MLR MODELS USED TO PREDICT EXCESS THERMODYNAMIC PROPERTIES

Cătălin LISA[1]

Department of Chemical Engineering, Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi" Technical University of Iasi, 73 Prof. dr. docent Dimitrie Mangeron Street, Iasi, 700050, Romania

Abstract

This paper describes the determination of the refractive index (n) and of the density (ρ) of the following two ternary systems: water-methyl ethyl ketone-isopropyl alcohol and water-methyl ethyl ketone-acetone, in a composition range specific to diluted solutions, at various temperatures and atmospheric pressure. Based on these experimental data, it was calculated the excess refractive indices and the excess molar volumes, and it was established the type of deviation from ideal behavior. The refractive index may be experimentally determined rather easily, with good measuring accuracy and low substance consumption. The development of theoretical or empirical correlations between this parameter and other properties that are more difficult to measure, like density, is of interest for researchers. Therefore, in this paper it was employed the multiple linear regression (MLR) method to predict the excess molar volumes and implicitly the density of ternary mixtures, based on experimental determinations of the refraction index.

Key words: Density, Refractive index, Excess molar volumes, MLR model

1. Introduction

Methyl ethyl ketone, acetone, isopropyl alcohol are solvents commonly used in chemical industry, and, when released in the atmosphere, their emissions may be extremely dangerous for human health [1, 2]. Methyl ethyl ketone may cause digestive tract irritations, and the ingestion of considerable amounts may cause headache, nausea, vomiting, dizziness, and it may also have a narcotic effect. Acetone and isopropyl alcohol have adverse effects on the liver, kidney and respiratory system. In practice, the removal of these volatile organic compounds (VOCs) is achieved by means of scrubbers, which, by absorption in water, lead to the release of minimal amounts of pollutants in the atmosphere. The design of efficient facilities or the improvement of the performance of existing

[1] Corresponding author: Email address: clisa@ch.tuiasi.ro

ones require the development of databases of properties for the pollutant and water mixtures. There are in literature studies on the density and refractive index only for a series of binary systems [3-6] containing one or two components of the ones tackled in this research; nevertheless, many of them are quite old [7, 8] and were carried out using equipment the accuracy of which was rather poor as compared to the accuracy of the devices that are currently used to measure density and refractive index.

In this paper it was report the findings of the experiments conducted to determine the refractive index and the density of the following ternary mixtures: water-methyl ethyl ketone-isopropyl alcohol and water-methyl ethyl ketone-acetone, at very small pollutant concentrations in water and temperatures of 293.15, 300.15, and 307.15 K. The excess refractive index n_{exc} and excess molar volumes were also determined, the findings indicating the type of deviation from the ideal value of these ternary systems. Considering that the refractive index may be determined by experiments rather easily, with quite good measuring accuracy and low substance consumption, by means of the multiple linear regression (MLR) method, it was were able to predict the excess molar volumes and implicitly the density of the ternary mixtures based on the experimental determinations of the refractive index.

2. Experimental

The purity of the fluids involved in the experiments, methyl ethyl ketone, isopropyl alcohol and acetone, was p.a., and the solutions were prepared by weighing, which enabled us to estimate molar fractions with ±0.0001 accuracy.
The experimental determination of the refractive index was done using a Kruss refractometer (digital Abbe refractometer) with wavelength corresponding to Na (589.3 nm) and a Lauda E100 thermostat for maintaining a constant temperature with 0.1 °C accuracy. The equipment was calibrated using bidistilled water. This type of refractometer has a standard uncertainty of reading the refractive index of ±0.0002 [9].

An Anton Paar type DMA 4500 densitometer was used to measure the density of the ternary fluid mixtures prepared by my. Equipment calibration was checked using air (ρ=0.001085 g/cm^3, at 20°C temperature) and bidistilled water (ρ=0.998203 g/cm^3, at 20°C temperature). The density of the ternary mixtures was measured with a standard uncertainty of ±0.001 g/cm^3 [9].

Thermodynamic excess properties were modelled by means of statistical experimental data processing based on the multiple linear regression (MLR) method. Sigmaplot 11.0 is the software used for experimental data processing.

3. Results and discussions

Tables 1 and 2 show the values of the refractive index and of the density, determined by means of experiments on pure fluids, whereas tables 3, 4, 5 and 6 show the same values, but for ternary mixtures. Both the refractive index values and the density values decrease with temperature increase.

Table 1

Refractive index for pure fluids

Temperature K	Water	Methyl ethyl ketone	Isopropyl alcohol	Acetone
293.15	1.3337	1.3800	1.3780	1.3597
300.15	1.3320	1.3762	1.3744	1.3555
307.15	1.3312	1.3733	1.3719	1.3527

Table 2

Density of pure fluids [g/cm^3]

Temperature K	Water	Methyl ethyl ketone	Isopropyl alcohol	Acetone
293.15	0.9982	0.8080	0.7874	0.7907
300.15	0.9955	0.8005	0.7829	0.7833
307.15	0.9944	0.7796	0.7750	0.7765

Table 3

Refractive index of ternary water (1)-methyl ethyl ketone (2)-isopropyl alcohol (3) mixtures

X_2	X_3	293.15	300.15	307.15
0.0097	0.0099	1.3394	1.3375	1.3372
0.0997	0.0298	1.3451	1.3427	1.3417
0.0099	0.0503	1.3502	1.3473	1.3461
0.0095	0.0689	1.3540	1.3516	1.3505
0.0293	0.0292	1.3506	1.3475	1.3468
0.0293	0.0500	1.3547	1.3518	1.3499
0.0288	0.0667	1.3747	1.3541	1.3528
0.0490	0.0480	1.3575	1.3556	1.3541
0.0496	0.0315	1.3552	1.3525	1.3522
0.0497	0.0684	1.3603	1.3576	1.3563

Table 4

Refractive index of ternary water (1)-methyl ethyl ketone (2)-acetone (3) mixtures

X_2	X_3	293.15	300.15	307.15
0.0101	0.0098	1.3392	1.3371	1.3361
0.0098	0.0294	1.3432	1.3410	1.3386
0.0100	0.0441	1.3446	1.3438	1.3426
0.0097	0.0648	1.3491	1.3473	1.3465
0.0278	0.0350	1.3489	1.3472	1.3458
0.0309	0.0505	1.3523	1.3492	1.3479
0.0296	0.0695	1.3536	1.3519	1.3498
0.0325	0.0497	1.3626	1.3496	1.3483
0.0492	0.0295	1.3646	1.3505	1.3496
0.0495	0.0662	1.3578	1.3542	1.3532

Table 5

Density of ternary water (1)-methyl ethyl ketone (2)-isopropyl alcohol (3) mixtures [g/cm^3]

X_2	X_3	293.15	300.15	307.15
0.0097	0.0099	0.9885	0.9866	0.9841
0.0997	0.0298	0.9802	0.9777	0.9746
0.0099	0.0503	0.9729	0.9696	0.9662
0.0095	0.0689	0.9663	0.9622	0.9580
0.0293	0.0292	0.9735	0.9702	0.9665
0.0293	0.0500	0.9656	0.9618	0.9577
0.0288	0.0667	0.9574	0.9565	0.9516
0.0490	0.0480	0.9582	0.9538	0.9493
0.0496	0.0315	0.9650	0.9607	0.9567
0.0497	0.0684	0.9498	0.9456	0.9404

Table 6.

Density of ternary water (1)-methyl ethyl ketone (2)-acetone (3) mixtures [g/cm^3]

X_2	X_3	293.15	300.15	307.15
0.0101	0.0098	0.9895	0.9873	0.9845
0.0098	0.0294	0.9827	0.9799	0.9767
0.0100	0.0441	0.9776	0.9745	0.9710
0.0097	0.0648	0.9698	0.9676	0.9637
0.0278	0.0350	0.9738	0.9705	0.9568
0.0309	0.0505	0.9679	0.9640	0.9595
0.0296	0.0695	0.9622	0.9579	0.9541
0.0325	0.0497	0.9673	0.9636	0.9590
0.0492	0.0295	0.9679	0.9640	0.9596
0.0495	0.0662	0.9531	0.9511	0.9457

The deviations from ideal behaviour may be accounted for by the quantity variation occurring during the mixing and may be determined by the excess molar volumes (1) and by the notion of excess refractive index (n_{exc}), defined by the following ratio (2):

$$V_{exc} = X_1 M_1 \left(\frac{1}{\rho} - \frac{1}{\rho_1} \right) + X_2 M_2 \left(\frac{1}{\rho} - \frac{1}{\rho_2} \right) + X_3 M_3 \left(\frac{1}{\rho} - \frac{1}{\rho_3} \right) \quad (1)$$

$$n_{exc} = n - X_1 \cdot n_1 - X_2 \cdot n_2 - X_3 \cdot n_3 \quad (2)$$

where M_i is the molar mass of each solution component, ρ is the density of ternary mixtures, ρ_i is the density of components in pure state, n is the refractive index of ternary solutions, and n_i is the refractive index of pure compounds and X_i the molar fractions.

The values of the excess values calculated for the two ternary systems at 293.15, 300.15 and 307.15 K temperatures are shown in tables 7, 8, 9 and 10.

Table 7

Excess refractive index of ternary water (1)-methyl ethyl ketone (2)-isopropyl alcohol (3) mixtures

X_2	X_3	293.15	300.15	307.15
0.0097	0.0099	0.00481	0.00465	0.00519
0.0997	0.0298	0.00546	0.00503	0.00509
0.0099	0.0503	0.01381	0.01273	0.01244
0.0095	0.0689	0.01681	0.01626	0.01610
0.0293	0.0292	0.01425	0.01297	0.01318
0.0293	0.0500	0.01743	0.01638	0.01543
0.0288	0.0667	0.03671	0.01800	0.01767
0.0490	0.0480	0.01940	0.01940	0.01888
0.0496	0.0315	0.01781	0.01697	0.01763
0.0497	0.0684	0.02127	0.02050	0.02022

Table 8

Excess refractive index of ternary water (1)-methyl ethyl ketone (2)-acetone (3) mixtures

X_2	X_3	293.15	300.15	307.15
0.0101	0.0098	0.00477	0.00442	0.00426
0.0098	0.0294	0.00828	0.00787	0.00636
0.0100	0.0441	0.00929	0.01032	0.01003
0.0097	0.0648	0.01326	0.01335	0.01350
0.0278	0.0350	0.01299	0.01314	0.01268
0.0309	0.0505	0.01585	0.01464	0.01431
0.0296	0.0695	0.01671	0.01695	0.01586
0.0325	0.0497	0.02609	0.01499	0.01466
0.0492	0.0295	0.02784	0.01562	0.01569
0.0495	0.0662	0.02007	0.01844	0.01849

Table 9

Excess molar volumes of ternary water (1)-methyl ethyl ketone (2)-isopropyl alcohol (3) [cm^3/mol]

X_2	X_3	293.15	300.15	307.15
0.0097	0.0099	-0.13809	-0.16160	-0.16358
0.0997	0.0298	-1.72169	-1.79639	-1.99763
0.0099	0.0503	-0.44049	-0.44453	-0.45159
0.0095	0.0689	-0.56318	-0.55196	-0.54960
0.0293	0.0292	-0.43926	-0.44987	-0.48012
0.0293	0.0500	-0.56981	-0.57250	-0.60418
0.0288	0.0667	-0.60907	-0.68470	-0.70404
0.0490	0.0480	-0.65788	-0.65488	-0.71606
0.0496	0.0315	-0.59181	-0.58992	-0.65686
0.0497	0.0684	-0.74340	-0.74784	-0.80110

Table 10

Excess molar volumes of ternary water (1)-methyl ethyl ketone (2)-acetone (3) mixtures [cm^3/mol]

X_2	X_3	293.15	300.15	307.15
0.0101	0.0098	-0.15437	-0.17491	-0.17067
0.0098	0.0294	-0.30382	-0.32209	-0.31812
0.0100	0.0441	-0.41428	-0.43341	-0.42995
0.0097	0.0648	-0.53417	-0.58299	-0.57861
0.0278	0.0350	-0.48183	-0.50218	-0.30207
0.0309	0.0505	-0.61549	-0.63058	-0.65074
0.0296	0.0695	-0.72471	-0.73727	-0.77875
0.0325	0.0497	-0.61482	-0.63501	-0.65577
0.0492	0.0295	-0.60133	-0.61667	-0.66908
0.0495	0.0662	-0.78890	-0.82471	-0.86475

The experimental findings reveal that the ternary mixtures under survey show negative deviations from the ideal value and generally increase with temperature increase. Probably, the main effects are the breakage of the dipole-dipole interactions.

The dependence between the refractive index and the density of binary and ternary fluid mixtures is calculated by means of empirical equations of the type $f(n) = k \cdot \rho$, where the k parameter depends on the type of fluids and wavelength used to measure the refractive index [10]. There are numerous equations of this type, the most common of which are: Lorentz–Lorenz ($f(n) = (n^2 - 1)/(n^2 + 2)$), Dale–Gladstone ($f(n) = n - 1$), Eykman ($f(n) = (n^2 - 1)/(n + 0.4)$), Oster ($f(n) = (n^2 - 1) \cdot (2n^2 + 1)/n^2$), Arago–Biot ($f(n) = n$) and New-ton ($f(n) = n^2 - 1$) [9]. These functions may be used to calculate the excess molar volumes according to the ratio suggested by Angel Pineiro et al. [11], which may also be extended to ternary systems:

$$Vm_{exc} = \sum_i Vm_i \cdot X_i \left(f_i / f - 1 \right) \tag{3}$$

where $f = f(n)$ for ternary fluid mixtures; $f_i = f(n_i)$ for pure compounds and X_i is the molar fraction. The writing of these equations is rather difficult and the resulting mathematical expressions are sometimes rather complex. A previous research suggested an modify Eykman equation to correlate the excess molar volumes with the refractive index for the binary water-propionic acid system [12]. For the ternary system: ethylbenzene–octane–propylbenzene it was preferred an MLR model that correlated the excess molar volumes with molar fractions, normalized temperature and refractive index and the findings were better, more precisely the standard deviation was only 0.03 [9].

In this paper, for the two ternary systems under survey, it was built mathematical MLR models by statistical processing of experimental data by using the Sigma Plot 11.0 software. It was achieved multi-linear regressions between the excess molar volumes and molar fractions, i.e. temperature and refractive index.

For the ternary water (1)-methyl ethyl ketone (2)-isopropyl alcohol (3) system, the MLR model has the following expression:

$$Vm_{exc} = -26.141 - (15.637 \cdot X_2) - (8.889 \cdot X_3) + (0.00290 \cdot T) + (19.525 \cdot n) \tag{4}$$

and the mean percentage deviation it was determined was 15.38%.

For the ternary water (1)- methyl ethyl ketone (2)-acetone (3) system, the MLR model has the following expression:

$$Vm_{exc} = 1.200 - (6.956 \cdot X2) - (6.975 \cdot X3) - (0.00169 \cdot T) - (0.889 \cdot n) \tag{5}$$

and the mean percentage deviation it was determined was 4.09%.

The results are shown in Figures 1 and 2. As one may notice, the correlation coefficients are superior to 0.9.

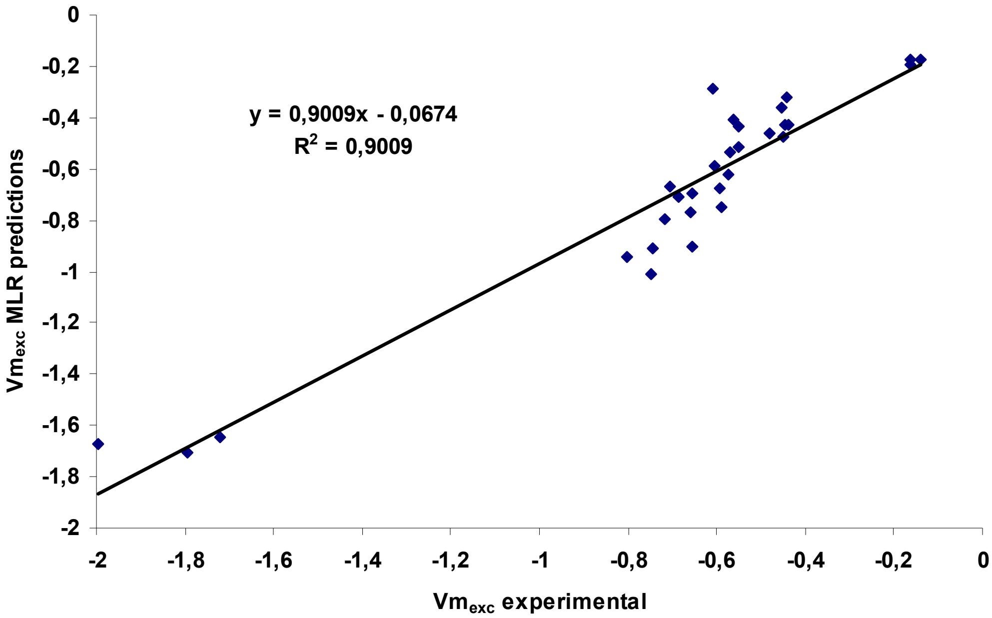

Fig. 1. Comparison of the experimental results to the ones calculated using the MLR model shown in equation 4 for: water - methyl ethyl ketone - isopropyl alcohol system

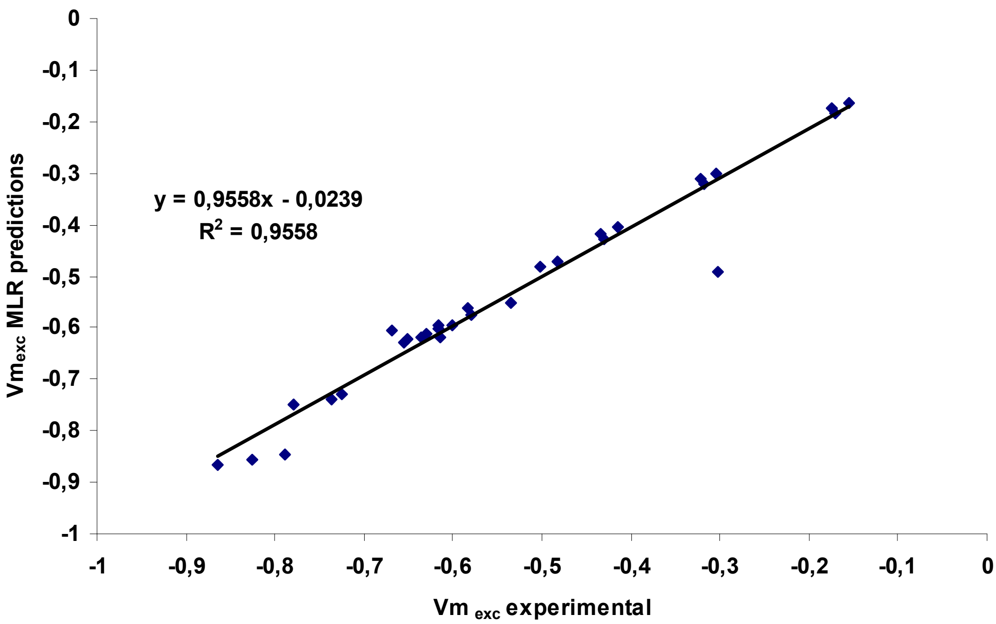

Fig. 2. Comparison of the experimental results to the ones calculated using the MLR model shown in equation 5 for: water- methyl ethyl ketone- acetone system

6. Conclusions

It was determined the refractive index (n) and the density (ρ) of the following ternary systems: water-methyl ethyl ketone-isopropyl alcohol and water-methyl ethyl ketone-acetone, in a composition range specific to diluted solutions, at the following temperatures: 293.15, 300.15 and 307.15 K, and atmospheric pressure. Based on these experimental data, it was calculated the excess refractive indices and the excess molar volumes, and it was established the type of deviation from ideal behavior. Bearing in mind that the refractive index may be experimentally determined much more easily, by means of the multiple linear regression (MLR) method it was were able to predict the excess molar volumes and implicitly the density of the ternary mixtures based on experimental determinations of the refractive index. The following models were suggested: $Vm_{exc} = a + b \cdot X_2 + c \cdot X_3 + d \cdot T + e \cdot n$. The correlation coefficients it was calculated were higher than 0.9.

Acknowledgment:
This work was supported by the "Program 4, Fundamental and Border Research, Exploratory Research Projects" financed by UEFISCDI, project No. 51/2017.

REFERENCES

[1] Rich J., Scheife R.T., Katz N., Caplan L.R., Isopropyl alcohol intoxication, *Archives of Neurology*, 47, (1990), 322-324.
[2] Mitran E., Callender T., Orha B., Dragnea P., Botezatu G., Neurotoxicity associated with occupational exposure to acetone, methyl ethyl ketone, and cyclohexanone., *Environmental Research*, 73, (1997), 181-188.
[3] Lisa G., Huhurez C., Matran R-M., Lisa C., Refractive indices of binary systems iso-propanol – water and iso-propanol – toluene, *Environmental Engineering and Management Journal*, 7, (2008), 309-312.
[4] Kyeong-Ho L., So-Jin P., Young-Yoon C., Density, refractive index and kinematic viscosity of MIPK, MEK and phosphonium-based ionic liquids and the excess and deviation properties of their binary systems, *Korean Journal of Chemical Engineering*, 34, (2017), 214-224.
[5] Almasi M., Iloukhani H., Densities, viscosities, and refractive indices of binary mixtures of methyl ethyl ketone + pentanol isomers at different temperatures, *Journal of Chemical & Engineering Data*, 55, (2010), 3918–3922.
[6] Mouli, J.C., Naidu, P.R., Choudary, N.V., Excess volumes, ultrasonic sound velocities, and isentropic compressibility's of 1-chlorobutane with isopropyl, isobutyl, and isopentyl alcohols, *Journal of Chemical & Engineering Data*, 31, (1986), 493-496.
[7] Kurtz Jr. S.S., Wikingsson A.E., Camin C.L., Thompson A.R., Refractive index and density of acetone-water solutions, *Journal of Chemical & Engineering Data*, 10, (1965), 330–334.
[8] Langdon W. M., Keyes D. B., Isopropyl alcohol-water system: density -composition data and pycnometric technique; plate factors in fractional distillation of isopropyl alcohol-water system, *Industrial and Engineering Chemistry*, 35, (1943), 459-469.
[9] Lisa C., Ungureanu M., Cosmatchi P.C., Bolat G., 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, *Thermochimica Acta*, 617, (2015), 76–82.
[10] Vuksanovic J.M., D.M. Bajic, G.R. Ivanis, Zivkovic E.M., Radovic I.R., Serbanovic S.P., Kijevcanin M.L.J, Prediction of excess molar volumes of selected binary mixtures from refractive index data, *Journal of the Serbian Chemical Society,* 79, (2014), 707–718.
[11] Pineiro A., Brocos P., Amigo A., Pintos M., Bravo R., Surface tensions and refractive indices of (tetrahydrofuran + n-alkanes) at T = 298.15 K, *The Journal of Chemical Thermodynamics*, 31, (1999), 931–942.
[12] Lisa G., Lisa C., Prediction of excess thermodynamic properties from experimental refractive index of binary mixtures 1. Water–propionic acid mixtures at 290.15, 300.15 and 310.15 K, *Revue Roumaine de Chimie*, 52, (2007), 647–653.