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Excess volumes and excess enthalpies of *N*-methyl-2-pyrrolidone with branched alcohols

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Abstract

Excess molar volumes (V^E) at 303.15 K and excess enthalpies (H^E) at 298.15 K and ambient pressure have been measured as a function of composition for the binary liquid mixtures of *N*-methyl-2-pyrrolidone (NMP) with branched alcohols. The branched alcohols include 2-propanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol and 3-methyl-1-butanol. The V^E values were measured using a dilatometer and are negative over the entire mole fraction range for all the systems. The H^E values for the above mixtures have been measured by a Paar 1451 solution calorimeter and are positive over the whole range of compassion. The experimental results have been correlated using Redilich–Kister polynomials and the results are interpreted on the basis of possible hydrogen bonding between unlike molecules and changes in molecular association equilibria as well as structural effects for these systems.

Keywords: *N*-Methyl-2-pyrrolidone; Branched alkanols; Binary mixture; Excess molar volumes; Excess enthalpies; Hydrogen bonding; Molecular interactions

1. Introduction

Experimental data of excess thermodynamic properties of liquids and liquid mixtures are fascinating and of great fundamental, practical importance and industrial points of view. Moreover, these properties allow one to draw information on the structure and interactions of mixed solvents. The chemical industries have recognized the importance of the thermodynamic properties in design calculations involving chemical separations, heat transfer, mass transfer and fluid flow.

N-Methyl-2-pyrrolidone (NMP) is a colorless, high-boiling, mobile, characteristic odor and low viscosity. NMP, known for its low toxicity and solvent power, is rapidly becoming the product of choice for paint strippers, agricultural chemicals, and process solvent applications. As a cosolvent, NMP can improve the gloss of floor polishes and it also has application in the electronic industry as a photoresist stripper. On the other hand, NMP is a strongly polar liquid and has the potential for use in solvent extraction process for separating polar substances from non-polar substances [1]. It is not on the Hazardous Air Pollutants (HAPs) list of the U.S. 1990 Clean Air Act Amendments. Recently, the demand for NMP is explicitly and incessantly increasing with the research and development of the electronics and chemical industry. It is an aprotic solvent with a large dipole moment and a high dielectric constant ($\mu = 4.09$ Debye and $\varepsilon = 32.2$ at 298.15 K) [2]. NMP is completely soluble with water at all temperatures and also soluble with most organic solvents. It is well known that amides (NMP) interact with water or alcohols by dipole–dipole interactions, and form some hydrogen-bonded complexes or hetero-associates [3–6].

Alkanols are polar liquids, strongly self-associated by hydrogen bonding to the extent of polymerization that may differ depending on temperature, chain length, and position of the OH group. For the alcohols which are highly associated in the pure state, breaking of the H-bonds followed by specific interactions

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occurs upon mixing with highly polar solvents. The alkanol chain length, and shifting the position of the hydroxyl group of the alkanol are important parameters that must be taken into account to explain the behavior interaction of the NMP + alkan-1-ol mixtures [7]. Due to the strong hydrogen bonding acceptor ability of the CO oxygen, NMP can interact with hydrogen bond donor alcohols [8], giving rise to the C=O· · ·H–O moiety [9]. The structure of the amide–water and amide–alcohol hetero-associations is different. The water molecule can participate in four hydrogen bonds, while alcohol molecules may create only two hydrogen bonds, forming linear polymeric structures [10]. On the basis of those studies, it will be interesting to explore the thermodynamic results of NMP with alcohols to obtain some information on the molecular interactions. Branching of alkyl group attached to the hydroxyl group results in abnormal behavior of alcohols. The branched alkanols are widely used as coupling and dispersing agents in the chemical, pharmaceutical and household industries and as carrier and extraction solvents for natural products. To investigate the study of polar NMP with water [11–14] or 1-alkanols [7,15–17], or *iso*-alkanols [C_3–C_5] [18] a series of measurements are in progress.

In other words, excess molar volumes (V^E) of binary mixtures containing NMP + aromatic hydrocarbons [19,20], +hydrocarbon [16,21], +chloroethanes and chloroethenes [22], +an ether [23] have been appeared in the literature. Moreover, several researchers explicitly elucidated in the literature for the excess enthalpies (H^E) of binary mixtures containing NMP + aromatic hydrocarbons [20,24], +hydrocarbon [21,25,26], or +*N*-methylcaprolactam [27], +chloroethanes and chloroethenes [28], +an ether [23]. However, no effort appears to have been made to collect the V^E and H^E for the mixtures of NMP with branched alkanols and there is no evidence for specific interactions between of NMP with branched alkanols. Molar excess volumes and molar excess enthalpies of these mixtures are also of interest from thermodynamic and structural points of view. In order to extend the our research programme to explore the interactions between the high polar groups with other solvents [22,28–33], and to characterize the type and magnitude of molecular interactions between the polar group solvents and also to study the effect of chain length of alkanols, we report here the V^E and H^E at 303.15 K and at 298.15 K, respectively, and atmospheric pressure of binary mixtures of containing NMP with branched alkanols, which are 2-propanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol and 3-methyl-1-butanol.

2. Experimental

2.1. Materials

The pure solvents, of highest purity commercially available were used in the present investigation. NMP (Merck >99%) was distilled at low pressure and stored over freshly activated 3A molecular sieves. The branched alcohols (Fluka) were purified by the methods described previously [34]. The purity of the chemicals assessed by comparing their measured densities (ρ) and refractive indices (n), which were in good agreement with literature values [2,35,36], as can be seen in Table 1. Densities of pure components were determined with a bicapillary-type pycnometer, of capacity 12 cm^3. The densities of the pure liquids were accurate to two parts in 10^5. Refractive index was determined using Abbe's refractometer with an accuracy of ±0.0002. The purities of the samples were further confirmed by GLC single sharp peaks.

Table 1
Densities (ρ) at 303.15 K and refractive indices (n) at 298.15 K of pure components

Compound	ρ ($g\,cm^{-3}$)		(n)	
	This work	Literature [34,35]	This work	Literature [2]
NMP	1.02340	1.02370[a]	1.4674	1.4675
2-Propanol	0.77688	0.77690	1.3750	1.3752
2-Butanol	0.79892	0.79895	1.3954	1.3953
2-Methyl-1-propanol	0.79434	0.79437	1.3939	1.3939
2-Methyl-2-propanol	0.77616	0.77620	1.3851	1.3852
3-Methyl-1-butanol	0.80176	0.80179	1.4053	1.4052

[a] Ref. [35].

2.2. Apparatus

The experimental V^E values for binary mixtures at 303.15 K were measured by using the dilatometer technique delineated in earlier articles [37,38]. The mixing cell contains two bulbs of different capacities that are connected through a U tube containing mercury to separate the two bulbs. One of the two bulbs was fitted with a capillary, and the other one was fitted with ground-glass stoppers. Each bulb of the dilatometer was filled with a component which mass was determined directly by weighing. Five dilatometers with different capacities are used to cover the entire composition range. The filled dilatometer was placed in a temperature controlled water bath maintained at (303.15 ± 0.01) K. The measured V^E values were accurate to ±0.003 $cm^3\,mol^{-1}$. The uncertainty in solution composition expressed in mole fraction was found to be less than 5×10^{-5}.

The H^E values of liquid mixtures were measured using a new Paar 1451 solution calorimeter. The measurements were performed in an isolated house at 298.15 K and atmospheric pressure. The detailed procedure and apparatus used in this work have been depicted in our previous papers [39,40]. In the measurement of excess enthalpies, known weight of 100 ml of one component as solvent is taken with the Dewar vessel and 20 ml of other component as solute is weighted in a sealed glass rotating cell. Both the components are kept in thermal contact with each other in the Dewar vessel by pushing the glass rod. The temperature change accompanying the mixing process is sensed by the thermistor and recorded on the strip chart recorder. These experiments were continued until the concentrations reach 50–60% and this procedure was repeated by taking solvent as solute and solute as solvent. The reliability of the apparatus and the method was established by measuring H^E values of standard systems, i.e., benzene with carbontetrachloride and chlorobenzene with toluene throughout the concentration range at 298.15 K. Results were in good agreement with the reported data in the literature [41]. The uncertainty in the measure H^E values are ±1%.