JOURNAL OF CHEMICAL & ENGINEERING DATA

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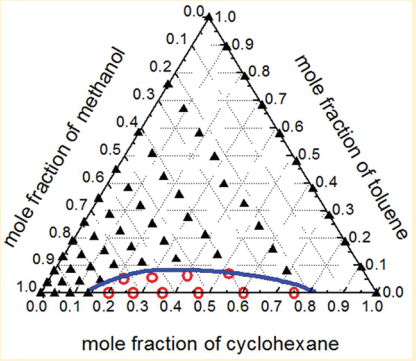
Measurements of Optical Properties in Binary and Ternary Mixtures Containing Cyclohexane, Toluene, and Methanol

Vitaliy Sechenyh, Jean Claude Legros, and Valentina Shevtsova*

Microgravity Research Center, CP-165/62, Université Libre de Bruxelles, 50, av. F.D. Roosevelt, B-1050 Brussels, Belgium

ABSTRACT: Refractive indices of ternary mixtures formed by cyclohexane, toluene, and methanol are reported over a wide range of mixture compositions. This mixture exhibits a miscibility gap and for a long time has attracted the attention of scientists from different areas of research. All measurements of refractive indices have been conducted at 298.15 K and atmospheric pressure using two light sources: one in the visible (λ = 670 nm) and the other in the infrared (λ = 925 nm) spectrum. The performance of the Lorentz−Lorenz mixing rule that is commonly used in modeling optical constants is examined. The concentration derivatives of the refractive index are an important parameter, as they are required for different experimental techniques and, particularly, for the measurements of the thermodiffusion coefficient. These derivatives have been determined from the experimental data on refractive indices. The mixture compositions, where these two wavelengths are applicable for the measurements of mass transport coefficients, are determined and discussed.



INTRODUCTION

The liquids appearing in nature and industrial applications are essentially multicomponent. The behavior of multicomponent systems is more complicated in comparison with pure fluids due to a complex interplay between heat and mass transfer processes. Specifically, the diffusive mass transport of a given component is induced not only by its compositional gradient (main or principal diffusion), but also by the compositional gradients of the other components (cross-diffusion) and the temperature gradient (thermodiffusion, also called the Soret effect).

Optical properties are the primary information needed to perform an investigation of mass transport processes in liquid mixtures or polymer solutions. The development of high-quality lasers has led to the emergence of a wide range of optical experimental methods that make use of refractive index variations. The variation of the refractive index with temperature and concentration is the basis for development of the experimental techniques aimed at studying convection and heat and mass transfer in transparent media.[1−3] By measuring the time evolution of the optical properties of a system one can obtain mass diffusion (thermodiffusion) coefficients. Among the existing methods for measurement of thermodiffusion (Soret) coefficients, modern optical techniques play an important role, such as the thermal lens technique,[4,5] beam deflection,[6,7] thermal diffusion forced Rayleigh scattering,[8,9] and optical digital interferometry.[10,11] They require accurate knowledge of refractive index derivatives with respect to concentration and temperature.

Nowadays, interest is focused on multicomponent mixtures. To extend the above-mentioned techniques to an N-component mixture, $N - 1$ beams of different wavelengths are required. Correspondingly, the wavelengths (or compositions) should be chosen in such a way that the matrix of the refractive index derivatives with respect to concentration (its elements are $a_{ij} = \partial n_{\lambda_i}/\partial c_j$, where $i, j = 1, N - 1$) would not be ill-conditioned.[12] There are only a few data on the refractive index and its compositional dependence for ternary mixtures containing dodecane, isobutylbenzene, 1,2,3,4-tetrahydronaphthalene, decane, and 1-methylnaphthalene at different wavelengths.[13,14] Looking forward to the investigation of mass transport coefficients in ternary mixtures, we examine optical properties at two different wavelengths: red (λ = 670 nm) and infrared (λ = 925 nm). The variations of concentration in these mixtures are expected to be very small, and so it is very important to have accurate information not only on the refractive indices n_λ but also on their derivatives, the so-called "contrast factors", that is, $\partial n_{\lambda_i}/\partial c_j$, where $i, j = 1$ or 2.

The first wavelength, visible light (λ = 670 nm), is often used in laboratory experiments, and the selection of the second one (λ = 925 nm) is related to the existence of this light source on the ISS (International Space Station) inside the SODI (Selectable Optical Diagnostics Instrument) instrument. Measurements of the mass transport coefficients on the ISS are planned by ESA (European Space Agency). A detailed description of the SODI instrument was published recently.[15] On the one hand the measurements at these wavelengths are necessary for the microgravity experiment preparation as available literature data are generally given for the D line of sodium (λ = 589.3 nm). On the other hand they will provide a valuable source of data for studying this scientifically attractive mixture.

The ternary liquid mixture cyclohexane−toluene−methanol exhibits a miscibility gap and for a long time attracts the attention of scientists from different areas of research.[16]

Received: August 23, 2011
Accepted: February 17, 2012
Published: February 27, 2012

   dx.doi.org/10.1021/je201277d | J. Chem. Eng. Data 2012, 57, 1036−1043

The concentration dependence of the mutual diffusion coefficients in the mixture has recently been measured[17,18] by the Taylor dispersion technique at 298.15 K. Previously the Soret coefficients were measured in a corresponding binary mixture of toluene−*n*-hexane[19−21] which does not contain a demixing zone.

EXPERIMENTAL SECTION

Materials and Measurements. Hereafter the binary liquid mixtures cyclohexane + toluene, cyclohexane + methanol, and toluene + methanol and ternary mixture cyclohexane + toluene + methanol are studied. Information about pure components of the mixtures was provided by the manufacturer and is shown in Table 1.

Table 1. Sample Information

chemical name	source	mole fraction purity	analysis method	molecular weight, g·mol^{-1}	CAS number
cyclohexane	Fisher Scientific	0.9999	GC[a]	84.16	110-82-7
toluene	Acros Organics	0.9985	GC	92.14	108-88-3
methanol	Fisher Scientific	0.9999	GC	32.04	67-56-1

[a]Gas−liquid chromatography.

For the refractive index measurements 10 g of each mixture was prepared from these high-quality products in its narrow-distributed concentration around the values of interest. An electronic balance manufactured by Sartorius with an accuracy of 10^{-2} mg/30 g was used. Before sample preparation pure ingredients were placed in smaller bottles to prevent evaporation and/or pollution of the basic solvents. Mixtures of the prescribed mass fraction were prepared directly on the weighing balance by adding the ingredients drop by drop with a Hamilton syringe. At the beginning 66 bottles of the investigated mixtures were filled with the less volatile component and carefully closed by a cover with Teflon sealing. The weight of each ingredient $m_{C_{i0}}$ was adjusted in such a way that it was in the range $m_{C_{i0}} \pm 10^{-3}$ g to generate concentrations C_{i0} very close to the values defined in the concentration matrix shown in Figure 1a. The weights of all components were measured with an accuracy of $5{\cdot}10^{-5}$ g. This procedure enables the calculation of derivatives in concentration space with high accuracy, for example, along the line with one really constant concentration.

The refractive index was measured with the Abbe refractometer manufactured by Bellingham and Stanley model 60/LR with a resolution of $1{\cdot}10^{-5}$ units of index of refraction. This refractometer does not include the light source. Two laser diodes, wavelengths 670 and 925 nm, were used for illumination, and their beams were alternatively directed into the refractometer through the optical window. As infrared light is invisible, the human eye was replaced by a high sensitivity camera. One crucial point for accurate measurements is the temperature stability. Constant temperature inside the instrument was maintained by water circulation through the thermostatically controlled high precision refrigerated circulating bath NESLAB RTE-300. The bath temperature was monitored to ± 0.01 K with a calibrated thermometer. Besides, all of the measurements were conducted in a room with controlled air temperature. The current temperature of measurement prism of refractometer was monitored using a built-in instrument with

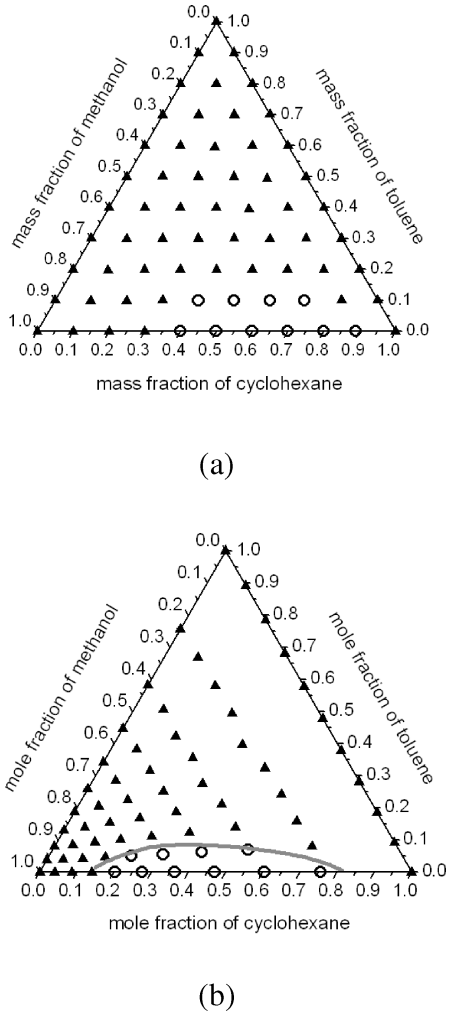


Figure 1. Concentration matrices. Triangles show the concentrations at which the refractive indices have been measured in the ternary mixture toluene + methanol + cyclohexane. Circles indicate the region with demixing at T = 298.15 K. The gray line (b) corresponds to the demixing gap data obtained by Nagata.[16] Triangles are given as (a) mass fraction and (b) molar fraction.

an uncertainty ± 0.1 K (according to manufacturer). The measurements are performed with uncertainties in mass fraction around ± 0.0001 and in the refractive index less than ± 0.00007.

Miscibility Gap and Sampling. For complete coverage of the mixture space, 36 ternary and 27 binary samples were prepared with 10 % sampling by mass fraction as shown in Figure 1a by dots. To mix components a gentle shaking was applied. In some samples we found demixing just after sample preparation. The demixing was determined by eye at T = 298.15 K and depicted by circles in Figure 1a. For a more accurate determination of a binodal boundary at T = 298.15 K the control samples were placed in a thermal bath, and mixing was checked once more. From the binary mixture methanol−cyclohexane the demixing gap occupies a large concentration range, $0.4 < C_{C_6H_{12}} < 0.9$. However in the concentration space for the ternary mixture this area is relatively small and leaves a large prospect for the selection of appropriate experimental points without demixing. Available literature data for demixing gap are given in molar fraction,[16−18] and for comparison our

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points are also shown in molar fraction in Figure 1b. The present results for the demixing gap are in an excellent agreement with literature data[16] shown by the gray line in Figure 1b.

RESULTS AND DISCUSSION

Refractive Index. To validate the accuracy of the experimental results, they should be compared with reliable literature data. Due to the lack of data at the wavelengths of interest we have made a comparison of the refractive index of the pure components with that at yellow light (λ = 589.3 nm) which is presented in Table 2. For the closest wavelengths, (λ = 589.3 nm and λ = 670 nm), the results are well comparable.

Table 2. Refractive Index and Density Data for Pure Liquids at T = 298.15 K

	refractive index			
	this work		literature	density
chemical name	λ = 925 nm	λ = 670 nm	λ = 589.3 nm	kg·m^{-3}
cyclohexane	1.41832	1.42253	1.42354[27]	773.89[27]
			1.42348[28]	773.65[28]
toluene	1.48176	1.48998	1.49413[29]	862.19[29]
			1.49432[24]	862.20[24]
methanol	1.32235	1.32603	1.32645[27]	786.64[27]
			1.32645[24]	786.60[24]

For validation of the results in the infrared spectrum the Cauchy dispersion relation[22] has been used:

$$n(\lambda) = n_\infty + \frac{A}{\lambda^2} \quad (1)$$

where two parameters (n_∞ and A) can be determined according to the measurements at different wavelengths. The analysis of the plots in the coordinates $[n(\lambda),(1/\lambda^2)]$ have shown that the points favorably lie around a straight line for all of the liquids.

Measurements were performed in 56 samples at temperature T = 298.15 K for the two different wavelengths λ = 670 nm and λ = 925 nm; 10 samples (six binary and four ternary) with demixing were not examined. The values of the measured indices are summarized in Table 3. On the basis of the measured refractive indices the fitting functions were constructed in the form $n_{1f} = n_f(C_1,C_2)$, $n_{2f} = n_f(C_2,C_3)$, $n_{3f} = n_f(C_1,C_3)$. The polynomial fit for $n_{1f}(C_1,C_2)$ was chosen as

$$n_{1f}(C_1, C_2) = \sum_{i,j=0}^{i,j=4} a_{ij} C_1^i C_2^j \quad (2)$$

where coefficients a_{ij} depend on the concentrations set and wavelength under consideration and they were sought by the nonlinear regression method. The polynomials for the other functions (n_{1f}, n_{2f}) were constructed in a similar way. On average

Table 3. Experimental Values of the Refractive Index for the Binary Liquid Mixtures Cyclohexane (1) + Toluene (2), Cyclohexane (1) + Methanol (3), Toluene (2) + Methanol (3), and Ternary Mixture Cyclohexane (1) + Toluene (2) + Methanol (3) at 298.15 K

			refractive index	
C_1	C_2	C_3	925 nm	670 nm
Cyclohexane (1) + Toluene (2)				
0.0996	0.9004	0.0000	1.47383	1.48158
0.2002	0.7998	0.0000	1.46618	1.47363
0.2995	0.7005	0.0000	1.45920	1.46616
0.4003	0.5997	0.0000	1.45229	1.45883
0.5004	0.4996	0.0000	1.44539	1.45162
0.6002	0.3998	0.0000	1.43956	1.44527
0.7000	0.3000	0.0000	1.43363	1.43903
0.8005	0.1995	0.0000	1.42825	1.43327
0.9001	0.0999	0.0000	1.42296	1.42768
Toluene (2) + Methanol (3)				
0.0000	0.1001	0.8999	1.33686	1.34089
0.0000	0.1994	0.8006	1.35152	1.35612
0.0000	0.3001	0.6999	1.36718	1.37219
0.0000	0.4000	0.6000	1.38279	1.38826
0.0000	0.4996	0.5004	1.39956	1.40560
0.0000	0.6000	0.4000	1.41564	1.42196
0.0000	0.6994	0.3006	1.43182	1.43865
0.0000	0.8001	0.1999	1.44951	1.45699
0.0000	0.8994	0.1006	1.46633	1.47418
Cyclohexane (1) + Methanol (3)				
0.1000	0.0000	0.9000	1.32811	1.33196
0.2004	0.0000	0.7996	1.33737	1.34128
0.2999	0.0000	0.7001	1.34602	1.34987
Cyclohexane (1) + Toluene (2) + Methanol (3)				
0.0987	0.1973	0.7040	1.35912	1.36380
0.0995	0.0991	0.8014	1.34393	1.34806
0.0997	0.2995	0.6008	1.37546	1.38034

			refractive index	
C_1	C_2	C_3	925 nm	670 nm
Cyclohexane (1) + Toluene (2) + Methanol (3)				
0.0997	0.6001	0.3002	1.42608	1.43269
0.0998	0.3999	0.5003	1.39150	1.39696
0.0999	0.5004	0.3997	1.40789	1.41378
0.0999	0.7999	0.1002	1.45901	1.46650
0.1002	0.7003	0.1995	1.44291	1.44992
0.1979	0.5955	0.2066	1.43272	1.43932
0.1995	0.4002	0.4003	1.40085	1.40649
0.1995	0.5002	0.3003	1.41746	1.42347
0.1997	0.1998	0.6005	1.36840	1.37314
0.2000	0.2998	0.5001	1.38443	1.38954
0.2003	0.0996	0.7001	1.35174	1.35621
0.2003	0.7002	0.0995	1.45092	1.45784
0.2996	0.2003	0.5001	1.37774	1.38258
0.2997	0.5001	0.2002	1.42682	1.43302
0.2998	0.4005	0.2997	1.41095	1.41670
0.2999	0.3000	0.4001	1.39409	1.39942
0.3002	0.1001	0.5997	1.36169	1.36609
0.3002	0.6004	0.0995	1.44422	1.45078
0.3940	0.3939	0.2121	1.41999	1.42565
0.3948	0.4937	0.1115	1.43610	1.44234
0.3992	0.3008	0.3000	1.40378	1.40894
0.4006	0.1996	0.3998	1.38763	1.39238
0.4998	0.2998	0.2005	1.41474	1.42022
0.5001	0.4002	0.0997	1.43287	1.43870
0.5007	0.1995	0.2998	1.39829	1.40330
0.5987	0.1993	0.2020	1.40839	1.41342
0.6006	0.3003	0.0991	1.42570	1.43129

dx.doi.org/10.1021/je201277d | J. Chem. Eng. Data 2012, 57, 1036−1043

the differences between the measured points and the fitting function at these points do not exceed 0.03 %, that is,

$$\frac{n(c_i) - n_f(c_i)}{n(c_i)} \cdot 100\,\% < 0.03\,\%$$

The residuals between the measured values and the fitting function are shown in Figure 2.

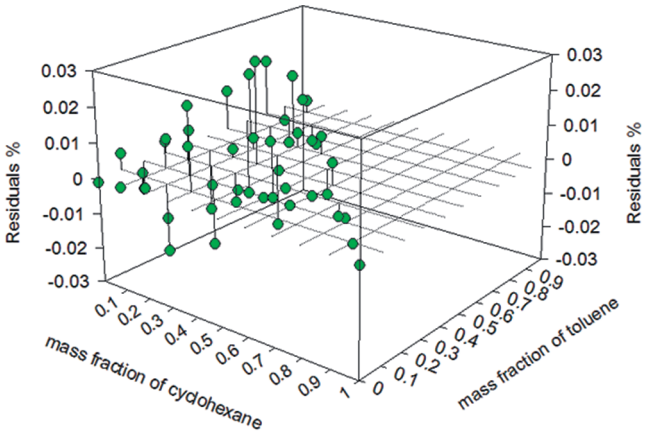

Figure 2. Residuals between the measured refractive indices and n_{1f} calculated by eq 3 (in %) for λ = 670 nm.

Choosing cyclohexane (C_1) and toluene (C_2) as independent concentrations in eq 2 the fitting function n_{1f} for λ = 670 nm is written as

$$\begin{aligned} n_{1f} = {} & -0.041731C_1^4 - 0.20227C_1^3C_2 + 0.043902C_1^3 \\ & - 0.35566C_1^2C_2^2 + 0.23932C_1^2C_2 + 0.023515C_1^2 \\ & - 0.25794C_1C_2^3 + 0.31308C_1C_2^2 - 0.06159C_1C_2 \\ & + 0.071329C_1 - 0.0582C_2^4 + 0.098214C_2^3 \\ & - 0.034384C_2^2 + 0.15905C_2 + 1.3254 \end{aligned} \quad (3)$$

and for λ = 925 nm

$$\begin{aligned} n_{1f} = {} & -0.035242C_1^4 - 0.16825C_1^3C_2 + 0.028464C_1^3 \\ & - 0.31542C_1^2C_2^2 + 0.19082C_1^2C_2 + 0.035051C_1^2 \\ & - 0.2438C_1C_2^3 + 0.28882C_1C_2^2 - 0.047356C_1C_2 \\ & + 0.068149C_1 - 0.052687C_2^4 + 0.088646C_2^3 \\ & - 0.029677C_2^2 + 0.15383C_2 + 1.3218 \end{aligned} \quad (4)$$

Using these functions n_{if} the variation of refractive index in the whole domain of the mass fractions is presented in triangles in Figure 3a for λ = 670 nm and in Figure 3b for λ = 925 nm. The shaded area corresponds to the demixing gap which is slightly increased as the sampling rate 10 % may lead to uncertainty in the refractive index in the vicinity of binodal boundary. The largest values on n are observed in a toluene-rich mixture with small additions of methanol, while the smallest values are observed in methanol-rich area.

Figure 4 demonstrates the comparative compositional behavior of the measured refractive indices with the literature data for two binary mixtures: (a) cyclohexane + toluene[23] (b) and methanol + toluene[24] at different wavelengths. The symbols correspond to measured points, and the continuous curves

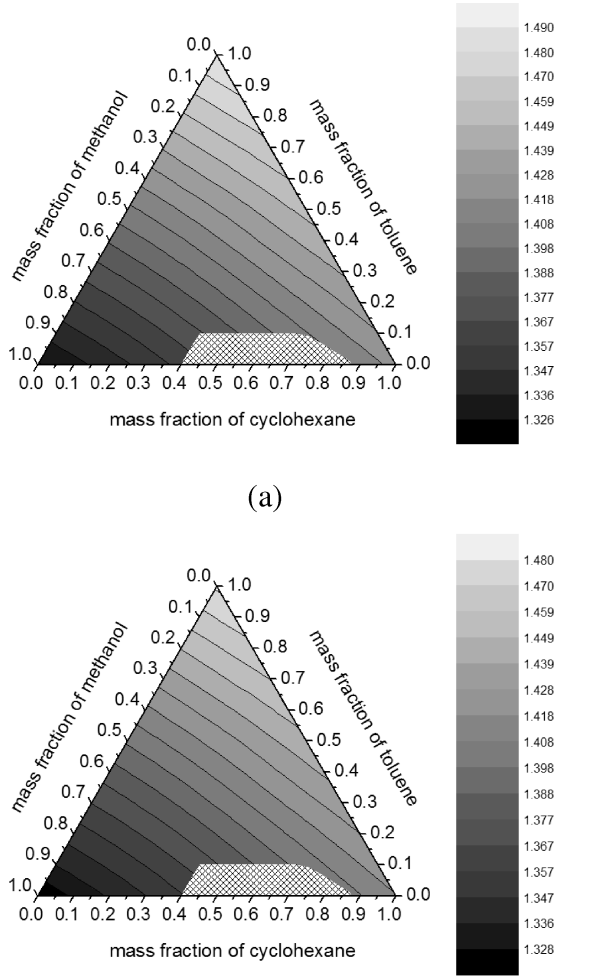

Figure 3. Refractive indices in the complete domain of mass fractions for the ternary mixture cyclohexane + toluene + methanol. (a) λ = 670 nm; (b) λ = 925 nm.

indicate the trend line. The refractive index behavior of the binary mixtures cyclohexane + toluene and methanol + toluene for the wavelengths λ_1 = 925 nm, λ_2 = 670 nm, and λ_2 = 589.3 nm is very complicated. Figure 4 shows the absence of similarity of the curve shapes in the wavelength range from (589.3 to 925) nm.

From the first look the surface of the refractive indices in Figure 3 resembles a linear function typical for thermodynamically ideal mixtures. However the slope of the lines is not constant, and lines themselves are slightly bended. The surface of the refractive index was calculated using the Lorentz–Lorenz rule:[25]

$$\text{Lorentz–Lorenz(L–L)}: \frac{n^2 - 1}{n^2 + 2} = \sum_{i=1}^{k} \left(\frac{n_i^2 - 1}{n_i^2 + 2} \right) \cdot \phi_i \quad (5)$$

$$\phi_i = \frac{x_i V_i}{\sum_{i=1}^{k} x_i V_i} \quad (6)$$

where ϕ_i is the volume fraction of the pure component i; x_i is the mole fraction of component i; V_i is the molar volume of the

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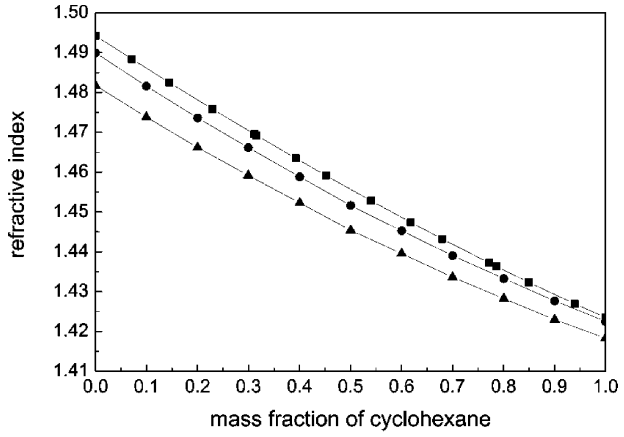
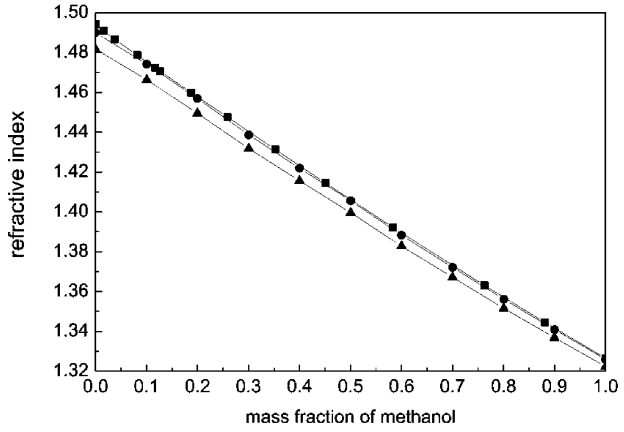


(a)



(b)

Figure 4. Comparison of the behavior of the refractive indices with composition at different wavelengths for two binary mixtures: (a) cyclohexane + toluene[23] and (b) methanol + toluene.[24] The data for the wavelengths λ_1 = 925 nm and λ_2 = 670 nm are measured in this work and for λ_3 = 589.3 nm are taken from the literature; triangles, circles, and cubes correspond to λ_1 = 925 nm, λ_2 = 670 nm, and λ_3 = 589.3 nm, respectively.

mixture component *i*. The molar volume values of the pure liquids V_i were calculated using the density data shown in Table 2 as there are no experimental densities available. The difference between the measured and the calculated refractive indices is shown in Figure 5. The Lorentz–Lorenz equation relates the macroscopic refractive index to the molecular refractivity and the volume density of particles. Thus the deviation from ideal behavior in Figure 5 represents entirely volumetric properties. The best agreement is observed for the ternary mixture with a low content of cyclohexane. The maximal difference is less than 0.4 %. It is better than for the recently measured aqueous ternary solutions where the difference attains 0.9 %.[26]

Derivative of Refractive Index. In this section we analyze the behavior of contrast factors for different wavelengths which are calculated as the derivatives of analytical functions n_{if} for the ternary mixture cyclohexane (1) + toluene (2) + methanol (3) given by eq 2. Figure 6 presents the surface of the derivative $(\partial n/\partial C_1)_{C_2}$ for λ = 670 nm (a) and λ = 925 nm (b). The appearance and amplitude of contrast factors are similar for

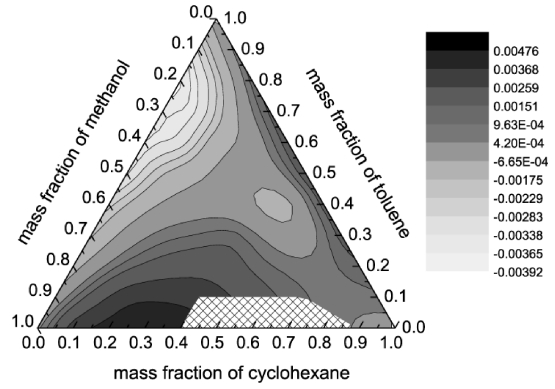
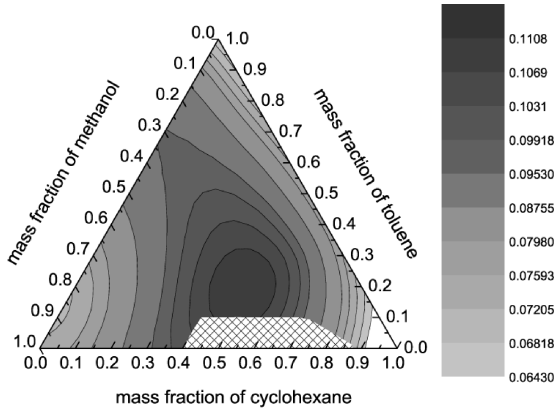
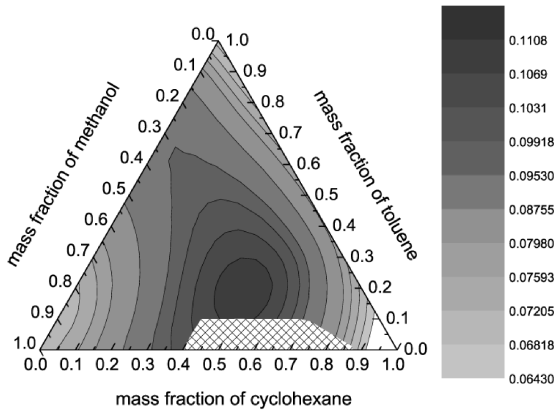


Figure 5. Difference between the measured values of refractive index for the ternary mixture cyclohexane + toluene + methanol and values calculated by the Lorentz–Lorenz equation eq 5 at λ = 670 nm.



(a)



(b)

Figure 6. Surface of the derivatives $(\partial n/\partial C_1)_{C_2}$. Plots are given for the wavelengths (a) λ = 670 nm and (b) λ = 925 nm.

both wavelengths. However the central area with the largest values of derivatives is wider in the case of λ = 670 nm. The shaded area in Figure 6 to 8 corresponds to the demixing region.

Figure 7 presents the surface of another derivative $(\partial n/\partial C_2)_{C_1}$ for λ = 670 nm (a) and λ = 925 nm (b). Its appearance, amplitude, and maximal values are very different from those in Figure 6.

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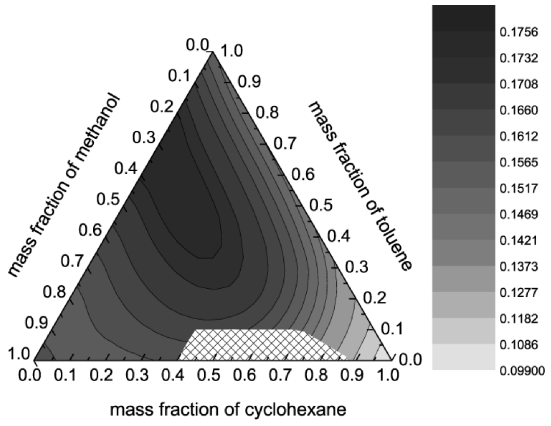
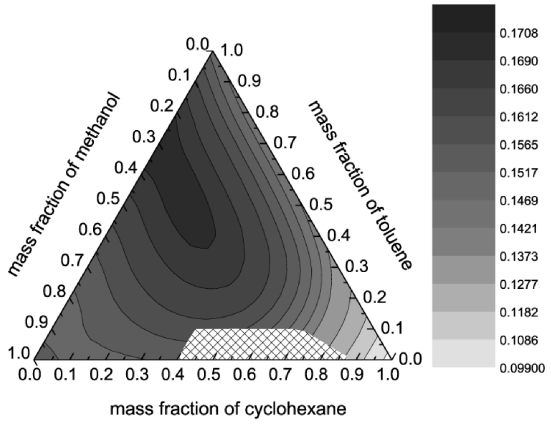
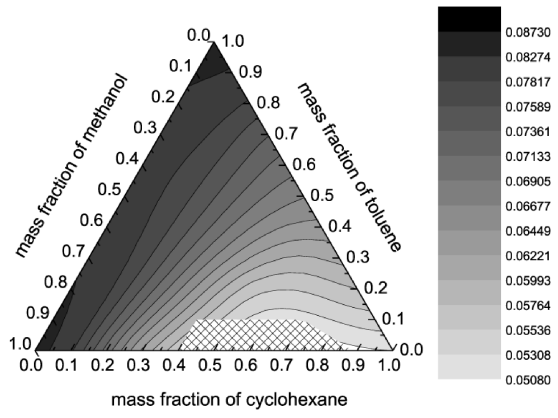


(a)

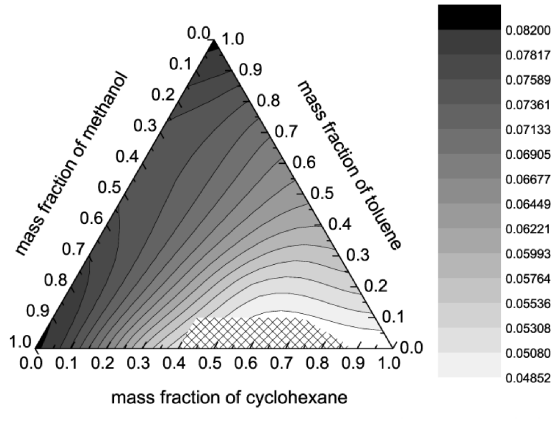


(b)

Figure 7. Surface of derivatives $(\partial n/\partial C_2)_{C_1}$. Plots are given for the wavelength values (a) λ = 670 nm and (b) λ = 925 nm.



(a)



(b)

Figure 8. Surface of derivatives $(\partial n/\partial C_2)_{C_3}$. Plots are given for the wavelength values (a) λ = 670 nm and (b) λ = 925 nm.

The region with the largest contrast factor values is located when the content of methanol is $0.2 < C_{\text{methanol}} < 0.4$ and that of toluene is more than 30 %. Although the amplitude in Figure 7 is only 20 % larger than in Figure 6, the maximal value of derivative of $(\partial n/\partial C_2)_{C_1}$ in 1.6 times larger than $(\partial n/\partial C_1)_{C_2}$. The only common point is that the smallest values of both derivatives take place in a cyclohexane-rich corner.

Figure 8 presents the space of the derivative $(\partial n/\partial C_2)_{C_3}$ for λ = 670 nm (a) and λ = 925 nm (b) which has also a different configuration. The derivative surface is rather smooth, and the contrast factor gradually increases with the increase of toluene concentration. The values of the derivative are larger for λ = 670 nm, but the amplitude is similar in both wavelengths and is about 0.036.

The analysis of all of the derivatives of the analytical functions n_{if} shown in Figure 6 to 8 indicate that the refractive index behavior of the ternary mixture does not correspond to an ideal liquid mixture. In the case of an ideal behavior the curves in the same plot for the different levels of the derivative would be parallel.

The application of the optical techniques to measurements of the mass transport coefficients in ternary mixtures is using the matrix A composed by derivatives at different wavelengths λ_1 and λ_2 and its inverse matrix (A^{-1}):[12]

$$A = \begin{pmatrix} \dfrac{\partial n_1}{\partial C_1} & \dfrac{\partial n_1}{\partial C_2} \\ \dfrac{\partial n_2}{\partial C_1} & \dfrac{\partial n_2}{\partial C_2} \end{pmatrix} \tag{7}$$

The dependences of the derivatives $\partial n_\lambda/\partial C_i$ on the wavelength could be weak, and they impose a serious obstacle to the practical implementation of the optical techniques, because the matrix can be ill-conditioned. Obviously, before carrying out the measurements, it is necessary to estimate the possible loss of precision by means of the analysis of the matrix A which is measured in advance. For this reason the concept of a condition number K was suggested.[12] On the basis of this concept the full surface of condition numbers using derivatives $(\partial n/\partial C_1)_{C_2}$ for the ternary mixture cyclohexane + toluene + methanol was calculated (see Figure 9). The smaller is the condition number K the smaller is the loss of accuracy due to condition of the matrix A. For planning an experiment, one can calculate the condition number for different pairs of light wavelengths and for different values of (C_1,C_2), searching for the minimum of K.

dx.doi.org/10.1021/je201277d | J. Chem. Eng. Data 2012, 57, 1036–1043

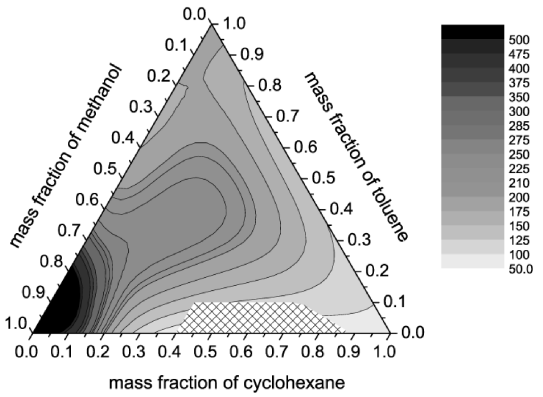


Figure 9. Condition number values for the derivative $(\partial n/\partial C_1)_{C_2}$.

Figure 9 demonstrates that the selected wavelengths λ_1 = 670 nm and λ_2 = 925 nm fit well for a large range of compositions for the cyclohexane + toluene + methanol mixture where condition number is at least $K < 200$; this concentration range is shown using light area. However, the most favorable region for the use of these wavelengths is the concentration space with a low content of methanol less than 15 %.

■ CONCLUSIONS

We reported extensive measurements of refractive indices in ternary mixtures of cyclohexane−toluene−methanol at two different wavelengths, λ = 670 nm and λ = 925 nm. The refractive index attains a maximum at the toluene-rich area and minimum at a methanol-rich area. We have analyzed the use of the Lorentz−Lorenz mixing rule for the evaluation of the refractive indices for this ternary system. We have demonstrated that the refractive indices provided by the Lorentz−Lorenz rule reproduce the measured values with a maximal relative error of about 0.4 %. However, the comparison between the experimental and calculated derivatives of refractive indices (contrast factors) shows unsatisfactory results within the whole range of mixture compositions. We have identified the region of compositions in the ternary mixture cyclohexane−toluene−methanol where the selected wavelengths for laser diodes installed inside the SODI instrument on the ISS for diffusion experiments fit the best.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: vshev@ulb.ac.be.

Funding

This work is supported by the PRODEX programme of the Belgian Federal Science Policy Office and ESA (European Space Agency).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are indebted to V. Yasnou (ULB, Brussels) for help in conducting the experiments and Dr. A. Mialdun (ULB, Brussels) for useful discussions.

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