Journal of Molecular Liquids 183 (2013) 31–44

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Measurements of some physical properties of binary liquid mixtures (N-methyl-2-pyrrolidone + an aliphatic ester) at several temperatures and data processing of viscosity and ultrasonic speed

D. Bala Karuna Kumar [a], K. Rayapa Reddy [a], G. Srinivasa Rao [b], P.B. Sandhyasri [c], Zareena Begum [a], C. Rambabu [a,*]

[a] Department of Chemistry, Acharya Nagarjuna University, Dr. M.R.A.R. Campus, Nuzvid, Andhra Pradesh 521201, India
[b] Department of Physics, Andhra Loyola College, Vijayawada, Andhra Pradesh 520 008, India
[c] Department of Physics, DAR College, Nuzvid, Andhra Pradesh 521201, India

ARTICLE INFO

Article history:
Received 2 November 2012
Received in revised form 3 April 2013
Accepted 4 April 2013
Available online 20 April 2013

Keywords:
Density
Viscosity
Ultrasonic speed
Excess molar volume
Binary mixture

ABSTRACT

The ultrasonic speed (U) studies are carried out using single crystal variable path fixed frequency (2 MHz) ultrasonic interferometer on some aliphatic esters in N-methyl-2-pyrrolidone (NMP) at temperatures of 303.15, 308.15, 313.15 and 318.15 K. Excess molar volume, excess isobaric thermal expansion coefficient, excess isentropic compressibility and excess ultrasonic speed are computed from the experimentally measured ultrasonic speeds and densities of pure liquids NMP, methyl acetate (MA), ethyl acetate (EA), butyl acetate (BA) and their binary mixtures over the entire range of composition of NMP. The variation of these properties with composition and temperature of the binary mixtures is discussed in terms of molecular interactions of component molecules. The excess parameters are fitted to a Redlich–Kister type polynomial and the corresponding standard deviations are calculated. Thermodynamic parameters under study suggest the existence of strong interactions between NMP and aliphatic esters. The experimental data of viscosity is used to test the applicability of empirical relations of Grunberg–Nissan, Katti–Chaudhri, Heric–Brewer and McAllister for the systems studied. Also, ultrasonic speeds are theoretically evaluated based on scaled particle theory and compared with the experimentally measured values. The study reveals a close agreement between experimental and theoretical values of ultrasonic speed of these mixtures at all the temperatures under study. An attempt is made to study the temperature effect on the shapes of the interacting molecules in the binary liquid mixture using scaled particle theory in the temperature range 303.15–318.15 K.

1. Introduction

The knowledge on variation of thermodynamic properties with temperature and mole fraction involving nonelectrolyte solutions is of substantial significance in the chemical industry connecting chemical separations, mass transfer, fluid flow and heat transfer. When two or more solvent molecules are associated with one another to form a liquid mixture, it brings about a marked effect on the intermolecular interactions, due to changes in free volume, energy and molecular orientations leading to corresponding variations in the thermodynamic properties. The nature and magnitude of this variation depend on the polarity and size of the molecules involved in the liquid mixture. Ultrasonic technique has become a powerful tool in providing information regarding the molecular behavior of liquids and solids owing to its ability of characterizing physico-chemical behavior of the medium. The ultrasonic speed may be considered as a thermodynamic property, provided that a negligible amount of ultrasonic absorption of the acoustic waves of low frequency and of low amplitude is observed; in which case, the ultrasonic absorption of the acoustic waves is negligible [1]. Derived acoustical and thermodynamic parameters like isentropic compressibility, excess molar volume, etc., are of great importance to understand liquid theory and provide information about molecular interactions [2–4].

Lactams are important class of amides that constitute a simple model system for proteins due to non polar region and a donor–acceptor CO–NH peptide linkage. One of the lactams, N-methyl-2-pyrrolidone (NMP) is an important solvent as it is water-miscible, hygroscopic, colorless, and strongly polar liquid. NMP has the potential for use in, solvent extraction process as strong solubilizing agent [5], purification and crystallization of drugs [6]. Esters, commonly used as solvents in the production of lacquers, are one of the best candidates with extensive applications in the pharmaceutical, food, and flavor industries; for instance, ethyl acetate is widely used in polymer processing industries as a plasticizer [7,8]. The increasing uses of NMP and acetates in many industrial processes have greatly stimulated the need for extensive information on

* Corresponding author. Fax: +91 8656 235200.
E-mail address: crbpublications@gmail.com (C. Rambabu).

0167-7322/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molliq.2013.04.003

the thermodynamic and transport properties of NMP, acetates and their mixtures. In pure state, alkyl acetates undergo dipolar association [9] as they are polar in nature possessing permanent dipole moment. When NMP is mixed with acetates, it is expected that the order present in the pure liquids get disturbed due to mutual interaction and also there is a possibility of interaction between unlike molecules.

Detailed literature survey shows that considerable amount of work has been done by different researchers on the binary mixtures of NMP. Letcher et al. [10–14] investigated the excess molar volumes of mixtures containing NMP + alkanol or hydrocarbon or ether or ketone, etc., Gnanakumari et al. studied the excess volumes and speeds of sound of NMP + chloroethanes, chloroethenes [15] and branched alcohols [3]. Chen et al. reported the densities and volumetric properties of NMP + xylenes [16]. The effect of molecular size, shape, chain length, and chain branching of alkyl acetates on solute–solvent interaction was reported by Sakurai et al. [17]. However, no effort appears to have been made to investigate the physico-chemical properties of the binary mixtures of NMP with methyl-, ethyl- and butyl acetates.

In order to elucidate the molecular interactions between NMP and alkyl acetates, the present work is focused on the measurement of physical properties such as density, ultrasonic speed and viscosity of binary mixtures of NMP with methyl acetate (MA), ethyl acetate (EA) and butyl acetate (BA) over the complete composition range at temperatures 303.15, 308.15, 313.15 and 318.15 K. Various excess quantities such as excess molar volume, excess isobaric thermal expansion coefficient, excess isentropic compressibility and excess ultrasonic speed are calculated from the experimental data to get insight into the intermolecular interactions that are present in these mixtures. An attempt is made to use FT-IR spectral analysis of these binary mixtures to understand the interactions present and to correlate them with thermodynamic findings. It is also aimed to compare the experimental values of ultrasonic speed and viscosity with those calculated by means of various theoretical models, and to investigate the effect of temperature on the shape of the interacting molecules in the temperature range 303.15–318.15 K using scaled particle theory.

2. Experimental section

The solvents, NMP procured from Merck with mass purity of 0.995, methyl acetate, ethyl acetate and butyl acetate of A.R grade procured from S.D fine chemicals (India) are further purified by standard methods [18] like fractional distillation and distillation under reduced pressure and only the middle fractions are collected. The purity analysis of chemicals is presented in Table 1. Before use, the chemicals are stored over 0.3 nm molecular sieves approximately for 72 h to remove traces of water and degassed. The measured densities (ρ), ultrasonic speeds (u) and viscosities (η) at 303.15 K for the pure liquids used in this investigation are compiled in Table 2 together with the literature data available [19–28]. These results are in good agreement with the reported data. The values of the isobaric thermal expansion coefficient ($\alpha_{p,i}^{*}$) and of the isobaric molar heat capacity, ($C_{p,i}^{*}$) of the pure components that are needed to calculate the ideal isentropic compressibility are included in Table 2. The mixtures are prepared gravimetrically using an electronic balance (Shimadzu AY120) with an uncertainty of $\pm 1 \times 10^{-7}$ kg and stored in air-tight glass bottles. The uncertainty in mole fraction is estimated to be 1×10^{-4}. It is ensured that the components are adequately mixed before being transferred into the apparatus. The required properties are measured within one day of the mixture preparation.

The ultrasonic speeds of pure components and their mixtures are measured by single crystal variable path fixed frequency interferometer provided by Mittal Enterprises, New Delhi (Model-F 05). The measurements of ultrasonic speed are taken at a fixed frequency of 2 MHz and the detailed procedure is described in our previous paper [29]. The standard uncertainty in the measured ultrasonic speed is estimated to be less than 0.1%. Temperature control for the measurement of densities, viscosities and ultrasonic speed is achieved by using a microprocessor assisted circulating water bath, (supplied by Mac, New Delhi) regulated to ± 0.01 K, using a proportional temperature controller. The densities, ρ, and viscosities, η, of the pure liquids and their mixtures are determined as described by us previously [30]. The standard uncertainty in the density obtained by triplicate replication at each temperature is found to be 2 in 10^4 parts whereas the standard uncertainty in viscosity is found to be less than 1%. IR measurements for all the three binary mixtures of NMP over the entire composition range were recorded using Bruker FT-IR spectrophotometer (Germany), alpha-T with universal module, with zinc optics operated by opus software, in the frequency range 4000 to 350 cm^{-1}.

3. Data processing and experimental results

The experimentally measured densities and ultrasonic speeds of the three systems under investigation viz., NMP + MA, NMP + EA and NMP + BA in the temperature range 303.15–318.15 K at atmospheric pressure over the entire composition range are presented in Table 3. It is evident from Table 3 that in all the three binary systems, the values of density and ultrasonic speed increase non-linearly, with the concentration of NMP and decrease with rise in temperature.

The excess functions are very useful in understanding molecular interactions between components of liquid mixtures. By definition, the excess function Y^E represents the excess of a given quantity Y of a real mixture over its value for an ideal mixture Y^{id} at the same conditions of pressure, temperature, and composition [31]. Using the measured densities of pure liquids and their mixtures, the excess molar volumes V_m^E are computed using the equation:

$$V_m^E = [(x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2] \quad (1)$$

in which x_1, x_2, M_1, M_2, ρ_1 and ρ_2 represent the mole fractions, molar masses and densities of pure components, respectively, and ρ is the density of the liquid mixture. The computed V_m^E values for all three binary mixtures at different temperatures are presented in Table 4. The variation in excess molar volumes with mole fraction of NMP is shown in Fig. 1; from the figure, it is observed that the excess molar volume is negative over the entire range of composition and the dependence of V_m^E on the composition of NMP is unsymmetrical, in all the three binary systems under study. Also, for each system the V_m^E values over the entire range of composition are decreasing with increasing temperature (Fig. 1) from 303.15 to 318.15 K.

Table 1
Purity analysis of the liquids used in the present investigation.

Chemical name	CAS number	Supplier	Purity	Purification technique	Purity GC	% water content KF
NMP	870-50-4	Merck	99.5	Vacuum distillation over P_2O_5	99.8	0.04
MA	79-20-9	S.D Fine	99.5	Fractional distillation & drying with K_2CO_3	99.8	0.17
EA	141-78-6	S.D Fine	99.5	Distillation over CaO & drying with K_2CO_3 and re-distillation	99.7	0.10
BA	123-86-4	S.D Fine	99.5	Fractional distillation	99.6	0.08