60	1240.09[r] 1240.37[s]	177.10[l]	0.9527	1.397139	1.39729[t] 1.39720[u]	2.5733	2.59[t] 2.563[u]
313.15	794.44		1190.52		187.29[l]	0.9667	1.391074		1.7696	

[a] Standard uncertainties u are $u(T) = 0.005$ K for densities and speeds of sound and $u(T) = 0.01$ K for the rest of properties, $u(p) = 0.003$ MPa, $u(\rho) = 0.1$ $kg \cdot m^{-3}$, $u(u) = 0.5$ $m \cdot s^{-1}$, $u(n_D) = 10^{-5}$, and $u(\eta) = 0.005$ mPa·s.
[b] Ref. [14].
[c] Ref. [15].
[d] Ref. [16].
[e] Ref. [12].
[f] Ref. [17].
[g] Ref. [18].
[h] Ref. [19].
[i] Ref. [20].
[j] Ref. [21].
[k] Ref. [22].
[l] Ref. [13].
[m] Ref. [23].
[n] Ref. [24].
[o] Ref. [25].
[p] Ref. [26].
[q] Ref. [27].
[r] Ref. [28].
[s] Ref. [29].
[t] Ref. [30].
[u] Ref. [31].