J. Chem. Thermodynamics 113 (2017) 291–300

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

Thermophysical approach to understand the nature of molecular interactions and structural factor between methyl isobutyl ketone and organic solvents mixtures

Faiza Ouaar [a], Amina Negadi [a], Indra Bahadur [b,*], Latifa Negadi [a,c,*]

[a] LATA2M, Laboratoire de Thermodynamique Appliquée et Modélisation Moléculaire, University of Tlemcen, Post Office Box 119, Tlemcen 13000, Algeria
[b] Department of Chemistry and Material Science Innovation & Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa
[c] Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, 4041 Durban, South Africa

ARTICLE INFO

Article history:
Received 21 April 2017
Received in revised form 3 June 2017
Accepted 8 June 2017
Available online 15 June 2017

Keywords:
MIBK
Biomass
Density
Speed of sound
Refractive index
Redlich-Kister polynomial equation

ABSTRACT

In this paper, we report the new experimental values of densities, speeds of sound, and refractive indices for four binary mixtures: {methyl isobutyl ketone (MIBK) + dimethyl sulfoxide (DMSO) or acetone or acetonitrile, or cyclohexane} over the entire composition range and in the temperatures range (293.15–313.15) K at 10 K intervals and pressure $p = 0.1$ MPa. From these experimental results, thermodynamics properties: excess molar volume, isentropic compressibility, deviation in isentropic compressibility and deviation in refractive indices were calculated. Excess molar volume, deviation in isentropic compressibility and deviation in refractive indices have been correlated using the Redlich–Kister equation. From the obtained results, a discussion was carried out in terms of nature of intermolecular interactions and structure factors in these binary mixtures.

1. Introduction

Because of intensive use of chemicals in pharmaceutical, and separation process, solvents have been a challenge to green chemistry. The majority of solvents used in academic and industrial laboratories are volatile organic compounds (VOC), which inevitably lead to environmental pollution. During the last decade, chemists have initiated action to address environmental issues in a safe and gainful manner under the name "green chemistry" to highlight the judicious use of chemistry for prevention of pollution through environmentally conscious designing of chemical processes.

As is well known, the solvents are very important in analytical chemistry, product purification, extraction and separation technologies. Therefore, to make chemistry more sustainable in these fields, knowledge of alternative, greener solvents is important in order to replace traditional organic solvents. Green solvents are environmentally friendly solvents, or bio-solvents, which are derived from the processing of agricultural crops [1]. By contrast, petrochemical solvents are the key to the majority of chemical processes but not without severe implications on the environment. Thus, green solvents were developed as a more environmentally friendly alternative to petrochemical solvents.

Methyl isobutyl ketone is the aliphatic ketone most produced worldwide; it places third after acetone and methyl ethyl ketone (MEK) in industry [2]. This compound has been industrially obtained by a conventional three-step process. Firstly, there is an aldol condensation of acetone on basic catalyst to form diacetone alcohol (DAA); secondly, there is dehydration onto an acidic catalyst to form mesityl oxide (MO); and thirdly, there is hydrogenation of unsaturated ketone (MO) to MIBK [3].

Nowadays, the complexity and the high operating costs of these processes lead to the production of MIBK in a one-step liquid-phase process from acetone and hydrogen using a multifunctional catalyst at (393–433) K and (1–10) MPa [4].

MIBK is largely used as solvent for extraction process, *e.g.* the extraction of platform chemicals from renewable resource (furfural, hydroxy methyl furfural) [5], the extraction and purification of some antibiotics and pharmaceuticals [6]. It can be also used as a reagent for separation of metals from solution of mixed

* Corresponding authors at: LATA2M, Laboratoire de Thermodynamique Appliquée et Modélisation Moléculaire, University of Tlemcen, Post Office Box 119, Tlemcen 13000, Algeria and Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, 4041 Durban, South Africa (L. Negadi).

E-mail addresses: bahadur.indra@nwu.ac.za (I. Bahadur), l_negadi@mail.univ-tlemcen.dz, latifanegadi@yahoo.fr (L. Negadi).

http://dx.doi.org/10.1016/j.jct.2017.06.008
0021-9614/

metals salts, in separation of plutonium from uranium, and even it is a useful material which can be applied in production of paint and stabilizers [7].

According to these considerations, several studies [8–18] have been advanced to thermodynamic and thermophysical properties of binary mixtures containing MIBK to explain the molecular interactions and the geometrical effect between the mixtures. Männistö et al. [8] reported LLE data for the mixtures (MIBK + furfural + water) at temperatures between (298 and 401) K. Negadi et al. [9] have studied the VLE of (2,5-dimethylfuran + methyl isobutyl ketone) binary mixtures at temperature between (313 and 393) K, Zaitseva et al. [10] have also studied the isothermal VLE of (furfural + MIBK) binary mixture at (333, 346 and 353) K, the isobaric VLE for (cyclohexane + MIBK) system at 100 kPa have been investigated by Marrufo et al. [11]. Additionally, measurements of the volume, speed of sound, and viscosity have been carried out for (N, N–dimethylaniline + MIBK) system at (303.15 & 308.15) K by Gowrisankar et al. [12]. Krishna et al. [13] have measured density and speed of sound data for (thiolane-1,1-dioxide + MIBK) system at (303.15, 308.15, and 308.15) K, where Kumari et al. [14] have reported the excess molar volumes and ultrasonic properties of N-methyl-2-pyrrolidone with MIBK at 303.15 K but no data have been found for (MIBK + acetone, or acetonitrile) systems. The excess molar volume of (dimethylsulphoxide + MIBK) system at 303.15 K was determined by Tiwari et al. [15] and Radhamma et al. [16]. Zarei et al. [17] have reported densities and volumetric properties of {MIBK + alkanols (C_1–C_4)} at (298.15–308.15) K. Lee et al. [18] have measured the excess volumes of (cyclohexane + MIBK) at 303.15 K. Karr et al. [19] have reported the density, refractive index and viscosity of (acetone + MIBK) at 298.15 K.

As a continuation of our systematic studies on thermodynamic and thermophysical properties of binary mixtures containing solvents derived from biomass, we report in this paper densities, speeds of sound and refractive indices of pure MIBK, DMSO, acetone, acetonitrile and cyclohexane and their binary mixtures over the entire composition range at (293.15, 303.15 and 313.15) K and pressure p = 0.1 MPa.

2. Experimental procedure

2.1. Chemicals

MIBK, DMSO, acetonitrile, and cyclohexane were Sigma Aldrich products, while acetone was of Merck. The purity of these chemicals was declared to be more than 0.99 on a mass fraction basis and have been used without further purification. The Table 1 shows the source and the purity of all chemicals employed in this work. As well, the purity was checked by comparing the measured densities, speed of sound and refractive index, which are in good accord with literature values [12–56] and these results are presented in Table 2.

2.2. Apparatus and procedure

The binary mixtures were prepared by mass, using an OHAUS analytical balance with a precision of ±0.0001 g. The estimated error in the mole fraction was ±0.0005. Density and speed of sound for pure components and binary mixtures were measured using a digital vibrating-tube densimeter and sound velocity analyzer (Anton Paar DSA 5000 M) with an accuracy of ±0.02 K in temperature. The speed of sound was measured using a propagation time technique with frequency of 3 MHz. The estimated errors in density and speed of sound velocity were ±0.003 $g{\cdot}cm^{-3}$ and ±1.2 $m{\cdot}s^{-1}$, respectively. The instrument can measure simultaneously density in the range of (0–3) $g{\cdot}cm^{-3}$ and speed of sound from (1000 to 2000) $m{\cdot}s^{-1}$ over the temperature range of (273.15–343.15) K with pressure variation from (0 to 0.3) × 10^5 Pa. The refractive indices of the pure liquids used in the present work were measured using an Abbe digital refractometer (Model Abbemat 300, Anton Paar), with an accuracy of ±0.02 K in temperature. The measured values of the refractive indices using the method and apparatus are estimated to be ±0.005 of their true values.

3. Results and discussion

3.1. Density

The values of density ρ was measured at (293.15, 303.15 and 313.15) K, and pressure p = 0.1 MPa for the binary systems (MIBK + DMSO or acetone or acetonitrile or cyclohexane) and are given in Table 3. It can be seen that the ρ values decreases with an increase in temperature, and increases with an increase of the concentration x_1 for all investigated binary systems except the system containing DMSO whereas a decreasing values of ρ with increasing concentration are observed. For the sake of comparison and clarity the ρ values of (MIBK + DMSO or cyclohexane or acetone) systems were plotted in Figs 1, 2(a) and 3(a) together with available literatures [15,16,18,19] and shows quite consistent and follow the trends for concentration and temperature with experimental data of literatures [18,19] except literature [18] at x_1 = 0.7512 and literatures [15,16] where higher deviation observed. This is probably due to lack of accuracy for the concentration preparation, accuracy of the instrument used in literatures as well as typographical error in literature [18]. In this work, an Anton Paar DSA 5000 M digital vibrating tube densimeter was used, whereas in literatures [15,16,18] an dilatometer and pycnometers (Blaubrand, Gay-Lussac type) which gives lower accuracy as compare to Anton Paar DSA 5000 M digital vibrating tube densimeter.

3.1.1. Speed of sound

Speed of sound, u, has been extensively employed to understand the nature of intermolecular interactions in pure liquids, binary, ternary and quaternary mixtures. In this regards, the speed of sound was also measured under the same conditions for all binary systems and are given in Table 3. It can be seen that the u values also decrease with an increase in temperature, and in general, decrease with an increase of the concentration for all binary systems excluding the system (MIBK + acetone), whereas an increasing values of u with increasing concentration are observed. For the sake of comparison and clarity, the u values of (MIBK + DMSO) system at 303.15 K are plotted in Fig. 2(b) together with available literature values [15,16] and show a similar trend for concentration and temperature

Table 1
Molar mass, CAS number, suppliers and purities of chemicals used in this study.

Chemical name	*Mass fraction purity (stated by supplier)	CAS number	Molar mass/($g{\cdot}mol^{-1}$)	Supplier	Lot #
MIBK	0.990	108-10-1	100.16	Sigma-Aldrich	BCBD7099V
Acetone	0.995	67-64-1	58.08	Merck	K25355014
Acetonitrile	0.999	75-05-8	41.05	Sigma-Aldrich	SZBE040AV
Cyclohexane	0.995	110-82-7	84.16	Sigma-Aldrich	SZBA0750
DMSO	0.995	67-68-5	78.13	Sigma-Aldrich	BCBX5164

*No further purification was done.