Thermodynamic properties of binary mixtures containing N,N-dimethylformamide + 2-alkanol: Cubic and statistical associating fluid theory-based equation of state analysis

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Mohammad Almasi *

Department of Chemistry, Science and Research Branch, Islamic Azad University, Khouzestan, Iran

A B S T R A C T

Densities and viscosities of mixtures of N,N-dimethylformamide with 2-propanol, 2-butanol, 2-pentanol, 2-hexanol, and 2-heptanol have been measured as a function of composition range at T = (298.15, 303.15, 308.15, 313.15) K and atmospheric pressure. Excess molar volumes V_m^E and viscosity deviations $\Delta\eta$ were calculated and correlated by the Redlich–Kister type function. The statistical associating fluid theory (SAFT), and perturbed chain statistical associating fluid theory (PC-SAFT) were applied to correlate and predict the volumetric behavior of the mixtures. The best predictions were achieved with the PC-SAFT equation of state. Also the Peng–Robinson–Stryjek–Vera (PRSV) equation of state (EOS) has been used to predict the binary viscosities.

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1. Introduction

Over the past decades, the modeling of processes has received a great deal of attention as a reliable tool to attain efficient, clean, and optimal new technologies [1]. The increasing development of process design, under the pressure of the growing of chemical and related industries, seeks to create environmentally friendly and low energy consuming conditions. Such modeling is critically dependent on the accurate knowledge of the thermodynamic behavior of the chemicals involved; therefore, the availability of suitable methods and the disposal of reliable physical property data are basic requirements to achieve a proper design [2,3]. On the other hand, knowledge of the pressure and temperature effects on the volume of complex fluid systems, either pure or mixed, is also required both for theoretical thermodynamics calculations and in engineering processes. However, despite the critical role played by *PVTx* data, so far the evaluation of such measurements over wide ranges of pressure, temperature, and composition often is not feasible because of economical and/or time-consuming requirements; hence, the modeling of *PVTx* data constitutes an alternative approach to the problem, in such a way that the modern process simulators include a variety of predictive models [4].

N,N-dimethylformamide (DMF) is a colorless, non-hydrogen bonded liquid, high-boiling, mobile, highly polar liquid with a faint, characteristic odor. DMF does not decompose at distilling at low pressure and is freely miscible with water, alcohols, ethers, ketones, esters, carbon disulfide, and chlorinated and aromatic hydrocarbons. Molecular interactions of N,N-dimethylformamide (DMF) with some solvents reported by various thermodynamic and thermophysical measurements. Several topics and examples of thermodynamic studies are depicted on the basis of the structural behavior of N,N-dimethylformamide (DMF) for binary and ternary mixtures of non-electrolytes. Valuable information on the behavior and factors governing of the liquid structure of the strongly associated solvents together with some properties such as excess volumes, viscosity deviations and ultrasonic studies of mixtures containing DMF with other solvents are reported in elsewhere [5].

Alkanols are organic compounds containing an –OH functional group bonded to a carbon atom. As the number of their carbon atoms increases, the non-polarity of the larger hydrocarbon chain offsets the polarity of the –OH group. The hydroxyl functional group strongly contributes to the physical properties of alkanols. The electronegativity of oxygen contributes to the unsymmetrical distribution of charge, creating a partial positive charge on the hydrogen and a partial negative charge on the oxygen. This uneven distribution of electron density in the –OH bond creates a dipole. Physical properties of alkanols are influenced by the hydrogen bonding ability of the –OH group. Hydrogen bonding raises the

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* Tel.: +98 6114431018; fax: +98 6114435288.
   E-mail addresses: m.almasi@khouzestan.srbiau.ac.ir,
almasi.mohammad@gmail.com

boiling point of alcohols. This is due to the combined strength of so many hydrogen bonds forming between oxygen atoms of one alcohol molecule and the hydroxyl H atoms of another. Alkanols of short chain length have a greater proton-donor capacity, so the strength of bonding is expected to decrease with an increase in their chain lengths. Moreover, because of the steric hindrance of alkyl groups, hydrogen bonds are weakened for higher length alkanols [5,6].

Continuing these investigations [7,8], present paper reports the densities, viscosities, excess molar volumes and viscosity deviations of mixing for the binary mixtures of N,N-dimethylformamide + 2-alkanols at T = (298.15, 303.15, 308.15, 313.15) K. In this work, the statistical associating fluid theory (SAFT), and perturbed chain statistical associating fluid theory (PC-SAFT), were applied to correlate and predict the volumetric behavior of the mixtures. Also the Peng–Robinson–Stryjek–Vera (PRSV) equation of state (EOS) has been used to predict the binary viscosities. Data available from literature, concerning deviations from ideality for this kind of mixtures mainly deal with excess molar volumes V_m^E and viscosity deviations [9,10], but few theoretical models to correlate and predict the experimental data can be found.

2. Materials and methods

2.1. Chemicals

The following materials with mass fraction purity were used N,N-dimethylformamide, 2-propanol, 2-butanol, 2-pentanol, 2-heptanol (Merck with mass purity > 0.99) and 2-hexanol (Aldrich with mass purity > 0.99). In Table 1, we compared the measured densities and viscosities at 298.15 K with values available in the literature [11–17].

2.2. Apparatus and procedure

An Anton Paar oscillating U-tube densimeter (DMA 4500 model) with automatic viscosity correction was used in this work. Densimeter was calibrated twice a day by air and bidistilled water. Uncertainty for density measurements is $\pm 5 \times 10^{-5}$ g/cm^3. Viscosities were measured with an Ubbleohde viscometer with an uncertainty of $\pm 2 \times 10^{-2}$ mPa/s. The equation for viscosity, according to Poiseuille's law, is

$$\eta = \rho \left(\frac{kt - c}{t} \right) \tag{1}$$

where k and c are the viscometer constants, t and η are the efflux time and dynamic viscosity, respectively. The k and c parameters were obtained by measurements on double distilled water and benzene at 298.15 K. In all measurements a thermostat was used at a constant digital temperature of ± 0.01 K. The mixtures were prepared just before 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 error in the mole fractions is $\pm 1 \times 10^{-4}$. Experimental procedures in this study essentially are similar to that of our previous works.

3. Results and discussion

3.1. Densities and derived properties

Excess molar volumes, V_m^E for studied mixtures, were calculated at different temperatures by use of the following equation

$$V_m^E = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}) \tag{2}$$

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. Calculated excess molar volumes for binary mixtures of N,N-dimethylformamide + 2-alkanols at T = 298.15 K are plotted in Fig. 1. The V_m^E values were fitted to the following type of Redlich–Kister polynomial [18]

$$Y^E = x_1 (1 - x_1) \sum_{k=0}^{N} A_k (1 - 2x_1)^k \tag{3}$$

where $Y^E \equiv V_m^E$ or $\Delta \eta$ and x_1 is the mole fraction of dimethyl carbonate. A_k is an adjustable parameter obtained by the

Table 1
Properties of the pure compounds at 298.15 K.

Chemical name	ρ (g/cm^3)		η (mPa/s)	
	Exptl.	Lit.	Exptl.	Lit.
N,N-Dimethylformamide	0.94409	0.9445[a]	0.803	0.802[a]
		0.9442[b]		0.805[d]
		0.944290[c]		0.80[e]
2-Propanol	0.78109	0.78126[e]	2.055	2.043[e]
		0.78114[d]		2.021[f]
		0.78128[d]		2.04[g]
2-Butanol	0.80270	0.80241[e]	3.105	2.998[e]
		0.80265[d]		3.12[g]
		0.8027[d]		3.11[g]
				2.98[d]
2-Pentanol	0.80541	0.80524[e]	3.478	3.478[e]
		0.80562[d]		3.5[g]
				3.49[d]
2-Hexanol	0.81014	0.81014[e]	4.101	4.100[e]
		0.81032[d]		4.14[d]
		0.81019[d]		3.9[g]
2-Heptanol	0.81318	0.81333[b]	5.003	5.331[b]
		0.81327[d]		5.128[d]
				4.9[g]

[a] Reference [11].
[b] Reference [12].
[c] Reference [13].
[d] Reference [14].
[e] Reference [15].
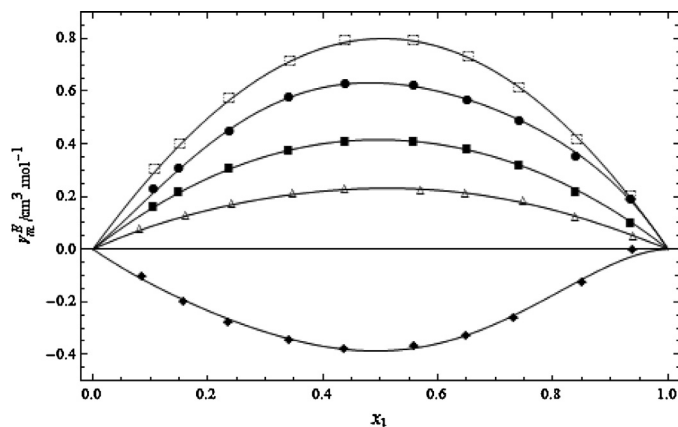[f] Reference [16].
[g] Reference [17].

Fig. 1. Excess molar volumes V_E^m vs. mole fraction of N,N-dimethylformamide for binary mixtures of N,N-dimethylformamide with (◆) 2-propanol, (△) 2-butanol, (■) 2-pentanol, (●) 2-hexanol, (□) 2-heptanol at T = 298.15 K. The solid curves were calculated from Redlich–Kister type equation.