Thermochimica Acta 617 (2015) 76–82

Contents lists available at ScienceDirect

Thermochimica Acta

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

The density, the refractive index and the adjustment of the excess thermodynamic properties by means of the multiple linear regression method for the ternary system ethylbenzene–octane–propylbenzene

C. Lisa*, M. Ungureanu, P.C. Cosmaţchi, G. Bolat

Gheorghe Asachi Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, 73 Prof.dr.doc D. Mangeron Street, 700050 Iasi, Romania

ARTICLE INFO

Article history:
Received 27 April 2015
Received in revised form 17 August 2015
Accepted 18 August 2015
Available online 22 August 2015

Keywords:
Density
Refractive index
Excess molar volume
Excess refractive index
MLR
Ethylbenzene–octane–propylbenzene

ABSTRACT

The density (ρ) and the refractive index (n) have been experimentally determined for the ethylbenzene (1)–octane (2)–propylbenzene (3) ternary system in the entire variation range of the composition, at three temperatures: 298.15, 308.15 and 318.15 K and pressure 0.1 MPa. The excess thermodynamic properties that had been calculated based on the experimental determinations have been used to build empirical models which, despite of the disadvantage of having a greater number of coefficients, result in much lower standard deviations in comparison with the Redlich–Kister type models. The statistical processing of experimental data by means of the multiple linear regression method (MLR) was used in order to model the excess thermodynamic properties. Lower standard deviations than the Redlich–Kister type models were also obtained. The adjustment of the excess molar volume (V^E) based on refractive index by means of the *Multiple linear regression* of the SigmaPlot 11.2 program was made for the ethylbenzene (1)–octane (2)–propylbenzene (3) ternary system, obtaining a simple mathematical model which correlates the excess molar volume with the refractive index, the normalized temperature and the composition of the ternary mixture: $V^E = A_0 + A_1X_1 + A_2X_2 + A_3(T/298.15) + A_4n$ for which the standard deviation is 0.03.

1. Introduction

The chemical industry frequently uses products such as solvents, heat-transfer fluids, cooling and refrigerant agents, etc. in its technological processes. After being used, these products can become chemical waste in our environment. Such waste that poses a risk to the environment generally contains complex, multiphase mixtures (e.g. water + organic compounds + electrolytes).

Volatile organic compounds, which are a class of potential contaminants, are frequently seen in wastewater. The environmental protection regulations indicate the strict limitations of the concentration of pollutants in water. Octane, ethylbenzene and propylbenzene, the substances that make the object of this paper, are toxic for aquatic organisms. Due to the high value of toxicity of propylbenzene, the discharge of this substance in wastewater or soil is forbidden.

Many groups of researchers have focused their activity on studying substances in liquid phase, be it pure compounds or mixtures of nonreactive organic compounds. The studies are based on analyzing the behavior of known classes of compounds, such as: alkanes, alcohols, esters, haloalkanes, etc., obtaining results for different thermodynamic quantities. The differences between the experimental and the theoretical quantities obtained are known as *excess quantities*, indicating the type and order of quantities of interactions that occur between compounds. The values of the excess quantities are used both for the study of interactions that occur in solutions, as well as for the design of various chemical engineering installations. They are further used to obtain and/or verify the theoretically developed dissolving models. The study of the physico-chemical properties of binary and ternary liquid mixtures, on a wide range of composition and temperature, is an important source of information in establishing the relation between the internal structure of the systems and their physical properties [1–7]. Iloukhani and Rezaei-Samati [8] have determined the excess molar volume for ternary systems (methylcyclohexane–cyclohexane–n-alkanes) and Rajasekhar and Sivakumar [9] respectively have determined the excess molar volume for ternary mixtures (1,3-dichlorobenzene-methyl ethyl ketone-1-propanol, 1-butanol, 1-pentanol, 1-hexanol). In order to predict excess molar volume, Iloukhani and Rezaei-Samati have

* Corresponding author.
E-mail address: clisa@ch.tuiasi.ro (C. Lisa).

http://dx.doi.org/10.1016/j.tca.2015.08.023
0040-6031/

Table 1
Sample information.

Solvents	Source	Molar mass (g/mol)	Mole fraction purity	Analysis method
Ethylbenzene	Merck, Germany	106.16	>0.99	GC[a]
Propylbenzene	Merck, Germany	120.19	>0.98	GC[a]
Octane	Merck, Germany	114.23	>0.99	GC[a]

[a] Gas–liquid chromatography.

tested seven empirical models proposed by various researchers and found that standard deviations, similar to values around 0.05, are obtained. Therefore, these models could be used, for example, by design engineers in order to predict the excess molar volume of the entire composition range of the ternary mixtures mentioned above [8].

Rajasekhar and Sivakumar have analyzed the influence of increasing the length of the carbon chain from alcohols used in the production of ternary mixtures with 1,3-dichlorobenzene and methyl ethyl ketone on the excess molar volume [9]. They have determined that the molar excess volume decreases with the increase of the length of the carbon chain according to the series: 1-propanol > 1-butanol > 1-pentanol > 1-hexanol. The negative values obtained for the excess molar volume have been attributed by the authors to the interactions between the hydroxyl and ketone groups which are manifested by creating hydrogen bonds. In order to link the excess molar volume to the mole fractions of the components in the mixture, the two authors used three types of empirical models proposed by Redlich and Kister, Kohler and Hwang [9]. The best estimate of the excess molar volume was obtained by Rajasekhar and Sivakumar [9] for the four ternary mixtures analyzed by means of the Kohler-type model.

Further to the research carried out in our laboratory, we shall present here the experimental results obtained on excess thermodynamic properties for the ternary system ethylbenzene–octane–propylbenzene, on the density and refractive index of which there is no data in the specialized literature. Modeling excess thermodynamic properties by applying statistical processing of the experimental data with the multiple linear regression method (MLR), for which there is no application in the case of ternary systems, is another important aim of this paper.

The analysis of the specialized literature revealed the existence of several studies that apply only the MLR method in order to predict certain thermodynamic properties. Kartritzky and his collaborators [10] have obtained a MLR-type model for predicting the viscosity of 361 organic compounds. The model's performance was highlighted by the correlation coefficient 0.854 and the standard deviation 0.22. The dependent variables of the model were a series of molecular descriptors obtained using the MOPAC 6.0 molecular modeling program [10].

On the other hand, Sapkota [11] used MLR for a series of organic compounds in order to predict the boiling point. The models obtained have led to correlation coefficients higher than 0.97. The density, the refractive index, the boiling point, the dielectric constant and the viscosity for a series of organic derivatives with the general structure X–CH_2–CH_2–Y have been estimated using MLR-type models by Cocchi and others [12]. The performance of the models obtained have been quantified by means of standard deviations, finding very good correlations between the values of the properties calculated using MLR models and those experimentally determined [12]. Another group of researchers [13] built MLR models in order to predict the enthalpy of formation for a series of 20 organic compounds. The molecular descriptors used as dependent variables in the model were obtained by molecular modeling using the Hyperchem program [13].

2. Experimental

The solvents involved in the experiments: ethylbenzene, octane and propylbenzene were used as received from supplier (Table 1). The ternary solutions were realized by weighing, making it possible to estimate the mole fractions with a standard uncertainty of ±0.0001. An XP105-type analytical balance from Mettler Toledo, with a measurement standard uncertainty of ±0.01 mg was used. Each solution was obtained in a sealed tube in order to prevent preferential evaporation. The density and the refractive index were then measured. The ternary graph shown in Fig. S1 from the Supporting Information demonstrates the fact that experimental determinations were made for the entire variation range of the mole fractions of the three components from the ternary system.

The density of the ternary mixtures was measured with a standard uncertainty of ±0.001 g cm^{-3} using a DMA 4500-type Anton Paar density meter additionally containing an oscillating U-tube and an additional reference oscillator. Due to the two integrated platinum thermometers Pt 100 this type of density meter

Table 2
The density and the refractive index of pure compounds from T = (298.15 to 318.15) K and pressure 0.1 MPa.[a]

Solvents	T/K	ρ/g cm^{-3}		n	
		Experimental (this work)	Literature	Experimental (this work)	Literature
Ethylbenzene	298.15	0.8627	0.8620 [18]	1.4928	1.49305 ± 0.00022[c]
	308.15	0.8538	0.8536 [16]	1.4879	1.4868 [17]
	318.15	0.8448	0.84605 ± 0.00034[c]	1.4832	1.48273 ± 0.00052[c]
Propylbenzene	298.15	0.8579	0.85771 ± 0.00023[c]	1.4892	1.48928 ± 0.00026[c]
	308.15	0.8494	0.84942 [22]	1.4844	[b]
	318.15	0.8409	0.84089 ± 0.00020[c]	1.4800	1.4810 [14] 1.4795[d]
Octane	298.15	0.6986	0.69840 [18]	1.3948	1.39507 ± 0.00024[c]
	308.15	0.6905	0.6901 [15]	1.3904	1.39052 [19]
	318.15	0.6822	0.68173 [21]	1.3868	1.38687 [20]

[a] Standard uncertainties u are $u(T)$ = ±0.01 K for density and $u(T)$ = ±0.1 K for refractive index, $u(\rho)$ = ±0.001 g cm^{-3}, $u(n)$ = ±0.0002 and $u(P)$ = ±0.001 MPa.
[b] There are no data in the literature at this temperature.
[c] Values from the NIST/TRC Web Thermo Tables, professional edition (thermophysical and thermochemical data).
[d] Values interpolated from TRC tables non-hydrocarbons, Thermodynamic Research Center, Texas A&M University, College Station, TX, 1991.