J. Chem. Thermodynamics 69 (2014) 48–55

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

Thermophysical properties of {R-fenchone + ethanol} at several temperatures and pressures

José F. Martínez-López, Ana M. Mainar, José S. Urieta, Juan I. Pardo *

Group of Applied Thermodynamics and Surfaces (GATHERS), Aragon Institute for Engineering Research (I3A), Universidad de Zaragoza, Facultad de Ciencias, Zaragoza 50009, Spain

ARTICLE INFO

Article history:
Received 8 July 2013
Received in revised form 16 September 2013
Accepted 17 September 2013
Available online 3 October 2013

Keywords:
R-fenchone + ethanol mixture
Excess enthalpy
P-ρ-T
UNIFAC
COSMO-RS, EOS

ABSTRACT

In this paper, experimental excess enthalpy and density values for the binary mixture {R-fenchone + ethanol} are reported at four temperatures (283.15, 298.15, 313.15 and 328.15) K and atmospheric pressure (virtually 0.1 MPa). Densities have been also measured at the same temperatures and pressures ranging from 20 MPa to 40 MPa. In all cases the whole composition range has been considered. Excess molar volumes, isothermal compressibilities and isobaric thermal expansions have been calculated from the volumetric data at the four working temperatures. Excess enthalpies have been predicted using the UNIFAC (Dortmund) method and the Quantum Continuum Method COSMO-RS: UNIFAC shows the best performance. Four equations of state (Peng–Robinson, Peng–Robinson–Stryjek–Vera with volume translation, SAFT, PC-SAFT) have been tested as predictive models of the *P-ρ-T* behavior. Stryjek–Vera EOS lead to the best results with an average in the percentage absolute average deviation of 0.6% and a maximum percentage absolute average deviation of 0.9%.

1. Introduction

In the last years our research group is carrying out a study of the thermophysical behavior of binary mixtures constituted by a compound present in volatile oils from plants and an alkanol (references to this work can be found in the literature cited in the papers of Ribeiro *et al.* [1], Gimeno *et al.* [2] and García-Abarrio *et al.* [3]. The objective of this study is to gather relevant information in order to optimize processes of supercritical carbon dioxide extraction of volatile oils from plants when using an alkanol, specially ethanol and propan-1-ol [4], as co-solvent. Given that those oils are usually themselves mixtures of several compounds whose composition varies depending on quite uncontrollable parameters it is advisable to study mixtures of one their major compounds with alkanols. In this paper the compound selected is the terpene R-fenchone or (1R,4S)-1,3,3-trimethylbicyclo [2.2.1] heptan-2-one. Fenchone is a terpene, present in a number of species of plants, such as wormwood and fennel. It is widely used as a flavor in foods and also in perfumes.

In this work, experimental excess enthalpy and density values for the binary mixture {R-fenchone (1) + ethanol (2)} are reported at four temperatures (283.15, 298.15, 313.15, and 328.15) K and atmospheric pressure (virtually 0.1 MPa). Densities (*P-ρ-T* equilibrium) have been also measured at the same temperatures and pressures ranging from (20 to 40) MPa in intervals of 5 MPa. In all cases the whole composition range has been considered. Densities at high pressures have been correlated using a modified Tait equation [5]. Excess molar volumes, isothermal compressibilities and isobaric thermal expansions have been calculated from the volumetric data at the four working temperatures. There are no data in the literature for these mixtures although Liu *et al.* [6] have measured the excess enthalpy of S-fenchone + ethanol at 298.15 K.

Several models have been used to predict the measured properties. In the case of excess enthalpies the UNIFAC (Dortmund version) method [7] and the Quantum Continuum Method COSMO-RS [8–12] have been applied. The equations of state of Peng–Robinson [13], Peng–Robinson–Stryjek–Vera [14] with volume translation according to Peneloux [15], SAFT [16–18], and PC-SAFT [19,20] have been tested as predictive models of the *P-ρ-T* behavior.

2. Experimental

2.1. Materials

The chemicals used are ethanol and R-fenchone for the mixtures under study and *n*-octane and water for the calibration of the densimeter Anton-Paar DMA 512-P. Their description can be found in table 1. A comparison between experimental and literature data [6,21–24] of densities of pure ethanol and fenchone at atmospheric pressure is reported in table 2. It can be observed that there is a good agreement between both sets of values.

* Corresponding author. Tel.: +34 976 762 386; fax: +34 976 761 202.
E-mail address: jupardo@unizar.es (J.I. Pardo).

0021-9614/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jct.2013.09.024

TABLE 1
Sample description.

Chemical name	Source	Purity	Purification method	Analysis method
R-fenchone	Aldrich	0.995[a]	None	GC[c]
Ethanol	Scharlau	0.999[b]	None	GC[c]
n-Octane	Aldrich	0.995[a]	None	GC[c]
Water	Laboratory	MilliQ[d]	None	Electrical resistivity

[a] Mass fraction purity.
[b] Volume fraction purity.
[c] Gas–Chromatography.
[d] 18.2 MΩ · cm.

TABLE 2
Experimental and literature densities for the pure liquids at T = (283.15, 298.15, 313.15, and 328.15) K and atmospheric pressure.

	T/(K)	ρ/(kg·m^{-3})	
		Experimental	Literature
R-fenchone	283.15	953.27	
	298.15	940.67	940.51[a]
			940.79[b]
	313.15	928.04	
	328.15	915.39	
Ethanol	283.15	797.99	797.9[c]
	298.15	785.20	785.49[d]
	313.15	772.15	772.1[c]
	328.15	758.71	758.61[e]

[a] Reference [21], at 298.12 K.
[b] Reference [6].
[c] Reference [22].
[d] Reference [23].
[e] Reference [24].

2.2. Equipments and procedures

The excess enthalpies were determined with a Thermometrics 2277 Thermal Activity Monitor maintained at ±0.0002 K and operating under constant flow conditions. The calorimeter has been tested with reference to recommended values [25] of the mixture of hexane with cyclohexane, being the agreement between our data and the bibliographic ones within ±1% of the maximum excess enthalpy value for the reference mixture. Two Shimadzu LC-10ADVP HPLC pumps were used to drive the liquids. The whole procedure is detailed elsewhere [1]. Given the uncertainty in the flow rate, the uncertainty in the mole fractions of the mixtures was estimated to be ±0.001. The relative uncertainty in the excess molar enthalpy is less than 0.03.

Densities at atmospheric pressure were obtained by means of a vibrating tube densimeter Anton Paar DMA 5000. For this apparatus, the accuracy in the control of the temperature is ±0.01 K. The expanded uncertainty ($k = 2$) for density is estimated to be ±0.04 kg · m^{-3}. In these measurements the composition of the binary mixtures was determined by weighing using an analytical balance Metter-Toledo model AB265-S with a precision of ±10^{-8} kg. Hence, the expanded uncertainty ($k = 2$) in the mole fraction was estimated to be ±0.0001.

For measuring densities at high pressures a vibrating tube densimeter Anton-Paar DMA 512-P was used. The samples were thermostated through an external bath Julabo F34 being the uncertainty in the control of the temperature ±0.01 K. The pressure in the system was controlled by a pressure transmitter (STW-A09) operating up to 70 MPa with an uncertainty relative to the full-scale of 0.001. A detailed description of the experimental device can be found in Lasarte *et al.* [26]. The overall experimental uncertainty in the reported density values was estimated to be ±0.5 kg · m^{-3}. As written above, the composition of the mixture samples, which were prepared with liquids degassed previously, was determined in the same way than at atmospheric pressure. The densimeter was calibrated with water (milli Q quality) and n-octane. For R-fenchone, values of density at high pressure have not been found in the literature.

3. Experimental results

3.1. Excess enthalpy

The values of excess enthalpy for the mixture {R-fenchone + ethanol (2)} at T (283.15, 298.15, 313.15, and 328.15) K and atmospheric pressure are listed in table 3 and plotted in figure 1. For each temperature, the property was fitted to the usual Redlich–Kister equation

$$H_m^E = x_1(1-x_1)\sum_{i=0}^{N} A_i(2x_1-1)^i, \quad (1)$$

the A_i are adjustable coefficients and N is the number of fitting coefficients used in the adjustment. The fitting of the data to equation (1) was carried out by using a Levenberg–Marquardt algorithm. The adjusting coefficients are listed in table 4 along with the corresponding standard deviations defined by

$$\sigma = \left[\frac{\sum_{j=1}^{m}\left\{\left(Y_j^E\right)^{\mathrm{exp}} - \left(Y_j^E\right)^{\mathrm{cal}}\right\}^2}{m-n}\right]^{\frac{1}{2}}, \quad (2)$$

where the superscript exp and cal indicate the experimental and calculated values, respectively, m is the number of experimental points, and n is the number of coefficients used in the fitting equation.

TABLE 3
Mole fraction, x_1, excess molar enthalpy, H_m^E, for the mixture {R-fenchone (1) + ethanol (2)} at T (283.15, 298.15, 313.15, and 328.15) K and atmospheric pressure.

	H_m^E/(J · mol^{-1})			
x_1	T/(K) = 283.15	T/(K) = 298.15	T/(K) = 313.15	T/(K) = 328.15
0.048	175	199	221	245
0.097	337	382	425	469
0.195	588	666	744	821
0.286	768	876	977	1080
0.395	914	1043	1163	1282
0.488	963	1109	1242	1365
0.601	960	1097	1219	1332
0.701	878	1000	1105	1198
0.801	719	807	884	950
0.894	437	503	550	586
0.945	238	272	297	318

$U(x_1) = \pm 0.001$ ($k = 2$); $U_r(H_m^E) = 0.03$.