J. Chem. Thermodynamics 73 (2014) 224–231

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

Contribution to study of the thermodynamics properties of mixtures containing 2-methoxy-2-methylpropane, alkanol, alkane

Pedro V. Verdes [a], Marta M. Mato [a,1], M.I. Paz Andrade [a,*], José Luis Legido [b]

[a] Departamento de Física Aplicada, Facultad de Física, Universidade de Santiago, Campus Universitario Sur, E-15782 Santiago de Compostela, Spain
[b] Departamento de Física Aplicada, Facultade de Ciencias, Universidade de Vigo, Campus Lagoas-Marcosende, E-36200 Vigo, Spain

ARTICLE INFO

Article history:
Available online 11 January 2014

Dedicated to the memory of the late Professor Manuel Ribeiro da Silva

Keywords:
Excess molar enthalpies
Ternary mixture
2-Methoxy-2-methylpropane (MTBE)
1-Pentanol
Hexane
Group contribution model

ABSTRACT

Excess molar enthalpies for the ternary system {x_1 2-methoxy-2-methylpropane (MTBE) + x_2 1-pentanol + $(1 - x_1 - x_2)$ hexane} and the involved binary mixture {x 1-pentanol + $(1 - x)$ hexane}, have been measured at T = 298.15 K and atmospheric pressure over the whole composition range. We are not aware of the existence of previous experimental measurement of the excess enthalpy for the ternary mixture under study in the literature currently available. Values of the excess molar enthalpies were measured using a Calvet microcalorimeter. The results were fitted by means of different variable degree polynomials. The ternary contribution to the excess enthalpy was correlated with the equation due to Verdes *et al.* (2004), and the equation proposed by Myers–Scott (1963) was used to fit the experimental binary mixture measured in this work. Smooth representations of the results are presented and used to construct constant excess molar enthalpy contours on Roozeboom diagrams. The excess molar enthalpies for the binary and ternary system are positive over the whole range of composition. The binary mixture {x 1-pentanol + (1 − x) hexane} is asymmetric, with its maximum displace toward a high mole fraction of decane. The ternary contribution is also positive with the exception of a range located around the rich compositions of 1-pentanol, and the representation is asymmetric.

Additionally, the group contribution model of the UNIFAC model, in the versions of Larsen *et al.* (1987) [18] and Gmehling *et al.* (1993) [19] was used to estimate values of binary and ternary excess enthalpy. The experimental results were used to test the predictive capability of several empirical expressions for estimating ternary properties from binary results.

1. Introduction

This work contributes to the systematic knowledge of several thermodynamic properties of ternary and binary mixtures containing 2-methoxy-2-methylpropane (MTBE), alkanols and alkanes as components. It is the continuation of previous papers [1–16] which are part of the scientific project entitled "Study on physical properties of mixtures hydrocarbon + alcohol + ether like alternative fuels". The main objective of this project has been the characterization of non-electrolyte liquids, and their mixtures, through experimental determination of thermophysical properties on mixing.

The series including the ternary systems {2-methoxy-2-methylpropane (MTBE) + 1-pentanol + alkane (decane [15], nonane [14], octane [9])} and {2-methoxy-2-methylpropane (MTBE) + 1-alkanol (ethanol [11], propanol [13], butanol [5]) + hexane}, are continued, considering hexane and 1-pentanol as components in this case.

This should help to study the molecular interactions of these mixtures and to examine the effect of the enlargement of the CH_2 unit in the alkanol or alkane. So, as an extension of these earlier investigations, the aim of this research was to measure, using a Calvet microcalorimeter, experimental excess molar enthalpies, over the whole composition range, for the ternary mixture {x_1 2-methoxy-2-methylpropane (MTBE) + x_2 1-pentanol + $(1 - x_1 - x_2)$ hexane}, at the temperature of 298.15 K and atmospheric pressure. Additionally, experimental data for the binary mixture {x 1-pentanol + $(1 - x)$ hexane} are reported. To correlate adequately the binary experimental data, a variable degree polynomial due to Myers–Scott [17] was used. The ternary contribution to the excess enthalpy was fitted on the basis of an equation proposed by Verdes *et al.* [15].

The experimental values were compared with the estimates obtained by applying the group contribution model of UNIFAC, the latter in the versions introduced by Larsen [18] and Gmehling *et al.* [19].

* Corresponding author. Tel.: +34 881814049.
E-mail address: inmaculada.paz.andrade@usc.es (M.I. Paz Andrade).
[1] Present address: Departamento de Física Aplicada, Facultad de Ciencias, Universidade de Vigo, E-36310 Vigo, Spain.

http://dx.doi.org/10.1016/j.jct.2014.01.002
0021-9614/

As the number of components in the mixture increases, the determination of thermodynamic properties becomes more laborious. Therefore, the applicability of predictive methods is of great interest for estimating ternary properties from the experimental data of the binaries involved. These methods allow us to estimate excess properties of generalised multi-component mixtures from the experimental correlated values of the binary mixtures.

So, deviations of the ternary enthalpies calculated on the basis of several empirical methods were also listed. The symmetric equations used were those introduced by Kohler [20], Jacob and Fitzner [21], Colinet [22], Knobeloch and Schwartz [23], and the asymmetric ones those due to Tsao and Smith [24], Toop [25], Scatchard *et al.* [26], Hillert [27], and Mathieson and Tynne [28].

2. Experimental

The chemical substances employed were commercial products of the best quality grade. Their sources and purities (stated by the supplier) are listed in Table 1. All products were used as supplied, no further purification being applied. In order to avoid hydration and to eliminate residual traces of water, the chemicals were dried over Union Carbide 0.4 nm molecular sieves. In addition, they were degassed by an ultrasound technique. The handling and disposal of the chemicals used have been done according to the recommendation of the *CRC Handbook of Chemistry and Physics* [29].

The mixtures were prepared by mass using a Mettler H51 balance (precision $\pm 1 \cdot 10^{-5}$ g), ensuring a probable error in the mole fraction less than 10^{-4}. All molar quantities are based on the IUPAC relative atomic mass table [30].

The experimental excess molar enthalpies were measured using a Calvet microcalorimeter with two calorimetric elements, equipped with a device allowing operation in the absence of vapour phase.

The experimental setups used to determine the heats of mixing, always conform to the conditions that owns each calorimeter, the kind of experience and to the systems to study characteristics. In our work we used an experimental setup designed by Paz Andrade [31] that operates at a constant pressure.

Figure 1 shows a scheme of the experimental device. It consists of a small stainless-steel cylindrical cell, having a volume of approximately 10 cm^3, which was partially filled with a known mass of one of the liquids, was screwed into a long pipe by means of a support with a Teflon stopper. It has a small hole where a silicon tablet was fitted and perforated by a long needle of the syringe where the other liquid was located. Further details about the experimental method of operation have been already published [31,32].

A Philips PM2535 multimeter and a data acquisition system were linked to the microcalorimeter. Calibration was performed electrically using a Setaram EJP30 stabilised current source. The apparatus and procedures were tested by determining the excess enthalpies for the standard system (cyclohexane + hexane) at T = 298.15 K.

TABLE 1
Sources and mass fraction purity of the chemical substances employed in this work.

Chemical name	Source	Mass fraction purity
MTBE[a]	Aldrich	>0.998
1-Pentanol	Aldrich	>0.990
Hexane	Fluka	>0.995
Cyclohexan	Aldrich	>0.995

[a] MTBE = 2-methoxy-2-methylpropane.

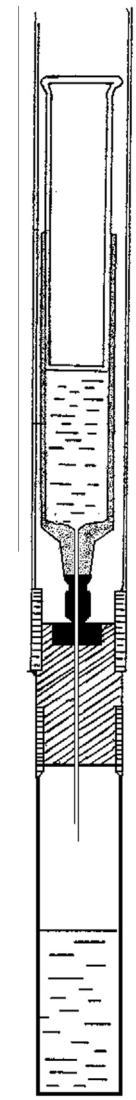

FIGURE 1. Mixing device for measurement of the enthalpy of mixing of liquids.

Table 2 summarizes experimental values of excess molar enthalpies obtained in this work for the binary mixture {x cyclohexane + $(1 - x)$ hexane} and the calculated values using the fitting curve published by Marsh [33] and Gmehling [34]. The Average Relative deviation was found to differ by lower than 1% in both cases.

The uncertainty in excess molar enthalpy measurements is estimated to be better than 1%.

Three experimental runs of measurements were carried out for the ternary compositions resulting from adding octane to an initial binary mixture of {x'_1 MTBE + x'_2 1-pentanol}. The ternary composition point may be regarded as a pseudo-binary mixture composed by the addition of hexane to the mentioned binary mixture. Thus, the ternary excess molar enthalpy at the pseudo-binary composition x_1, x_2, and $x_3 = 1 - x_1 - x_2$ can be expressed as

$$H^E_{m,123} = H^E_{m,\phi} + (x_1 + x_2)H^E_{m,12}, \tag{1}$$

where $H^E_{m,\phi}$ is the measured excess molar enthalpy for the pseudo-binary mixture and $H^E_{m,12}$ is the excess molar enthalpy of the initial binary mixture {x'_1 MTBE + x'_2 1-pentanol}. Values of $H^E_{m,12}$ at three mole fractions were interpolated by using a spline-fit method.