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Excess molar enthalpy measurement and modelling of (oxygenated compounds + hydrocarbon) mixtures: Binary and ternary mixtures containing 2-(2-methoxyethoxy)ethanol, 1-hexene and cyclohexane at (298.15 and 313.15) K

Mohamed Lifi^{a,b}, Natalia Muñoz-Rujas^a, Eduardo A. Montero^a, Latifa Negadi^c, Fernando Aguilar^a and Fatima Ezzahrae M'hamdi Alaoui^{b,}*

^aDepartamento de Ingeniería Electromecánica, Escuela Politécnica Superior, Universidad de Burgos, Burgos, Spain.

^bEcole Nationale des Sciences Appliquées, Université de Chouaib Doukkali d'El Jadida, El Jadida, Morocco.

^cFaculty of Sciences, University Abou Bekr Belkaid of Tlemcen, Algeria.

*Corresponding author. E-mail: mhamdialaoui.f@ucd.ac.ma. Tel. +212 5 23 39 56 79 . Fax: +212 5 23 39 49 15.

ABSTRACT

New measurements and modelling data of excess molar enthalpy H^E at atmospheric pressure and temperatures of (298.15 and 313.15) K using a quasi-isothermal flow calorimeter are presented in this work for the ternary system diethylene glycol monomethyl ether glycol (2-(2-methoxyethoxy)ethanol) + 1-hexene + cyclohexane and the corresponding binary systems over the whole composition range. All the binary and ternary systems present an endothermic behaviour at the chosen temperatures. The experimental data of the binary and ternary systems were correlated using the modified Redlich-Kister equation, NRTL and UNIQUAC models.

Keywords

Excess molar enthalpy; Oxygenated compound; Glycol ether, Diesel.

1. Introduction

Various researches have been realised to study mixtures of glycol ethers with diesel fuel, demonstrating a significant decline in the amount of toxic air pollutants such as CO, hydrocarbon and particulate emissions. As well, the results established by this research reveal that the addition of oxygen to glycol ether is more effective than the addition of oxygen to alcohol. Although the viscosity of the diesel is reduced with the use of glycol ether, the oxidation stability of the fuel and the carbon residues of Conradson remains the same [1]. Diethylene glycol monomethyl ether glycol (2-(2-methoxyethoxy)ethanol) belongs to the family of glycol ethers, known by its commercial name methylcarbitol and some of their utilizations are as additives in jet fuels, diesel fuels, marine fuels and fuel oils for the antimicrobial control of fungi and bacteria contained in hydrocarbon fuel systems. They are also used for anti-icing control, as brake fluid component and as solvent used in paints, printing inks, resins and waxes.

In this work, binary and ternary systems containing diethylene glycol monomethyl ether glycol (2-(2-methoxyethoxy)ethanol) as glycol ether, 1-hexene as representative of alkenes category and cyclohexane as representative of cycloalkane category, are studied at two different temperatures 298.15 K and 313.15 K.

This work presents a study on excess molar enthalpies at 298.15 K or / and 313.15 K of mixtures of: (i) 1-hexene + cyclohexane, (ii) 2-(2-methoxyethoxy)ethanol + 1-hexene, and + cyclohexane, and (iii) 2-(2-methoxyethoxy)ethanol (1) + 1-hexene (2) + cyclohexane (3). Excess molar enthalpies are measured with a quasi-isothermal flow calorimeter at atmospheric pressure. Furthermore, the experimental data are fitted using a modified Redlich-Kister equation [2], NRTL [3] and UNIQUAC [4] models.

2. Experimental

The 2-(2-methoxyethoxy) ethanol; $C_5H_{12}O_3$, 1-hexene; C_6H_{12} , cyclohexane; C_6H_{12} , with a stated mole fractionpurity > 0.99 , were purchased from Sigma-Aldrich, Arcos and Honeywell,

respectively. Table 1 shows the purity of the chemicals used in this work, which were examined by gas chromatography. The experimental technique used to determine the excess molar enthalpy of the binary and ternary systems under study at $T = (298.15 \text{ and } 313.15) \text{ K}$ and atmospheric pressure, is a quasi-isothermal flow calorimeter, previously described [5]. The measurements are determined two by isocratic positive displacement pumps (Agilent, Serie 1100, G1310A) that inject the liquids supposed to be mixed through the cell with a programmable and constant flow into the mixing coil sitting placed in the measuring cell. For binary systems, the two injected liquids are pure compounds, and for ternary systems, one of them is a pure compound and the other is a binary system whose excess molar enthalpy H^E is known at the whole range of composition. The measuring cell is immersed in a thermostatic bath, (Hart Scientific, model 6020E) and it is responsible for maintaining the cell at a set point temperature. The temperature stability achieved with thermostatic system is better than $\pm 0.01 \text{ K}$. Knowing the flow rates, molecular weights and densities of each liquid, we could subsequently find the different mole fractions (x_i) of the studied binary and ternary mixtures with a standard uncertainty $u(x) = 0.0008$. Densities of pure liquids are obtained from Riddick et al. [6] at the measured temperature of delivery. Estimated densities at (298.15 and 313.15) K are listed in Table 1. Mixtures of different compositions are studied and in this way, the dependence of excess molar enthalpy on mole fraction (x_i) can be determined. Therefore, the determination of the excess molar enthalpy of mixing for each composition is obtained by dividing the mixture power $Q_{mixture}$ by the number of moles per second $\dot{n}_{mixture}$ that circulated in the measuring cell while mixing, with $H^E = \frac{Q_{mixture}}{\dot{n}_{mixture}}$. The relative expanded uncertainty ($k = 2$) $U_r(H^E) = 1\%$ for excess enthalpy.

3. Results and discussion

The binary mixtures (1-hexene + cyclohexane) and (2-(2-methoxyethoxy)ethanol + 1-hexene) were measured at 298.15 K and 313.15 K, while the binary mixture (2-(2-methoxyethoxy)ethanol + cyclohexane) with the ternary mixtures (2-(2-methoxyethoxy)ethanol (1) + 1-hexene (2) + cyclohexane (3)) were measured at 313.15 K. These experimental data, reported in Tables 2, 3 and 6 with a graphic representation shown in Figures 1, 2, 3, 4 and 5.

For binary systems, the H^E measurements were fitted using the modified Redlich-Kister mathematical equation, given by Eq. (1), where the A_i coefficients are given by the unweighted least-squares method.

$$H^E = \frac{x \cdot (1-x) \cdot \sum_{i=1}^n A_i \cdot (2x-1)^{i-1}}{1 + A_0 \cdot (2x-1)} \quad (1)$$

The optimal number of modified Redlich-Kister coefficients A_i was selected using the F -test [7].

The studied binary systems have also been fitted using UNIQUAC model, where the excess molar enthalpy is given by using the following equation:

$$H^E = \sum_{i=1}^n q_i x_i \frac{\sum_{j=1}^n g_j \Delta u_{ji} \tau_{ji}}{\sum_{j=1}^n g_j \tau_{ij}} \quad (2)$$

With: $g_i = \frac{q_i x_i}{\sum_j q_j x_j}$ and q_i is the molecular surface area, obtained by summing the contributions of the functional groups present in the compound.

The NRTL model has also used to fit the H^E measurements of the studied binary systems, using the following equation:

$$H^E = -RT \sum_{i=1}^n x_i \eta_i \quad (3)$$

where:

x_i : the composition of the component i and the coefficient η_i is obtained by :

$$\eta_i = \frac{\sum_{k=1}^p x_k \tau_{ki} G_{ki} \left[\alpha \left(\tau_{ki} - \left(\frac{\sum_{n=1}^p x_n \tau_{ni} G_{ni}}{\sum_{l=1}^n x_l G_{li}} \right) \right) - 1 \right]}{\sum_{l=1}^p x_l G_{li}} \quad (4)$$

$$G_{ji} = \exp(-\alpha \tau_{ij}) \quad (5)$$

$$\tau_{ij} = (g_{ij} - g_{ii})/RT \quad (6)$$

g_{ji} represents the interaction energy between each pair of i - j molecules. x is the mole fraction and α is the non-randomness factor in the mixture. The NRTL theory supposed that the H^E of multi-component mixture conditioned by the binary parameters. In this study, the non-randomness parameter α is an adjustable parameter for the three-parameter.

Correlation results of excess molar enthalpy H^E of binary systems using Eq.(1), Eq. (2) and Eq. (3), are summarized in Table 4 and 5, with root mean square deviation, rms , absolute difference maximum, $\max |\Delta H^E|$, maximum relative deviation, $\max (|\Delta H^E|/H^E)$, which are calculated by the following equations:

$$rms = \left[\frac{\sum_i^{n_{dat}} (H_{exp}^E - H_{calc}^E)^2}{n_{dat} - n_{par}} \right]^{1/2} \quad (7)$$

$$\max |\Delta H^E| = \max |H_{exp}^E - H_{calc}^E| \quad (8)$$

$$\max (|\Delta H^E| / H^E) = \max \left(\frac{|H_{exp}^E - H_{calc}^E|}{H_{exp}^E} \right) \quad (9)$$

where H_{exp}^E , H_{calc}^E , n_{dat} and n_{par} are respectively the values of the experimental and correlated data of H^E , the number of measured data and the number of parameters of the corresponding model.

Concerning the first binary system (1-hexene + cyclohexane) at 298.15 K and 313.15 K, the best fit of measured data is obtained with modified Redlich-Kister equation. The root mean

square deviation, rms ΔH^E , is 0.1 J·mol⁻¹ and 0.3 J·mol⁻¹, at both temperatures, respectively. Deviations of rms ΔH^E obtained with the NRTL and the UNIQUAC models are almost the same, they are about 1.3 J·mol⁻¹ and 1.5 J·mol⁻¹ for NRTL model, then 0.6 J·mol⁻¹ and 0.8 J·mol⁻¹ for UNIQUAC model, at both temperatures, respectively. This binary system shows an endothermic behaviour ($H^E > 0$) throughout the whole range of composition (Figure 1). The maximum value of H^E at 298.15 K is 236.46 J·mol⁻¹, while at 313.15 K the maximum value of H^E slightly decreased until 218.50 J·mol⁻¹. For both temperatures, the maximum of H^E is shifted to the cyclohexane rich region ($x = 0.45$). For the same binary system and at temperature $T = 298.15$ K, the comparison with data reported by Zhaohui *et al.* [8] and Letcher *et al.* [9], shows that our experimental data agree to within 0.65% and 5%, respectively. No reference data in the literature at $T = 313.15$ K for comparison.

The second binary system (2-(2-methoxyethoxy)ethanol + 1-hexene) shows also an endothermic behavior ($H^E > 0$) at 298.15 K and 313.15 K, at any mole fraction (Figure 2). The maximum value of H^E at 298.15 K is 1012.16 J·mol⁻¹ and when the temperature is increased to 313.15 K the maximum value of H^E reaches 1162.98 J·mol⁻¹, both at the mole fraction $x = 0.45$. The best fit of experimental data at both temperatures is obtained with the modified Redlich-Kister equation with a root mean square deviation, rms ΔH^E , of 4.8 J·mol⁻¹ and 4.4 J·mol⁻¹, at 298.15 K and 313.15 K, respectively. The correlated results of H^E obtained with NRTL and UNIQUAC models are not good enough, they are about 15.2 J·mol⁻¹ and 19.0 J·mol⁻¹ for NRTL model, then 82.8 J·mol⁻¹ and 77.6 J·mol⁻¹ for UNIQUAC model, at both temperatures, respectively. No data were found in the literature to compare our experimental data of this binary system at 298.15 K and 313.15 K.

The third binary system (2-(2-methoxyethoxy)ethanol + cyclohexane) presents also an endothermic behaviour at 313.15 K and at the whole range of composition (Figure 3). With a maximum value of excess molar enthalpy H^E of 1266.03 J·mol⁻¹, obtained at equimolar

composition. Modified Redlich-Kister equation gave also the best fit with a root mean square deviation, rms ΔH^E , of 10.5 J·mol⁻¹. The other used models (NRTL and UNIQUAC) gave a worse fit, with a rms ΔH^E , 28.4 J·mol⁻¹ for NRTL model and 120.3 for UNIQUAC model. No data were found of this binary system in the literature.

The ternary mixtures 2-(2-methoxyethoxy)ethanol (1) + 1-hexene (2) + cyclohexane (3) at $T = 313.15$ K were formed by adding the 2-(2-methoxyethoxy)ethanol (1) to the binary mixtures of fixed composition of 1-hexene (2) + cyclohexane (3). Four different starting binaries were used, with values of the ratio x_2/x_3 of 0.2499, 0.6999, 1.4010 and 4.0025, respectively. The measured excess molar enthalpies H^E presented in Table 6 are determined by Eq. (10), using the calculated values of H_{23}^E from the Redlich-Kister fit of the data of the binary system 1-hexene (2) + cyclohexane (3):

$$H_{123}^E = H_{1+23}^E + (1 - x_2)H_{23}^E \quad (10)$$

To fit the H^E experimental data, the following equation is used:

$$H_{123}^E = H_{12}^E + H_{13}^E + H_{23}^E + x_1x_2x_3\Delta H_{123}^E \quad (11)$$

with

$$\Delta H_{123}^E = B_0 + B_1x_1 + B_2x_2 + B_3x_1^2 + B_4x_2^2 + B_5x_1x_2 + B_6x_1^3 + B_7x_2^3 \quad (12)$$

The coefficients B_i were obtained by the unweighted least-squares method.

The following equation is also used to calculate ΔH_{123}^E :

$$\Delta H_{123}^E = B_1x_1 + B_2x_2 + B_3x_3 \quad (13)$$

The correlation results obtained for the ternary systems with Eqs. (11)-(13) and the NRTL and UNIQUAC models, are illustrated in Table 7. Also, the prediction results obtained for the same ternary systems using parameters of binary systems are presented in Table 7.

The studied ternary systems, 2-(2-methoxyethoxy)ethanol (1) + 1-hexene (2) + cyclohexane (3) at $T = 313.15$ K, presents an endothermic behaviour ($H^E > 0$) in the whole range of composition (Figure 4). The maximum value of H^E is 1363.3 J·mol⁻¹. The best fit of measured

data of H^E is obtained with Eq.(11). With a root mean square deviation, rms ΔH^E , of 27.7 J·mol⁻¹, and the maximum value of the absolute deviation, max $|\Delta H^E|$, of 118.0 J·mol⁻¹. The correlated results obtained with the other models (NRTL and UNIQUAC) and Eq. (13) are also good. No reference data in the literature of this studied ternary systems for comparison.

Figure 5 presents the graphical comparison of measured and predicted data of the studied ternary mixtures using parameters of binary mixtures of NRTL and UNIQUAC models. The NRTL model shows the best qualitative description of studied ternary H^E curves, with a root mean square deviation, rms ΔH^E , of 42.8 J·mol⁻¹. While the prediction data of the studied ternary from binary parameters obtained with UNIQUAC model is slightly worse, with a root mean square deviation, rms ΔH^E , of 70.9 J·mol⁻¹.

Generally, two effects contribute to the value of the excess molar enthalpy H^E of the n components at fixed T and P and in their actual stable states. The first effect is a phase change of at least one of the compounds during the mixing process. The second effect is the non-ideality of the mixture which is revealed when the molecules making up the mixture are different in terms of size, shape and interactions which they exert on one another [10], this dissimilarity determined either the increase or the drop of excess molar enthalpy amount, for the hydrocarbon-hydrocarbon mixtures, and according to the present study (1-hexene + cyclohexane) and to our previous published work [11], we drive as a conclusion that the excess molar enthalpy amount decreases during the temperature change from 298.15 K to 313.15 K, while for the n-alkoxyethanol-hydrocarbon mixtures as the binary system (2-(2-methoxyethoxy)ethanol + 1-hexene), this amount increases. When the molecules are few polar, few associating and are sufficiently alike from the point of view of their shapes and sizes (e.g., hydrocarbon-hydrocarbon mixtures) and when phase change does not occur during the mixing process, the values of excess molar enthalpy H^E are heavily small comparing with the high values of H^E obtained by other mixtures as n-alkoxyethanol-hydrocarbon and n-

alkanols-hydrocarbon, that their molecules are self-associated and form intermolecular H-bonds. The significantly higher excess molar enthalpy H^E values found in this work and more precisely in alkoxyethanol-hydrocarbon mixtures (e.g., in this work: 2-(2-methoxyethoxy)ethanol with 1-hexene or cyclohexane), in comparison with the well-known values for homomorphic mixtures on n-alkanols with the same used hydrocarbons (1-hexene and cyclohexane) that are previously published by our group [5, 12-13], suggest that the mixtures containing n-alkoxyethanol have an intermolecular H-bonds that are formed between the O and OH groups of the same cellosolve [14-15]; and also have a strong dipolar interactions, which are actually more important than those in mixtures with n-alcohols, exist. This may be due to a larger dipole moment of n-alkoxyethanol compared to those of homomorphic n-alkanols [16], or to the formation of the mentioned intramolecular H-bonds may enhance these dipolar interactions as molecules become more anisotropic [15]. The excess molar enthalpy curves for alkoxyethanol-hydrocarbon mixtures are more symmetrical than those for alcoholic solutions, which are skewed towards low concentration of the self-associated compound. This also demonstrates that the contribution to the thermodynamic properties from the dipole–dipole interactions is higher in solutions with alkoxyethanols than in the corresponding mixtures with the homomorphic n-alkanols [17].

4. Conclusion

Isothermal excess molar enthalpies H^E at $T = 313.15$ K for the ternary systems 2-(2-methoxyethoxy)ethanol (1) + 1-hexene (2) + cyclohexane (3) and their corresponding binary systems at 298.15 K and 313.15 K were measured by using an isothermal flow calorimeter at atmospheric pressure. All the binary systems show an endothermic and strongly asymmetric H^E behaviour at the chosen temperatures. The binary system containing 1-hexene and cyclohexane shows a decreasing value of H^E with increasing temperature from 298.15 K to 313.15 K, while 2-(2-methoxyethoxy)ethanol with 1-hexene or cyclohexane show the

opposite behaviour. Intermolecular and association effects involved in these systems have been discussed. The excess molar enthalpies experimental data were correlated and predicted with modified Redlich-Kister polynomial equation, NRTL and UNIQUAC models.

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LIST OF SYMBOLS

H^E ; excess molar enthalpy, T ; temperature, P ; pressure, x_i ; mole fraction, i ; constituent identification, $u(P)$, $u(T)$ and $u(x)$; the standard uncertainties for pressure, temperature and mole fraction, respectively, R ; universal gas constant.

REFERENCES

- [1] S.C. Bhupendra, K.S. Ram, H.M. Cho, H.C. Lim, Practice of diesel fuel blends using alternative fuels. A review, *Renewable and Sustainable Energy Reviews.*, 2016, 59, 1358-1368.
- [2] O. Redlich, A.T. Kister, Algebraic Representation of Thermodynamic Properties and Classification of Solutions, *Ind. & Eng. Chem.*, 1948, 40, 345-348.
- [3] Renon, H., and J.M. Prausnitz, J.M., *AIChE Journal*, 14, (1968), 135-14

- [4] D.S. Abrams, J.M. Prausnitz, Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems, *AIChE Journal.*, 1975, 21, 116-128.
- [5] F. Aguilar, F.E.M. Alaoui, C. Alonso-Tristán, J.J. Segovia, M.A. Villamañán, E.A. Montero, Excess enthalpies of binary and ternary mixtures containing dibutyl ether (DBE), cyclohexane and 1-butanol at 298.15 K, *J. Chem. Eng. Data.*, 2009, 54, 6, 1672-1679.
- [6] J.A. Riddick, W.B. Bunger, T.K. Sakano, *Organic Solvents. Physical Properties and Methods of Purification*; Wiley; New York, 1986.
- [7] P.R. Bevington, D.K. Robinson, *Data Reduction and Error Analysis for the Physical Sciences*, WCD/McGraw-Hill, Boston, Mass, 1992.
- [8] W. Zhaohui, G.C. Benson, B.C.-Y. Lu, Excess Molar Enthalpies of Binary Mixtures of 1-Hexene with Some Cyclic and Aromatic Hydrocarbons at 298.15 K, *J. Thermochemica. Acta.*, 2004, 414, 31-33.
- [9] T. M. Letcher, J. Sack, The excess enthalpy of mixing of some hydrocarbon mixture. *J. South African Chem. Inst.*, 1975, 28, 316-320
- [10] J.W. Qian, R. Privat, J-N. Jaubert, P. Duchet-Suchaux, Enthalpy and Heat Capacity Changes on Mixing: Fundamental Aspects and Prediction by Means of the PPR78 Cubic Equation of State, *J. Energy & Fuels.*, 2013, 27, 11, 7150-7178.
- [11] M. Lifi, N. Muñoz-rujas, E.A. Montero, Y. Chhiti, F. Aguilar, F.E.M. Alaoui, Measurement and Modeling of Excess Molar Enthalpies of Binary Mixtures Involving Hydrocarbon Components of Fuel, *J. Chem. Eng. Data.*, 2020, 65, 2, 717-724.
- [12] F.E.M. Alaoui, F. Aguilar, M.J. González-Fernández, E.A. Montero, Excess enthalpies of ternary mixtures of (oxygenated additives + cycloalkane) in fuels and bio-fuels: (dibutyl ether + 1-propanol + cyclohexane), or methylcyclohexane, at $T = (298.15 \text{ and } 313.15) \text{ K}$, *J. Chem. Thermodynamics.*, 2017, 105, 6, 112-122.

- [13] F. Aguilar, F.E.M. Alaoui, J.J. Segovia, M.A. Villamañán, E.A. Montero, Ether + alcohol + hydrocarbon mixtures in fuels and bio-fuels: Excess enthalpies of binary mixtures containing dibutyl ether (DBE) or 1-butanol and 1-hexene or methylcyclohexane or toluene or cyclohexane or 2,2,4- trimethylpentane at 298.15 K and 313.15 K, *Fluid Phase Equilib.*, 2012, 315, 1– 8.
- [14] R.L. Brinkley, R.B. Gupta, Intra- and intermolecular hydrogen bonding of 2-methoxyethanol and 2-butoxyethanol in n-hexane. *Ind. Eng. Chem. Res.* 1998, 37, 4823-4827.
- [15] J.C. Cobos, I. García, C. Casanova, Excess properties of mixtures of some n-alkoxyethanols with organic solvents. V. Excess enthalpies of 2-butoxyethanol with normal alkanes at 298.15 K. *Can. J. Chem.* 1988, 66, 2618-2620.
- [16] J.A. Riddick, W.B. Bunger, T.K. Sakano, In *Organic Solvents, Techniques of Chemistry*; Weissberger, A., Ed.; Wiley: New York, 1986, Vol. II.
- [17] J.A. González, J.C. Cobos, F. J. Carmona, I. García de la Fuente, V.R. Bhethanabotla, S.W. Campbell, Thermodynamics of mixtures containing alkoxyethanols Part XV. DISQUAC characterization of systems of alkoxyethanols with n-alkanes or cyclohexane, *Phys. Chem. Chem. Phys.*, 2001, 3, 2856-2865.
- [18] R. Francesconi, C. Castellari, F. Comelli, Excess Molar Enthalpies and Excess Molar Volumes of Diethyl Carbonate + Some n-Alkoxyethanols at (298.15 and 313.15) K, *J. Chem. Eng. Data* 1999, 44, 1373-1378.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

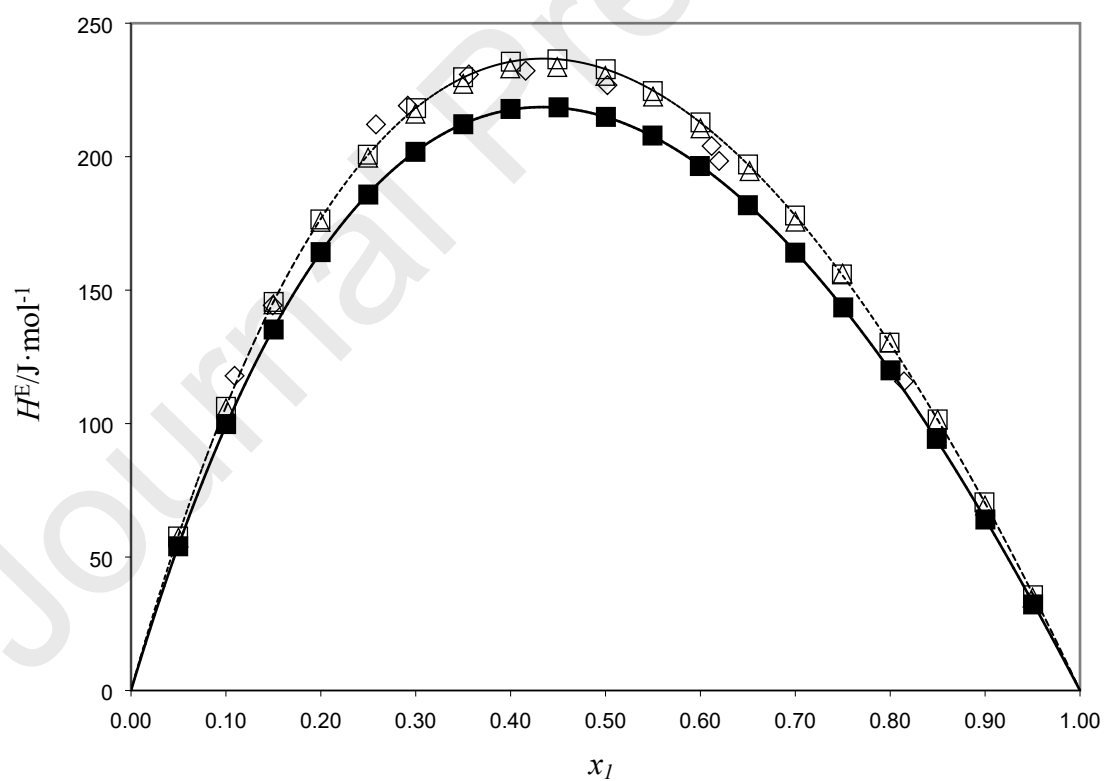
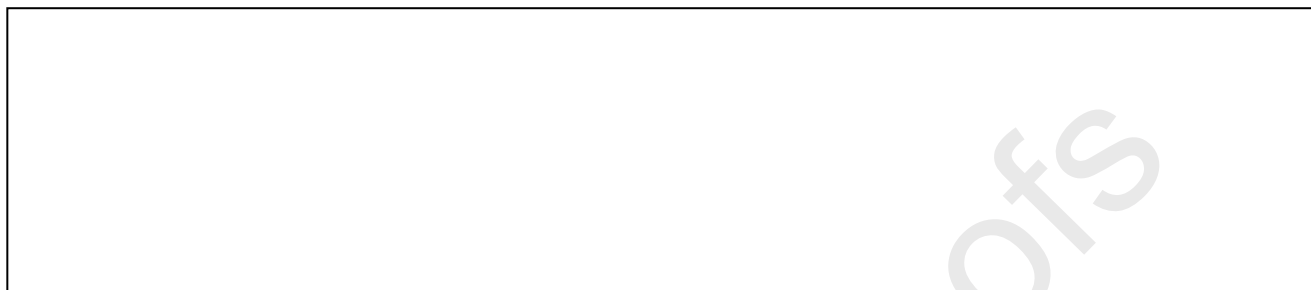


Figure 1. Excess molar enthalpy H^E of 1-hexene (1) +cyclohexane (2). At $T = 298.15$ K: (□), experimental data; (Δ), data from Ref. [8]; (◇), data from Ref. [9]; (----), calculated values

with Eq. (1), using parameters of Table 4. At $T = 313.15$ K: (■), experimental data; (—), calculated values with Eq. (1), using parameters of Table 5.

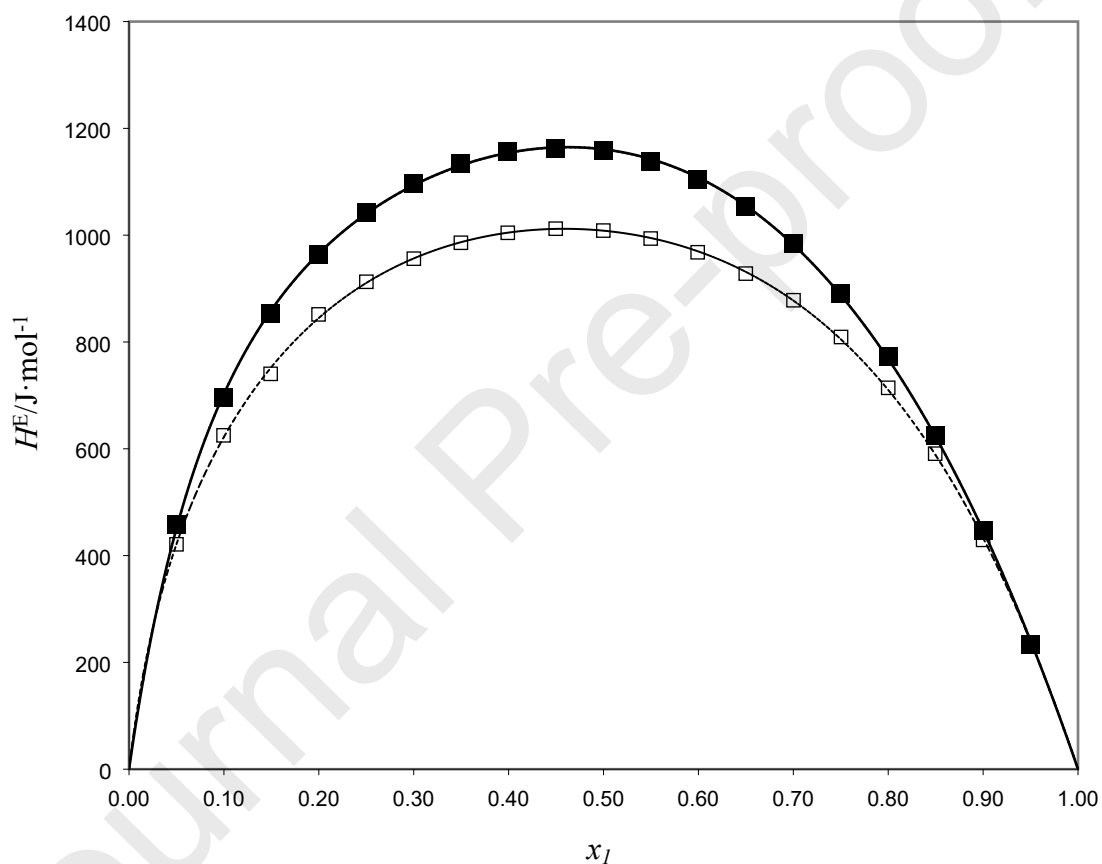


Figure 2. Excess molar enthalpy H^E of 2-(2-methoxyethoxy)ethanol (1) + 1-hexene (2). At $T = 298.15$ K: (□), experimental data; (---), calculated values with Eq. (1), using parameters of Table 4. At $T = 313.15$ K: (■), experimental data; (—), calculated values Eq. (1), using parameters of Table 5.

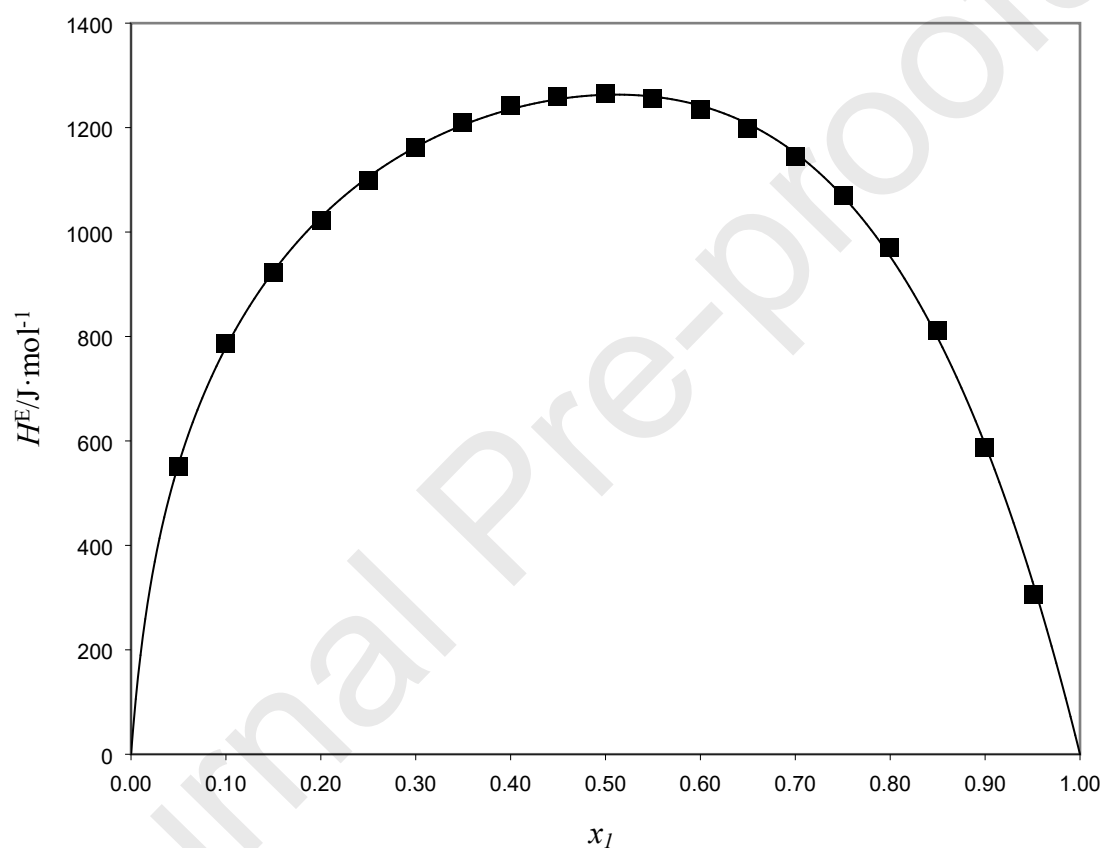


Figure 3. Excess molar enthalpy H^E of 2-(2-methoxyethoxy)ethanol (1) + cyclohexane (2). At $T = 313.15$ K: (■), experimental data; (—), calculated values with Eq. (1), using parameters of Table 5.

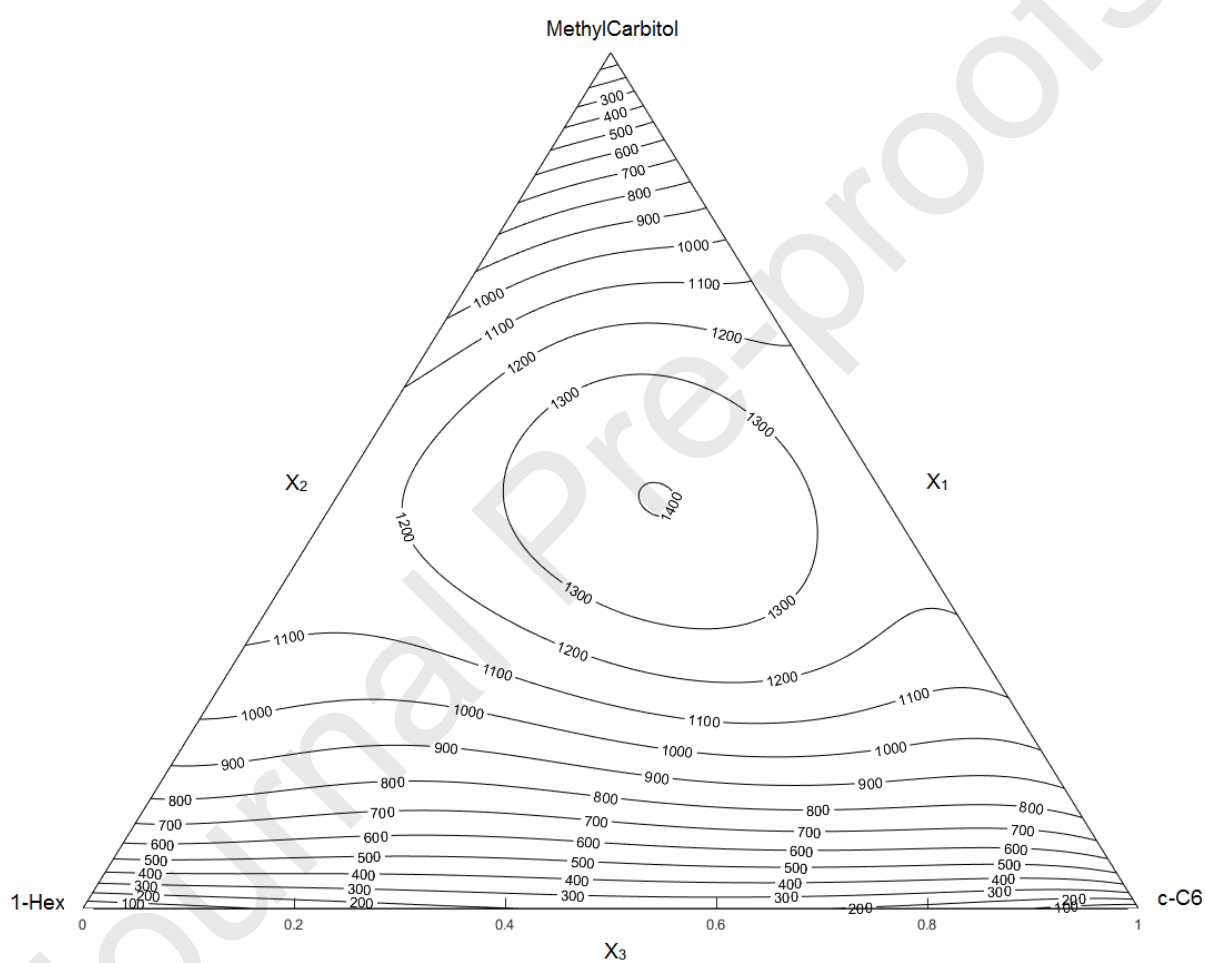
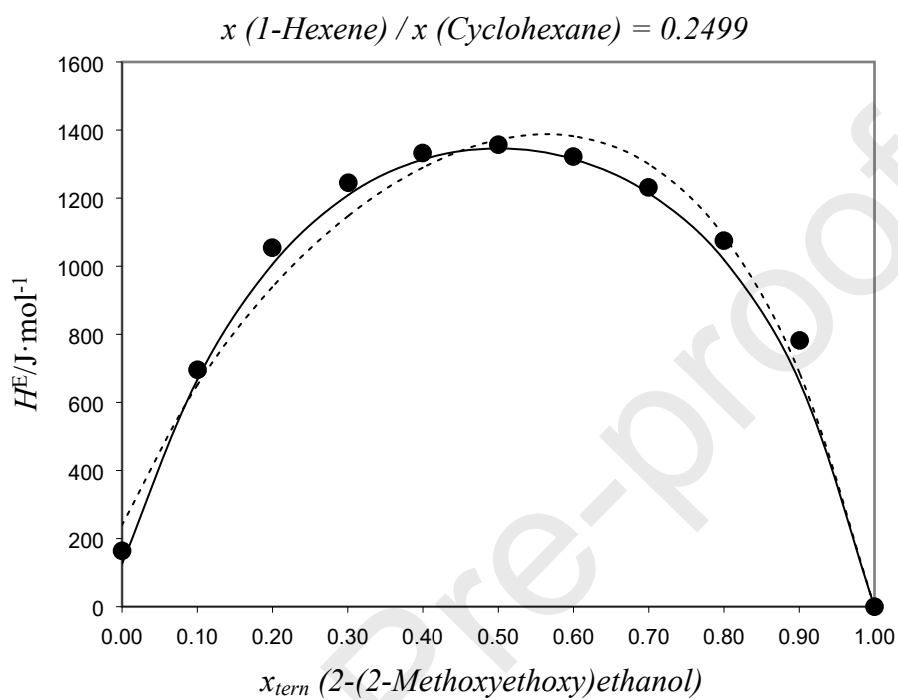
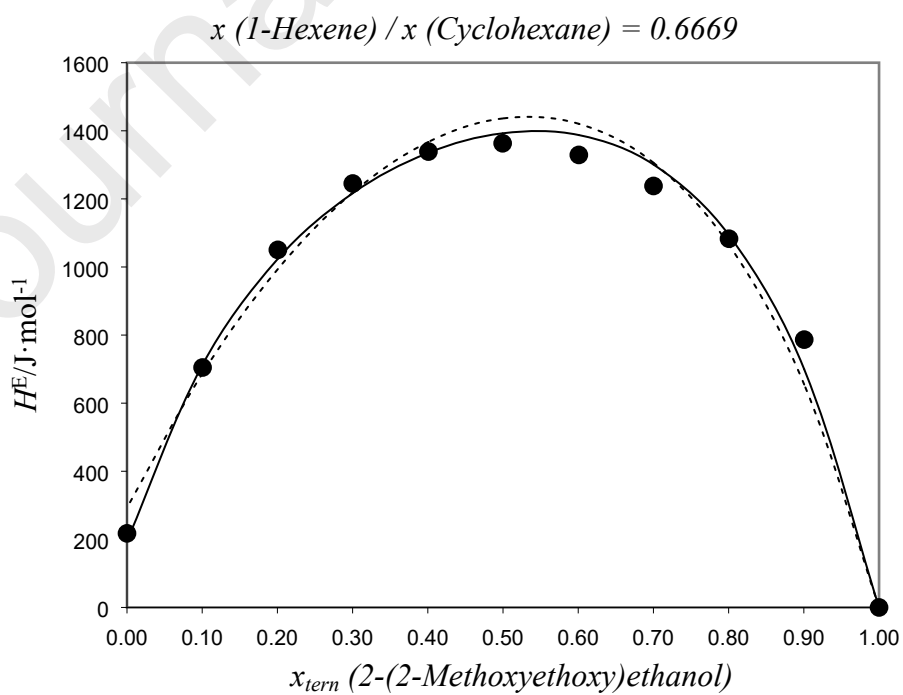


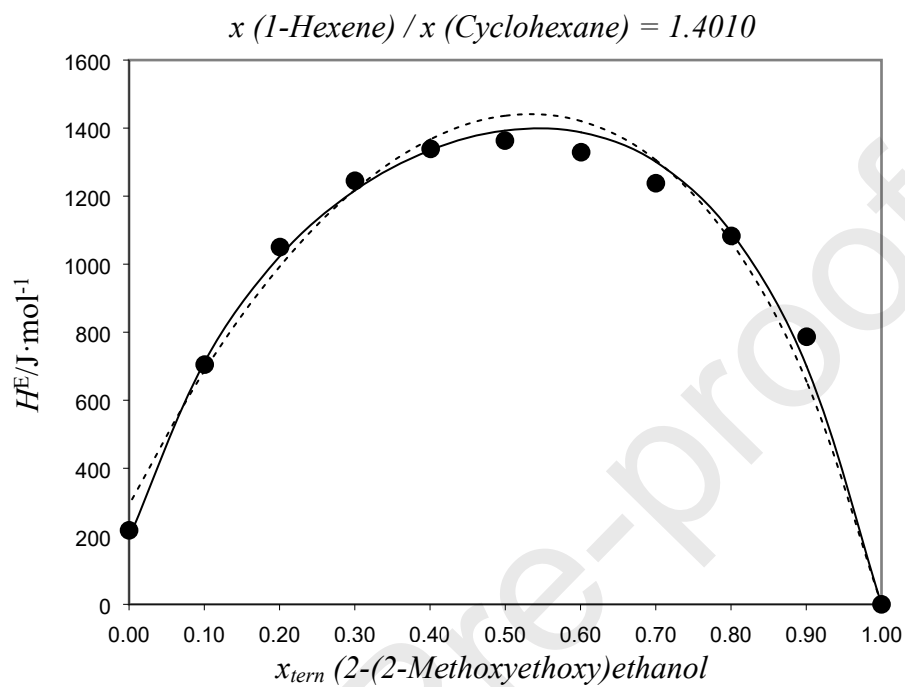
Figure 4. Contours for constant values of H_{123}^E for 2-(2-methoxyethoxy)ethanol (1) + 1-hexene (2) + cyclohexane (3) at $T = 313.15$ K.



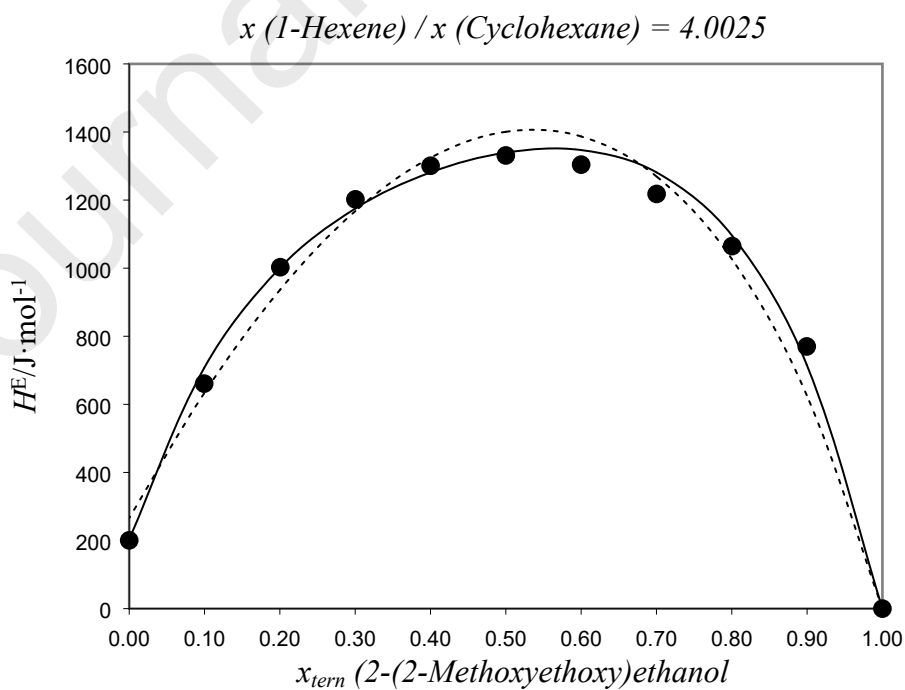
(a)



(b)



(c)



(d)

Figure 5. Excess molar enthalpy H^E for 2-(2-methoxyethoxy)ethanol (1) + 1-hexene (2) + cyclohexane (3) at $T = 313.15$ K: (●), experimental data; (—), NRTL model; (----), UNIQUAC model.

Table 1. Purity and chemical data of used liquids.

Compound	formula	Molar mass /(g·mol ⁻¹)	Density /(g·cm ⁻³)		Stated mole fraction	CAS number
			298.15 K	313.15 K		
2-(2-Methoxyethoxy) ethanol	C ₅ H ₁₂ O ₃	120.15	1.0167 ^a	1.0026 ^b	>0.990 ^d	111-77-3
1-Hexene	C ₆ H ₁₂	84.16	0.6685 ^a	0.6538 ^c	>0.993 ^e	592-41-6
Cyclohexane	C ₆ H ₁₂	84.16	0.7739 ^a	0.7605 ^c	>0.999 ^f	110-82-7

^a Riddick *et al.* [6]. ^b Francesconi *et al.* [18]. ^c Lifi *et al.* [11].

^d Determined by gas chromatography (GC) by the supplier Sigma-Aldrich.

^e Determined by gas chromatography (GC) by the supplier Arcos.

^f Determined by gas chromatography (GC) by the supplier Honeywell.

Table 2. Experimental data of excess molar enthalpies of studied mixtures (x 2-(2-methoxyethoxy)ethanol + (1- x) 1-hexene) and (x 1-hexene + (1- x) cyclohexane) at 298.15 K and at 0.1 MPa.^a

x	$H^E/\text{J}\cdot\text{mol}^{-1}$	x	$H^E/\text{J}\cdot\text{mol}^{-1}$	x	$H^E/\text{J}\cdot\text{mol}^{-1}$	x	$H^E/\text{J}\cdot\text{mol}^{-1}$
x 1-Hexene + (1- x) cyclohexane							
0.0496	57.7	0.3004	218.2	0.5498	224.6	0.7992	130.3
0.1000	106.3	0.3499	229.8	0.6001	212.9	0.8500	101.6
0.1503	145.6	0.4002	235.6	0.6502	197.1	0.8993	70.5
0.1995	176.5	0.4493	236.5	0.6997	178.0	0.9505	35.7
0.2495	200.7	0.5002	232.8	0.7491	155.9		

x 2-(2-Methoxyethoxy)ethanol + $(1-x)$ 1-hexene							
0.0500	421.1	0.3001	956.0	0.5497	993.7	0.8000	714.2
0.0996	625.2	0.3497	985.8	0.5992	968.0	0.8495	590.9
0.1492	740.3	0.3991	1004.5	0.6499	928.0	0.9000	429.4
0.1997	851.7	0.4496	1012.2	0.7002	878.2	0.9501	231.2
0.2501	912.8	0.4998	1008.6	0.7503	809.3		

^a Standard uncertainties of pressure P , temperature T and mole fraction x are as follows: $u(P) = 0.01$ MPa, $u(T) = 0.05$ K, $u(x) = 0.0008$. The relative expanded uncertainty ($k = 2$) is $U_r(H^E) = 0.01$ for excess molar enthalpy.

Table 3. Experimental data of excess molar enthalpies of studied binary mixtures (x 2-(2-methoxyethoxy)ethanol + $(1-x)$ 1-hexene), (x 2-(2-methoxyethoxy)ethanol + $(1-x)$ cyclohexane), (x 1-hexene + $(1-x)$ cyclohexane) at 313.15 K and at 0.1 MPa.^a

x	$H^E/\text{J}\cdot\text{mol}^{-1}$	x	$H^E/\text{J}\cdot\text{mol}^{-1}$	x	$H^E/\text{J}\cdot\text{mol}^{-1}$	x	$H^E/\text{J}\cdot\text{mol}^{-1}$
x 1-Hexene + $(1-x)$ cyclohexane							
0.0497	54.0	0.2997	201.8	0.5495	207.9	0.8003	120.0
0.1002	99.8	0.3501	212.2	0.5994	196.5	0.8491	94.3
0.1503	135.3	0.3999	217.9	0.6500	181.8	0.9003	64.1
0.1998	164.2	0.4505	218.5	0.6999	164.0	0.9506	32.3
0.2500	185.8	0.5004	214.9	0.7505	143.5		
x 2-(2-Methoxyethoxy)ethanol + $(1-x)$ 1-hexene							

0.0500	457.7	0.3001	1096.7	0.5495	1137.6	0.7999	773.2
0.0998	696.0	0.3497	1134.7	0.5990	1104.6	0.8494	625.6
0.1492	853.9	0.3991	1156.6	0.6497	1053.9	0.8999	446.6
0.1998	964.7	0.4494	1163.0	0.7001	984.8	0.9501	232.7
0.2501	1042.7	0.4996	1158.1	0.7502	891.1		
<i>x</i> 2-(2-Methoxyethoxy)ethanol + (1- <i>x</i>) cyclohexane							
0.0501	552.0	0.2994	1161.9	0.5494	1256.0	0.7997	971.2
0.0994	787.4	0.3494	1209.6	0.6001	1234.0	0.8495	811.7
0.1505	922.9	0.3998	1242.2	0.6498	1197.3	0.8998	588.2
0.2006	1022.4	0.4493	1259.4	0.6998	1145.3	0.9505	305.0
0.2498	1099.3	0.5005	1266.0	0.7503	1070.8		

^a Standard uncertainties of pressure P , temperature T and mole fraction x are as follows: $u(P) = 0.01$ MPa, $u(T) = 0.05$ K, $u(x) = 0.0008$. The relative expanded uncertainty ($k = 2$) is $U_r(H^E) = 0.01$ for excess molar enthalpy.

Table 4. Sets of parameters needed for the graphical representation of excess molar enthalpies H^E by Redlich-Kister equation, NRTL and UNIQUAC models, for studied binary mixtures 2-(2-methoxyethoxy)ethanol (1) + 1-hexene (2) and 1-hexene (1) + cyclohexane (2) at 298.15 K and at 0.1 MPa.

Binary Systems ^a			
1-Hexene (1) + cyclohexane (2)	Redlich-Kister	NRTL	UNIQUAC
A_0	0.2854	-0.1330	-159.6
A_1	931.2	0.6370	391.1
A_2	29.1		
A_3	5.2		
A_4			
α_{12}		0.30	

rms $\Delta H^E/\text{J}\cdot\text{mol}^{-1}$	0.1	1.3	0.6
Max $ \Delta H^E /\text{J}\cdot\text{mol}^{-1}$	0.3	2.1	0.9
Max $(\Delta H^E /H^E)$	0.8%	2.8%	1.2%
2-(2-Methoxyethoxy)ethanol (1) + 1-hexene (2)	Redlich-Kister	NRTL	UNIQUAC
A_0	0.9184	2.1289	82.6
A_1	4033.6	2.8933	762.6
A_2	3364.5		
A_3	1650.9		
A_4	1103.0		
α_{12}		0.29	
rms $\Delta H^E/\text{J}\cdot\text{mol}^{-1}$	4.8	15.2	82.8
Max $ \Delta H^E /\text{J}\cdot\text{mol}^{-1}$	10.9	42.3	166.3
Max $(\Delta H^E /H^E)$	3.3%	17.9%	40.9%

^a Equivalence between parameters: NRTL $A_0=\tau_{12}$ and $A_1=\tau_{21}$; UNIQUAC $A_0=\Delta u_{12}$; $A_1=\Delta u_{21}$.

Table 5. Sets of parameters needed for the graphical representation of excess molar enthalpies H^E by Redlich-Kister equation, NRTL and UNIQUAC models, for studied binary mixtures 2-(2-methoxyethoxy)ethanol (1) + 1-hexene (2), 2-(2-methoxyethoxy)ethanol (1) + cyclohexane (2), 1-hexene (1) + cyclohexane (2) at 313.15 K and at 0.1 MPa.

Binary Systems ^a			
1-Hexene (1) + cyclohexane (2)	Redlich-Kister	NRTL	UNIQUAC
A_0	-0.1491	-0.1596	-188.1
A_1	859.6	0.6111	407.5
A_2	-345.6		
A_3	112.2		
A_4	-49.2		
α_{12}		0.30	
rms $\Delta H^E/\text{J}\cdot\text{mol}^{-1}$	0.3	1.5	0.8

Max $ \Delta H^E /\text{J}\cdot\text{mol}^{-1}$	0.5	3.0	1.7
Max $(\Delta H^E /H^E)$	1.5%	3.5%	1.7%
2-(2-Methoxyethoxy)ethanol (1) + 1-hexene (2)	Redlich-Kister	NRTL	UNIQUAC
A_0	0.7691	2.0012	44.5
A_1	4643.1	2.9494	954.2
A_2	3139.9		
A_3	1363.7		
A_4			
α_{12}		0.27	
rms $\Delta H^E/\text{J}\cdot\text{mol}^{-1}$	4.4	19.0	77.6
Max $ \Delta H^E /\text{J}\cdot\text{mol}^{-1}$	6.0	42.7	157.3
Max $(\Delta H^E /H^E)$	3.3%	16.3%	36.0%
2-(2-Methoxyethoxy)ethanol (1) + cyclohexane (2)	Redlich-Kister	NRTL	UNIQUAC
A_0	0.9422	2.9633	901.1
A_1	5051.3	3.4310	326.1
A_2	4869.4		
A_3	2800.7		
A_4	1594.5		
α_{12}		0.24	
rms $\Delta H^E/\text{J}\cdot\text{mol}^{-1}$	10.5	28.4	120.3
Max $ \Delta H^E /\text{J}\cdot\text{mol}^{-1}$	17.2	77.9	252.4
Max $(\Delta H^E /H^E)$	7.4%	23.6%	47.8%

^a Equivalence between parameters: NRTL $A_0 = \tau_{12}$ and $A_1 = \tau_{21}$; UNIQUAC $A_0 = \Delta u_{12}$; $A_1 = \Delta u_{21}$.

Table 6. Experimental data of H_{1+23}^E for the addition of 2-(2-Methoxyethoxy)ethanol (1) to 1-Hexene (2) + Cyclohexane (3) to form x_1 2-(2-Methoxyethoxy)ethanol + x_2 1-Hexene + (1- x_1 - x_2) Cyclohexane at 313.15 K and at 0.1 MPa, and values of H_{123}^E are calculated from Eq. (10) using H_{23}^E data that obtained from Redlich-Kister (Eq. (1)) with coefficients from table 5.

^a

x_1	$H_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$	$H_{123}^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$	$H_{123}^E/\text{J}\cdot\text{mol}^{-1}$
$x_2/x_3 = 0.2499; H_{23}^E/\text{J}\cdot\text{mol}^{-1} = 164.2$					
0.9005	765.8	782.2	0.3994	1234.0	1332.6
0.7998	1042.3	1075.2	0.3007	1130.5	1245.3

0.6995	1182.3	1231.7	0.1995	923.2	1054.6
0.5996	1256.4	1322.2	0.1003	548.2	695.9
0.5000	1275.0	1357.1			

$$x_2/x_3 = \mathbf{0.6669}; H_{23}^E/\text{J}\cdot\text{mol}^{-1} = 217.6$$

0.9005	765.0	786.7	0.4008	1208.6	1339.0
0.8005	1039.6	1083.0	0.3002	1092.9	1245.2
0.7001	1172.7	1238.0	0.2006	876.3	1050.3
0.6008	1242.3	1329.2	0.1005	509.1	704.8
0.4995	1254.4	1363.3			

$$x_2/x_3 = \mathbf{1.4010}; H_{23}^E/\text{J}\cdot\text{mol}^{-1} = 200.6$$

0.8995	749.9	770.1	0.4001	1180.6	1300.9
0.8005	1024.9	1064.9	0.3003	1061.9	1202.2
0.7002	1157.9	1218.0	0.2006	842.5	1002.8
0.6000	1223.9	1304.1	0.0995	480.3	660.9
0.5000	1230.8	1331.1			

$$x_2/x_3 = \mathbf{4.0025}; H_{23}^E/\text{J}\cdot\text{mol}^{-1} = 119.8$$

0.8997	711.1	723.1	0.4000	1134.7	1206.6
0.8000	985.0	1008.9	0.2997	1013.8	1097.7
0.6996	1121.9	1157.9	0.2000	798.7	894.5
0.6000	1180.6	1228.5	0.0997	445.4	553.3
0.4997	1186.5	1246.5			

^a Standard uncertainties of pressure P , temperature T and mole fraction x are as follows: $u(P) = 0.01$ MPa, $u(T) = 0.05$ K, $u(x) = 0.0008$. The relative expanded uncertainty ($k = 2$) is $U_r(H^E) = 0.01$ for excess molar enthalpy.

Table 7. Summary of the data reduction and prediction results obtained for the studied ternary system 2-(2-methoxyethoxy)ethanol (1) + 1-hexene (2) + cyclohexane (3) at 313.15 K and at 0.1 MPa.

Correlation ^a	ΔH_{123}^E , Eq. (11) / J·mol ⁻¹	ΔH_{123}^E , Eq. (13) / J·mol ⁻¹	NRTL	UNIQUAC
B ₀	-3448.6	1852.6	0.6750	660.9
B ₁	-4760.7	-926.0	1.8018	12515.0
B ₂	72788.9	5837.9	-0.3695	-21.7
B ₃	33482.6		0.8604	249.9
B ₄	-193739.2		4.0366	1163.5
B ₅	-25698.0		0.0375	210.0
B ₆	-35553.1			
B ₇	150211.0			
α			0.16	
rms ΔH^E /J·mol ⁻¹	27.7	34.0	58.5	51.5
Max $ \Delta H^E $ /J·mol ⁻¹	118.0	138.7	142.6	158.0
Max ($ \Delta H^E /H^E$)	15.1%	17.7%	19.8%	26.8%
Prediction ^a			NRTL	UNIQUAC
B ₀			2.4454	-95.4
B ₁			3.3899	1109.4
B ₂			0.3463	197.5
B ₃			135.5373	17680.4
B ₄			3.0333	2935.1
B ₅			2.4016	-578.0
α_{12}			0.27	
α_{13}			0.24	

α_{23}	0.30	
rms $\Delta H^E/\text{J}\cdot\text{mol}^{-1}$	42.8	70.9
Max $ \Delta H^E /\text{J}\cdot\text{mol}^{-1}$	122.3	143.2
Max $(\Delta H^E /H^E)$	23.4%	46.4%

^a Equivalence between parameters : NRTL $B_0 = \tau_{12}$; $B_1 = \tau_{21}$; $B_2 = \tau_{13}$; $B_3 = \tau_{31}$; $B_4 = \tau_{23}$; $B_5 = \tau_{32}$; UNIQUAC $B_0 = \Delta u_{12}$; $B_1 = \Delta u_{21}$; $B_2 = \Delta u_{13}$; $B_3 = \Delta u_{31}$; $B_4 = \Delta u_{23}$; $B_5 = \Delta u_{32}$.

CRediT author statement

Mohamed Lifi: Writing - Original Draft, Investigation, Formal analysis.

Natalia Muñoz-Rujas: Investigation, Visualization.

Eduardo Atanasio Montero: Project administration, Writing - Review & Editing, Validation, Supervision.

Latifa Negadi: Visualization.

Fernando Aguilar: Writing - Review & Editing, Supervision, Software, Validation.

Fatima Ezzahrae M'hamdi Alaoui: Writing - Review & Editing, Supervision, Methodology, Validation.

> New excess molar enthalpy data for 1-hexene + cyclohexane, 2-(2-methoxyethoxy)ethanol + 1-hexene, and + cyclohexane, and 2-(2-methoxyethoxy)ethanol (1) + 1-hexene (2) + cyclohexane (3) are reported. > 5 binary systems at 298.15 K and 313.15 K and 1 ternary systems at 313.15 K were measured by means of an isothermal flow calorimeter > Experimental data were fitted using Redlich-Kister equation, NRTL and UNIQUAC models. > Intermolecular and association effects involved in these systems have been discussed