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MULTIPLE LINEAR REGRESSION (MLR) MODELS USED FOR THE PREDICTION OF EXCESS THERMODYNAMIC PROPERTIES BASED ON EXPERIMENTAL DETERMINATION OF REFRACTIVE INDEX

BY

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Abstract. In engineering, it is very important to have thorough knowledge of the thermodynamic and conveying properties of fluid mixtures, as they are mainly used to study the interactions that occur in fluids with several components, as well as to design various equipment for separation by distillation, fractional distillation and solvent extraction, and to achieve a scientific approach of the risk factors that affect separation processes. Our research group used the statistical processing of experimental data by the multiple linear regressions (MLR) method in order to estimate the excess molar volume starting from the experimental values of the refractive index for ternary systems. In this paper we will prove that this type of experimental data processing could also be used to predict other excess thermodynamic properties such as excess viscosity and excess surface tension (P^E). In order to achieve this goal, we will use both the literature data and experimental data obtained in our laboratory on the thermodynamic properties of certain fluid mixtures. The created mathematical models correlate the excess thermodynamic properties with the refractive index, the standard temperature and the fluid mixture composition: $P^E=A_0+A_1X_1+A_2X_2+A_3(T/298.15)+A_4n$, where X_1 and X_2

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are the molar fractions, T is the temperature expressed in Kelvin and n is the refractive index. These models are extremely useful in practice. The refractive index can be easily determined, with rather good accuracy and low substance consumption. These mathematical models also allow the determination of other properties, such as density, viscosity and surface tension, which are more difficult to determine by experimental methods.

Keywords: MLR models; density; viscosity; surface tension; refractive index; multicomponent systems.

1. Introduction

The thermodynamic and transport properties of liquid mixtures are very important for the designing and optimization of chemical processes. The studies from the specialized literature (Guevara-Carrion *et al*., 2012; Hendriks *et al*., 2010; Kabo *et al.*, 2019; O'Connell *et al.*, 2009) show that there is a critical need of accurate and consistent thermodynamic experimental data, which can cover a wide range of temperature, pressure and composition and, also of models that can make property-related predictions (Albà *et al.*, 2020; Hill and Justice, 2011; Speybroeck *et al*., 2010). The most well-known and used model for representing excess properties is the one proposed by Redlich and Kister, which correlates any excess volume of a molar fraction multicomponent system of the mixture components (Redlich and Kister, 1948). As opposed to the Redlich-Kister model, the Jouyban-Acree model (Jouyban *et al*., 2005; Rodriguez *et al.*, 2011) used for predicting the density and molar volume, has the advantage of including the temperature effects among the model constants, so that, by using the interpolation technique, the properties can be determined at other temperatures as well. The Redlich-Kister model does not allow this, because the model constants are valid for one temperature only.

Our research group proved that the modelling of the excess thermodynamic properties can be made by applying statistical processing to the experimental data, along with multiple linear regression method (MLR) (Lisa *et al*., 2015). The MLR method was used for estimating the excess molar volume, based on the experimental values of the refractive index for the ternary system ethylbenzene-octane-propylbenzene (Lisa *et al.*, 2015). In this paper, we aim at showing that this type of experimental data processing can also be used to predict other excess thermodynamic properties: excess viscosity and excess surface tension. In order to achieve this objective, we shall use both data from specialized literature and experimental data obtained in our laboratory, which concern the thermodynamic properties of certain liquid mixtures. The mathematical models obtained will correlate the excess thermodynamic properties with the refractive index, normalized temperature and composition of the liquid mixture. These models are extremely useful on a practical level. The refractive index can be easily determined, both with good precision and lower

consumption of substances. By means of these mathematical models, other properties can be obtained, such as density, viscosity and surface tension, since it is more difficult to measure them through experiments.

2. Materials and Methods

The excess thermodynamic volume modelling was performed through statistical processing of experimental data by using the SigmaPlot 11.0 software, along with the application of the multiple linear regression (MLR) method.

The mathematical models obtained correlate the excess thermodynamic properties (P^E) with the refractive index, normalized temperature and composition of the liquid mixture:

$$P^E = A_0+A_1X_1+A_2X_2+A_3(T/298.15)+A_4n \quad (1)$$

where: X_1 and X_2 are molar fractions, T is temperature given in Kelvin and n is the refractive index.

The applicability verification of such models was carried out by processing our own experimental data (Lisa *et al*., 2008; Lisa and Lisa, 2007) concerning the density and refractive index for the water-propionic acid binary system for a wide range of composition and the following temperatures: 292.15, 299.15, 305.15, 311.15 and 317.15 K.

In addition, there were created models which correlate excess molar volume, excess surface tension and excess viscosity with the refractive index, normalized temperature and composition for the ternary system 2,2,4-trimethylpentane (isooctane) + cyclohexane + n-decane (Gomez-Diaz *et al*., 2003). There were processed experimental data from literature (Gomez-Diaz *et al.*, 2003) for density, viscosity and surface tension at temperatures of 308.15, 313.15, 318.15 and 323.15 K and a wide range of composition and the excess thermodynamic properties were calculated: excess molar volume, excess surface tension and excess viscosity.

3. Results and Discussions

Based on the experimental data (Lisa *et al*., 2008; Lisa and Lisa, 2007), regarding the density of certain water/ propionic acid binary mixtures, the values of the excess molar volume were calculated as it follows:

$$Vm^E = \sum_{i=1}^{k} X_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \quad (2)$$

where: M_i represents the molar mass of each solution component, ρ is the mixture density, ρ_i is the density of the pure components and X_i are the molar fractions. The results obtained for different temperature values are shown in Fig. 1.

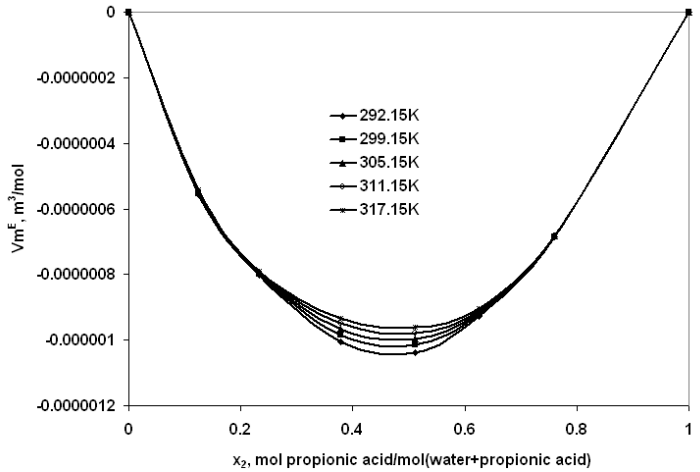


Fig. 1 – Variation of excess molar volume with molar fraction of propionic acid in water at different temperatures.

The excess molar volume is negative over the entire composition range and it decreases with increasing temperature. The results are consistent with what other researchers (Estrada-Baltazar *et al.*, 2003), have reported for this binary system, but at other temperature values, within the 283-323K range. Fig. 2 also shows the experimental values of the refractive index at different temperatures for the propionic acid-water binary system. We notice that it increases with the increase of the molar fraction of propionic acid and decreases as the temperature increases.

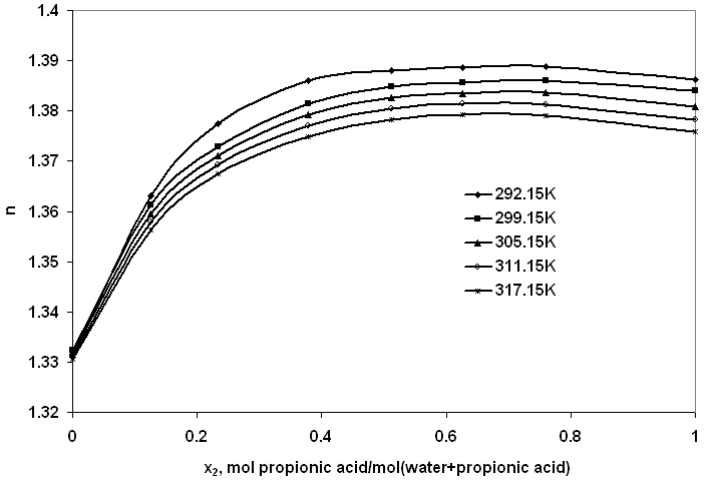


Fig. 2 – Variation of refractive index with molar fraction of propionic acid in water at different temperatures.

Considering the fact that the refractive index can be determined more easily, and also with a lower consumption of substances than the density, in this paper, the excess molar volume was correlated through statistical processing of experimental data by using the SigmaPlot 11.0 software, with the refractive index, normalized temperature and composition of the liquid mixture:

$$Vm^E = A_0+A_2X_2 +A_3(T/298.15)+A_4n \quad (3)$$

The standard deviation was calculated to evaluate the performance of the model given by Eq. (3), with the following relation:

$$\delta = \sqrt{\sum_{i=1}^{k}\left[(P^E)_{exp} - (P^E)_{model}\right]^2/(n-p)} \quad (4)$$

where: n represents the number of experimental data, and p the number of parameters.

Table 1 shows the coefficients in the model given by Eq. (3) and the standard deviation. Fig. 3 compares the experimental values for Vm^E with those calculated with model 3. It is found that they fall within a confidence interval of ±14%.

In order to show that models of the type given by Eq. (1) can also be used to predict other properties, such as excess surface tension and excess viscosity, experimental data from literature (Gomez-Diaz *et al.*, 2003) for the ternary system 2,2,4-trimethylpentane (isooctane) + cyclohexane + n-decane were processed. The excess thermodynamic quantities were calculated: the excess molar volume with Eq. (2), the excess surface tension with Eq. (5) and the excess viscosity with Eq. (6) starting from the experimental values of density, viscosity and surface tension over a wide range of composition variation and temperatures of 308.15, 313.15, 318.15 and 323.15 K.

$$\eta^E = \eta - x_1\eta_1 - x_2\eta_2 - x_3\eta_3 \quad (5)$$

$$\sigma^E = \sigma - x_1\sigma_1 - x_2\sigma_2 - x_3\sigma_3 \quad (6)$$

where: x_1 – molar fraction of isooctane, x_2 – molar fraction of cyclohexane, x_3 – molar fraction of n-decane, η – viscosity of ternary mixture, σ – surface tension of ternary mixture, η_i – viscosity of pure compounds and σ_i – surface tension of pure compounds.

Fig. 4 shows the results obtained for the temperature of 308.15 K. For excess molar volume (Fig. 4*a*), there were found both positive and negative deviations and the trend is also maintained with increasing temperature, while greater deviations from the ideal behavior are being recorded. In the case of

excess viscosity (Fig. 4*b*), there were found negative deviations from the ideal behavior over the entire range of composition variation. As the temperature increases, the values of excess viscosity decrease. Fig. 4 also shows the variation of the excess surface tension (Fig. 4*c*) and of the refractive index (Fig. 4*d*) with the molar fractions of isooctane (x_1) and cyclohexane (x_2) for the temperature of 308.15 K.

Table 1
Coefficients in MLR Models and Standard Deviation Values

System/ Property	propionic acid-water / Vm^E, m^3/mol	isooctane-cyclohexane-n-decane / Vm^E, m^3/mol	isooctane-cyclohexane-n-decane /η^E, Pa*s	isooctane-cyclohexane - n-decane/σ^E, mN/m
A_0	$4.46\cdot10^{-5}$	$-2.73\cdot10^{-4}$	$-4.42\cdot10^{-4}$	-0.894
A_1	-	$2.67\cdot10^{-6}$	$-1.38\cdot10^{-5}$	1.047
A_2	$8.23\cdot10^{-7}$	$-2.04\cdot10^{-8}$	$-3.34\cdot10^{-5}$	-0.152
A_3	$-3.43\cdot10^{-6}$	$2.05\cdot10^{-5}$	$9.71\cdot10^{-5}$	-1.837
A_4	$-3.07\cdot10^{-5}$	$1.8\cdot10^{-4}$	$2.35\cdot10^{-4}$	2.894
δ	$5.25\cdot10^{-8}$	$1.168\cdot10^{-6}$	$1.360\cdot10^{-5}$	0.5266

The excess surface tension is positive over the entire composition range and it decreases with increasing temperature.

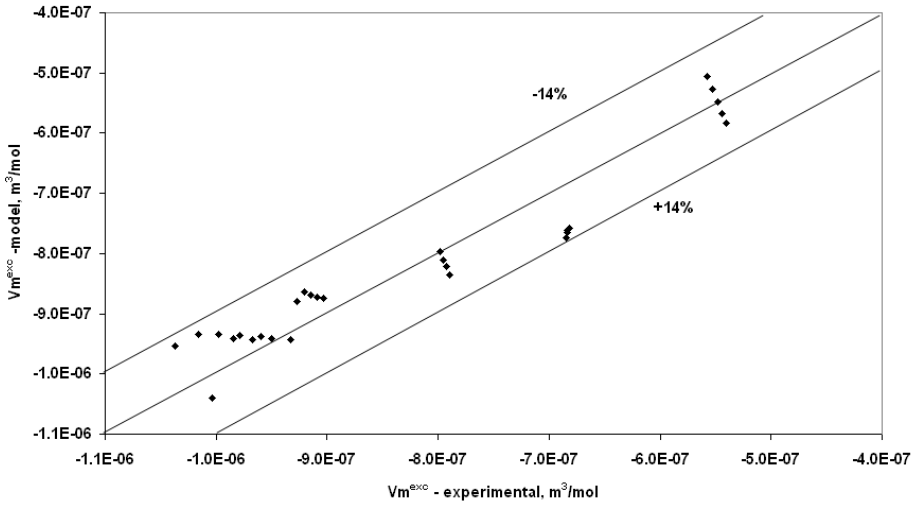
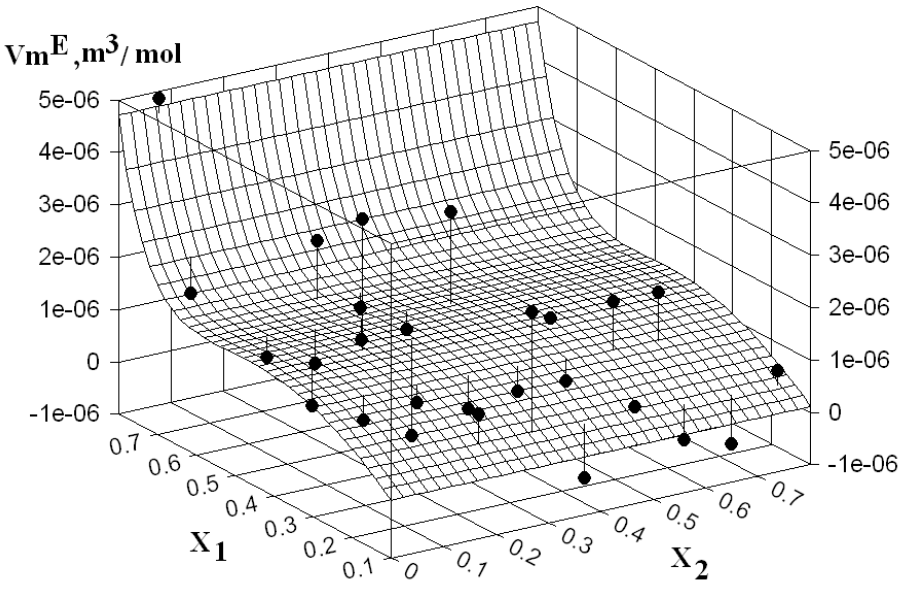
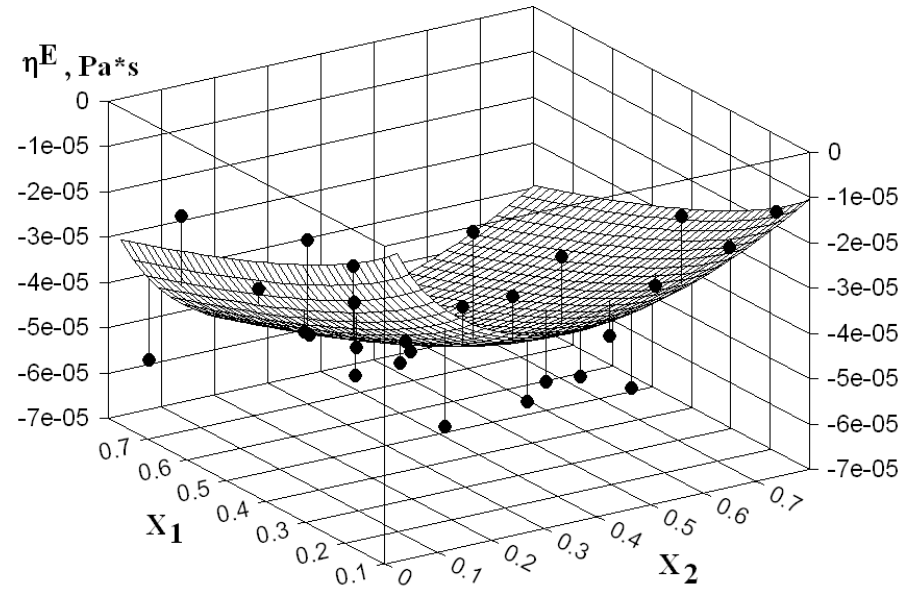


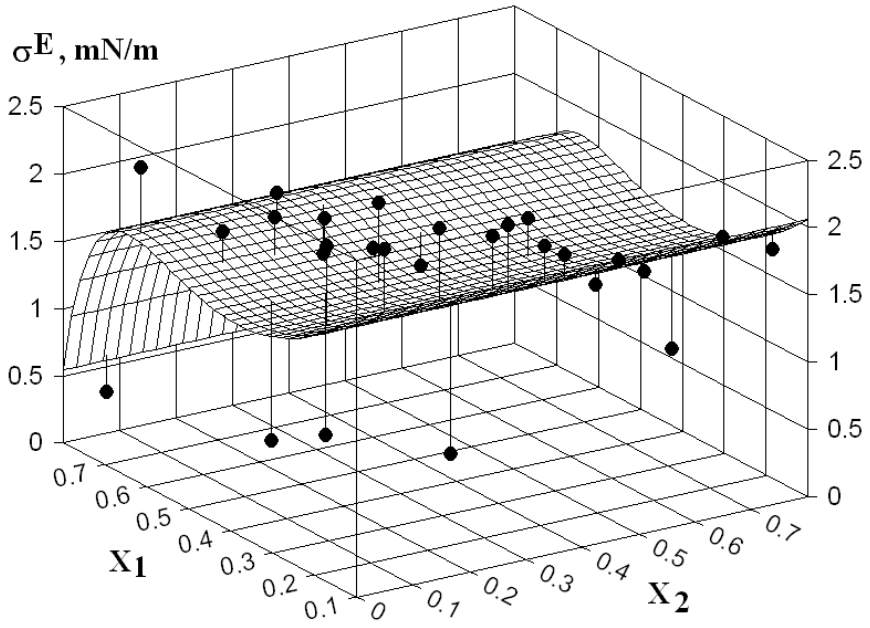
Fig. 3 – Comparison of experimental results with those calculated with the model given by Eq. (3).



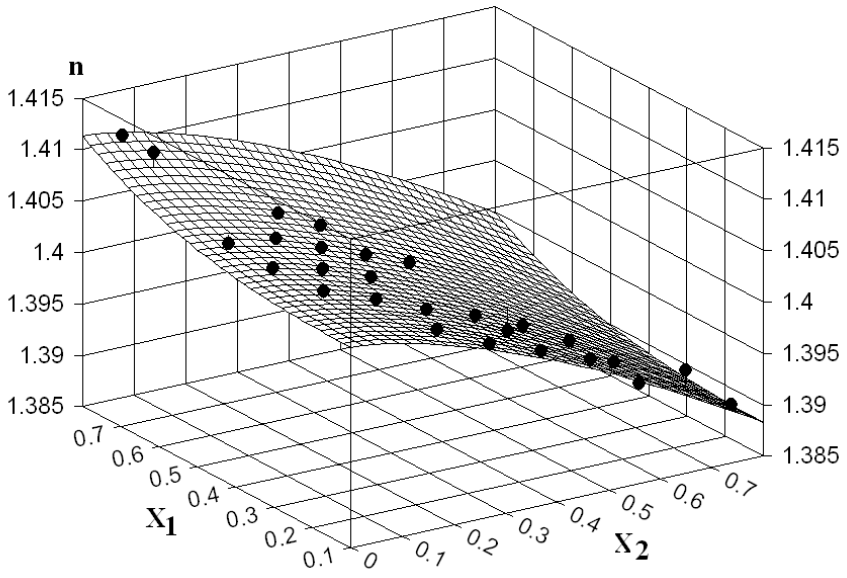
a – Excess molar volume.



b – Excess viscosity.



c – Excess surface tension.



d – Refractive index.

Fig. 4 – Variation of excess thermodynamic quantities and refractive index for the ternary system isooctane + cyclohexane + n-decane at a temperature of 308.15 K.

The excess thermodynamic quantities, obtained for the ternary system isooctane + cyclohexane + n-decane, based on experimental data from literature (Gomez-Diaz *et al.*, 2003), were also processed by applying the multiple linear regression (MLR) method along with using the SigmaPlot 11.0 software. There were created models which correlate the excess thermodynamic properties with the refractive index (n), molar fractions (X_1, X_2) and normalized temperature (T/298.15).

$$Vm^E = A_0 + A_1X_1 + A_2X_2 + A_3(T/298.15) + A_4n \quad (7)$$

$$\eta^E = A_0 + A_1X_1 + A_2X_2 + A_3(T/298.15) + A_4n \quad (8)$$

$$\sigma^E = A_0 + A_1X_1 + A_2X_2 + A_3(T/298.15) + A_4n \quad (9)$$

The A_i coefficients in the obtained models are presented in Table 1, together with the values of the standard deviations. Fig. 5, 6 and 7 show the comparative experimental values and those calculated with models (7), (8) and (9). It is found that in the case of all excess thermodynamic properties, the values fall within a confidence interval of ±25%. The performance of the obtained models is clearly influenced by the measurement accuracy of the equipment used for measuring the refractive index, density, viscosity and surface tension.

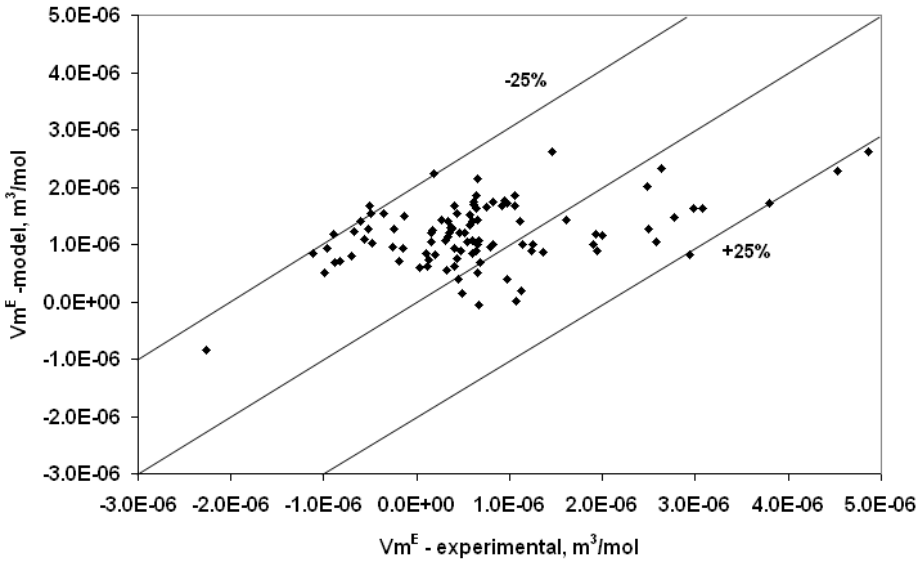


Fig. 5 – Comparison of experimental results with those calculated with the model given by Eq. (7).

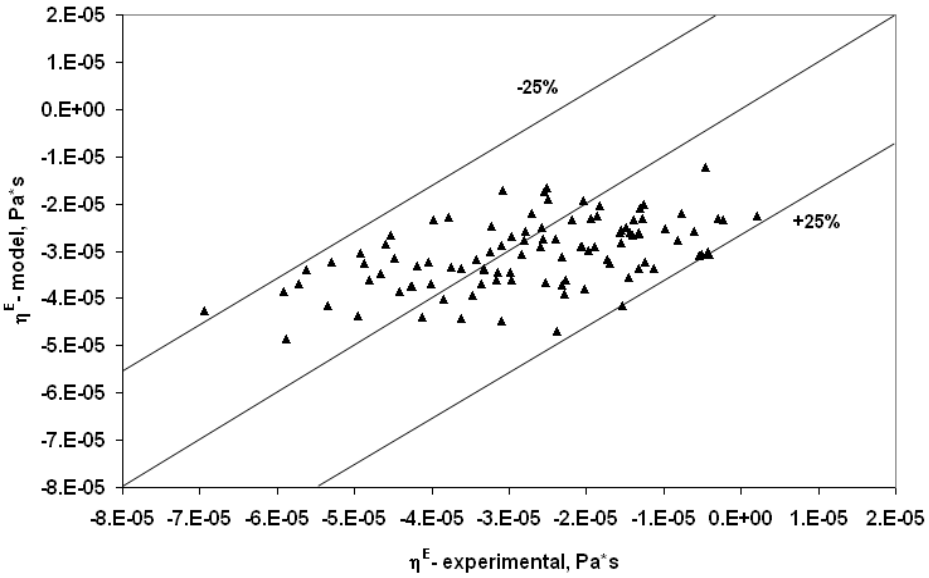


Fig. 6 – Comparison of experimental results with those calculated with the model given by Eq. (8).

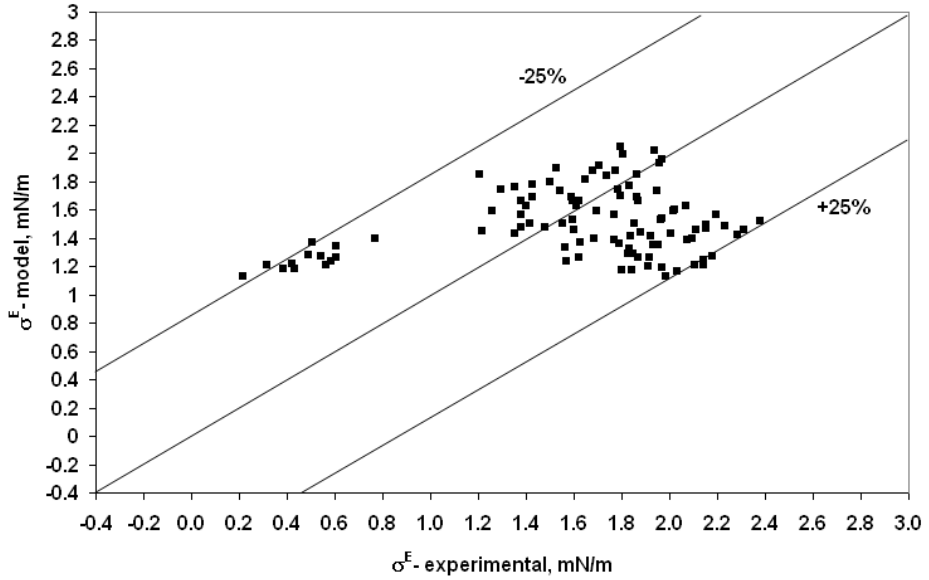


Fig. 7 – Comparison of experimental results with those calculated with the model given by Eq. (9).

4. Conclusions

Knowledge of the thermodynamic properties for different liquid mixtures is very important for the design and optimization of the installation operation in the chemical industry. Some properties, such as the refractive index, can be more easily determined by means of experiment and with a lower consumption of substances.

In this paper, we propose a series of mathematical models obtained through statistical processing of experimental data by using the multiple linear regression (MLR) method. These models correlate the excess thermodynamic properties P^E (excess molar volume, excess viscosity and excess surface tension) with the refractive index, normalized temperature and composition: $P^E=A_0+A_1X_1+A_2X_2+A_3(T/298.15)+A_4n$. The Vm^E prediction for the propionic acid+water binary system falls within a confidence interval of ±14%, while for the ternary system isooctane + cyclohexane + n-decane, the P^E prediction falls within a confidence interval of ±25%. It was noted that the performance of the obtained models is clearly influenced by the measurement accuracy of the equipment used for measuring the refractive index, density, viscosity and surface tension.

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MODELE DE REGRESIE LINIARĂ MULTIPLĂ (MLR) UTILIZATE PENTRU PREDICȚIA PROPRIETĂȚILOR TERMODINAMICE DE EXCES PE BAZA DETERMINĂRILOR EXPERIMENTALE ALE INDICELUI DE REFRACȚIE

(Rezumat)

În inginerie este foarte important să existe o bună cunoaștere a proprietăților termodinamice și de transport ale amestecurilor de lichide. Aceasta, deoarece sunt utilizate, în principal, pentru studiul interacțiunilor ce apar în amestecuri lichide multicomponente, dar și pentru proiectarea diferitelor instalații de separare prin distilare, fracționare, extracție cu solvenți și pentru elaborarea științifică a factorilor de risc pentru procesele de separare. Grupul nostru de cercetare a utilizat prelucrarea statistică a datelor experimentale cu metoda regresiei liniare multiple (MLR) pentru estimarea volumului molar de exces, plecând de la valorile experimentale ale indicelui de refracție pentru sisteme ternare. În această lucrare vom demonstra că acest tip de

prelucrare a datelor experimentale poate fi utilizat și pentru predicția altor proprietăți termodinamice de exces: vâscozitate de exces și tensiune superficială de exces (P^E). Pentru îndeplinirea acestui obiectiv vom utiliza atât date din literatura de specialitate cât și date experimentale obținute în laboratorul nostru cu privire la proprietățile termodinamice ale unor amestecuri de lichide. Modelele matematice obținute corelează proprietățile termodinamice de exces cu indicele de refracție, temperatura normalizată și compoziția amestecului de lichide: $P^E=A_0+A_1X_1+A_2X_2+A_3(T/298.15)+A_4n$, în care X_1 și X_2 sunt fracțiile molare, T este temperatura exprimată în Kelvin și n este indicele de refracție. Aceste modele sunt extrem de utile din punct de vedere practic. Indicele de refracție se determină cu ușurință, dar și cu o precizie destul de bună și consum mic de substanțe. Cu ajutorul acestor modele matematice se pot obține alte proprietăți cum ar fi densitatea, viscozitatea și tensiunea superficială care se măsoară experimental mai anevoios.