

## Changes of refractive indices in ternary mixtures containing chlorobenzene + *n*-hexane + (*n*-heptane or *n*-octane) at 298.15 K

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(Received 11 August, revised 5 December 2003)

**Abstract:** The refractive indices of ternary mixtures of chlorobenzene + *n*-hexane + (*n*-heptane or *n*-octane) have been measured at 298.15 K and at atmospheric pressure over the whole composition diagram. Parameters of polynomial equations which represent the composition dependence of physical and derived properties are gathered. The experimental refractive indices and the ternary derived properties are compared with the data obtained using several predictive semi-empirical models. The use of the Soave–Redlich–Kwong (SRK) and the Peng–Robinson (PR) cubic equations of state with the Van der Waals one-fluid mixing rule, which incorporate different combining rules to predict refractive indices on mixing, are tested against the measured results, good agreement being obtained.

**Keywords:** refractive index, chlorobenzene, alkanes, cubic equation of state.

### INTRODUCTION

The chemical industry may be able to design processes with waste minimization, and dispose of generated chemical waste in a manner consistent with legal requirements in force. In order to design an effective remediation strategy for the contamination of air, ground and surface water with halogenated aromatic and hydrocarbon compounds of different nature, the physical, chemical and biodegradation potential of each contaminant must be researched. Nevertheless, contamination with these kinds of chemicals of different nature is perhaps one of the most serious problems facing mankind today. Although the properties of pure compounds are usually available in accessible literature, the availability of mixing properties are limited. Due to this fact, over the last few years we have conducted systematic studies on the thermodynamic properties of mixtures related to industrial processes (modified rectification, liquid extraction, etc.),<sup>1,2</sup> food technology<sup>3,4</sup> and pharmacological mixtures.<sup>5,6</sup>

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The purpose of this study was to continue our work in the field of thermochemical properties in order to obtain a better understanding of mixing trends of chemicals related to contamination with chlorobenzene and hydrocarbons.<sup>7,8</sup> In this way, the first step is the thermodynamic characterization of the mixtures (physical properties, vapor-liquid equilibria, liquid-liquid equilibria, *etc.*) involved in separation problems and then an engineering study to evaluate, optimize and design adequate unit operations. From a remediation standpoint, chlorobenzene is moderately soluble in water, exhibiting a strong tendency to vaporize to ambient air at moderate air temperatures but these characteristics are strongly dependent on the kind of solvents and relative concentration on mixing.

In this paper new measurements of refractive indices of ternary mixtures of chlorobenzene + *n*-hexane + (*n*-heptane or *n*-octane) that were measured at 298.15 K and atmospheric pressure over the whole composition diagram, as well as the corresponding derived changes of refractive index on mixing, are presented. Parameters of polynomial equations which represent the molar fraction dependence of physical, and derived properties are gathered. Different procedures for estimating the derived property by application of binary contributions were employed, comparative accuracy being obtained.

A real predictive procedure of this property was attempted using different cubic equations of state with simple mixing rules. An interpretation in terms of structure and length of the molecular chain of the aliphatic alkanes was made from the obtained results.

## EXPERIMENTAL

### Chemicals

The substances employed were supplied by Merck (LiChrosolv quality). Their molefraction purities were better than 0.99 for *n*-octane and better than 0.995 for the other chemicals used. The values of the refractive indices were in accordance with those published in the open literature<sup>9</sup> as is shown in Table I. Molecular sieves (3Å or 4Å) were used to dehydrate the solvents and ultrasonic treatment for degassing them. The manipulation procedure of the chemicals and the techniques applied in our laboratory have been commented in a previous paper.<sup>10</sup>

TABLE I. Comparison of experimental data with literature values for pure liquids at 298.15 K

Component	$n_D$	
	Exptl.	Lit. <sup>a</sup>
Chlorobenzene	1.52378	1.52138
<i>n</i> -Hexane	1.37234	1.37226
<i>n</i> -Heptane	1.38512	1.3850
<i>n</i> -Octane	1.39514	1.39505

<sup>a</sup>TRC Thermodynamic tables (1994)<sup>9</sup>

### Methods of measurement

The refractive indices were measured by an automatic refractometer ABBEMAT-HP Dr. Kernchen with a precision of  $\pm 0.00001$ . The refractometer was thermostated using a control bath PolyScience model 9510, with a temperature stability of  $\pm 10^{-2}$  K. The samples, covering the whole composition

range of the ternary mixtures, were prepared by weight using a Mettler AT-261 Delta Range balance with a precision of  $\pm 10^{-4}$  g. Before each series of measurements, the instrument was calibrated in accordance with the instruction manual. No systematic errors were detected in the measurements. The accuracy of both the changes of the refractive indices on mixing and the mole fractions was estimated to be better than  $10^{-4}$ . A wider explanation of the technical device used in this work can be obtained from the available literature or previous papers.<sup>10,11</sup>

## RESULTS AND DISCUSSION

### *Data correlation*

The refractive indices and changes of refractive indices on mixing are given in Tables II and III, for the *n*-heptane and *n*-octane systems, respectively. Eq. (1) being applied to compute the corresponding derived magnitude:

TABLE II. Refractive indices and changes of refractive indices on mixing chlorobenzene+*n*-hexane+*n*-heptane at 298.15 K

$x_1$	$x_2$	$n_D$	$\delta n_D$
0.0484	0.0482	1.38950	-0.0015
0.0988	0.0952	1.39386	-0.0036
0.1967	0.0967	1.40397	-0.0070
0.2953	0.0961	1.41540	-0.0093
0.3903	0.0976	1.42685	-0.0110
0.5001	0.0965	1.44117	-0.0120
0.6027	0.0999	1.45546	-0.0119
0.6974	0.0988	1.46922	-0.0113
0.7981	0.1010	1.48588	-0.0086
0.9030	0.0475	1.50430	-0.0054
0.0992	0.1980	1.39292	-0.0033
0.1955	0.1972	1.40326	-0.0063
0.3000	0.1960	1.41504	-0.0091
0.3990	0.1986	1.42781	-0.0100
0.4992	0.1981	1.44130	-0.0104
0.6029	0.1972	1.45518	-0.0110
0.6936	0.2045	1.46871	-0.0099
0.0779	0.3075	1.38948	-0.0024
0.1954	0.2997	1.40212	-0.0061
0.3014	0.3040	1.41411	-0.0088
0.3964	0.3012	1.42660	-0.0095

TABLE II. Continued

$x_1$	$x_2$	$n_D$	$\delta n_D$
0.5014	0.2960	1.44091	-0.0099
0.5990	0.2985	1.45477	-0.0096
0.0976	0.3993	1.39062	-0.0028
0.1978	0.4020	1.40146	-0.0058
0.3010	0.3993	1.41368	-0.0080
0.3945	0.4035	1.42545	-0.0091
0.4979	0.3997	1.43992	-0.0091
0.1017	0.4975	1.38964	-0.0031
0.1911	0.5122	1.39943	-0.0055
0.3001	0.4959	1.41258	-0.0077
0.4012	0.4988	1.42658	-0.0077
0.1018	0.6004	1.38882	-0.0026
0.2016	0.5958	1.39989	-0.0055
0.2965	0.6019	1.41174	-0.0067
0.1011	0.6955	1.38690	-0.0033
0.1971	0.7023	1.39852	-0.0049
0.1009	0.7975	1.38540	-0.0034
0.0495	0.9025	1.37889	-0.0015

TABLE III. Refractive indices and changes of refractive indices on mixing chlorobenzene+n-hexane+n-octane at 298.15 K

$x_1$	$x_2$	$n_D$	$\delta n_D$
0.0492	0.0453	1.39827	-0.0021
0.0980	0.0953	1.40120	-0.0043
0.1998	0.0960	1.41026	-0.0084
0.2965	0.0979	1.41976	-0.0112
0.3996	0.0979	1.43074	-0.0135
0.5008	0.0964	1.44304	-0.0143
0.6014	0.0941	1.45586	-0.0145
0.7019	0.0931	1.46996	-0.0133
0.8028	0.0975	1.48592	-0.0103
0.9028	0.0467	1.50383	-0.0064

TABLE III. Continued

$x_1$	$x_2$	$n_D$	$\delta n_D$
0.0994	0.1950	1.39979	-0.0036
0.2005	0.1951	1.40894	-0.0075
0.2957	0.1994	1.41857	-0.0100
0.4015	0.1949	1.41031	-0.0320
0.4957	0.2005	1.44140	-0.0129
0.6040	0.1969	1.45578	-0.0125
0.6979	0.1994	1.46944	-0.0109
0.0998	0.2957	1.39791	-0.0033
0.1969	0.2995	1.40689	-0.0067
0.2983	0.2957	1.41717	-0.0096
0.3958	0.2960	1.42844	-0.0108
0.4991	0.3000	1.44142	-0.0110
0.6044	0.2964	1.45602	-0.0101
0.1009	0.4143	1.39610	-0.0025
0.2012	0.3990	1.40571	-0.0062
0.2961	0.3966	1.41589	-0.0083
0.3981	0.3991	1.42749	-0.0097
0.5012	0.4001	1.44048	-0.0100
0.0971	0.5041	1.39367	-0.0024
0.1962	0.5010	1.40351	-0.0054
0.2822	0.5130	1.41230	-0.0074
0.4012	0.4940	1.42643	-0.0090
0.0981	0.6023	1.39176	-0.0022
0.1995	0.5984	1.40155	-0.0056
0.2988	0.6002	1.41252	-0.0073
0.0980	0.6987	1.38911	-0.0027
0.2034	0.6962	1.40021	-0.0052
0.0986	0.8009	1.38698	-0.0025
0.0488	0.9020	1.37964	-0.0011

$$\delta n_D = n_D - \sum_{i=1}^N x_i n_{Di} \quad (1)$$

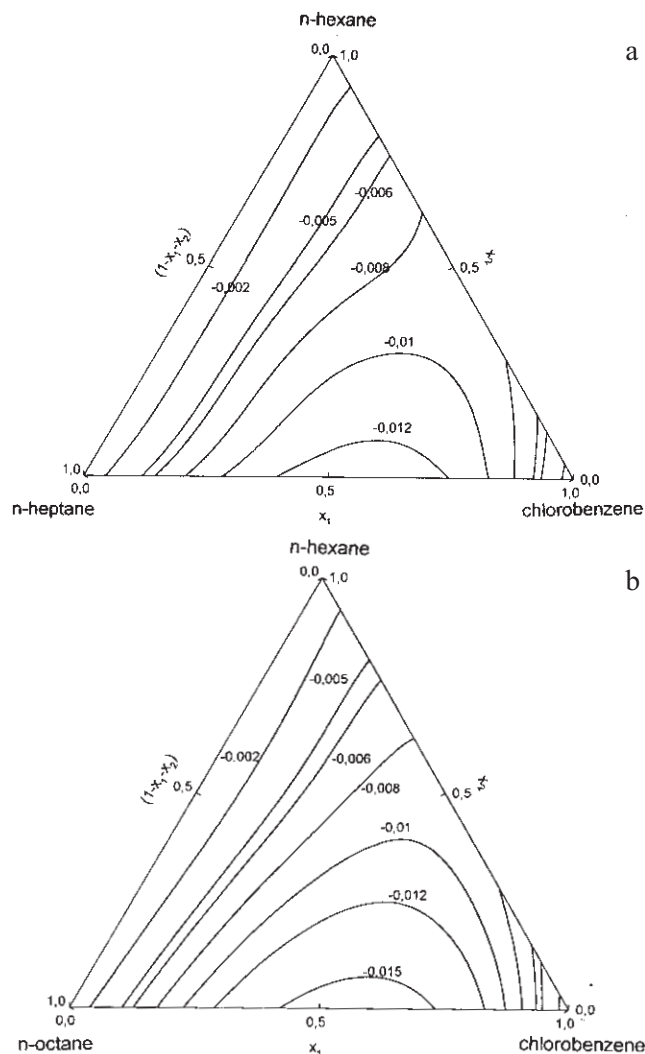


Fig. 1. Curves of constant changes in refractive indices on mixing at 298.15 K for (a) chlorobenzene + *n*-hexane + *n*-heptane and (b) chlorobenzene + *n*-hexane + *n*-octane.

In this equation,  $n_D$  is the refractive index of the mixture,  $n_{Di}$  is the refractive index of the pure component  $i$ ,  $x_i$  is the mole fraction of component  $i$  in the mixture.  $N$  is the number of components and  $\delta$  signifies the variation of a magnitude. A Redlich–Kister type equation<sup>12</sup> was used to correlate the changes of refractive indices on mixing of the corresponding binary mixtures. The parameters for these binary mixtures are those corresponding to the Redlich–Kister equation which is expressed as:

$$\delta Q = x_i x_j \sum_{p=0}^m B_p (x_i - x_j)^p \quad (2)$$

where  $m$  is the limit of the expansion (Bevington test<sup>13</sup>) and  $B_p$  are the fitting parameters. The ternary correlation was realized by means of a Nagata type equation<sup>14</sup> as follows:

$$\delta Q_{123} = \delta Q_{12} + \delta Q_{13} + \delta Q_{23} + x_1 x_2 x_3 RT (B_0 - B_1 x_1 - B_2 x_2 - B_3 x_1^2 - B_4 x_2^2 - B_5 x_1 x_2 - B_6 x_1^3 - B_7 x_2^3 - B_8 x_1^2 x_2) \quad (3)$$

where  $\delta Q_{12}$ ,  $\delta Q_{13}$  and  $\delta Q_{23}$  are the binary contributions of the Redlich-Kister expression for each binary mixture. Fig. 1a and 1b show the derived property as fitted curves against molar fraction. In the whole composition diagram, the mixtures show a miscible trend. The correlation was realized taking into account the binary contributions,<sup>7,15</sup> by the least squares method with all points being equally weighted by means of a routine developed in accordance with the Marquard algorithm.<sup>16</sup>

No values of these properties for the investigated ternary systems have been published in currently available literature. The parameters of Eq. (3) and the corresponding root mean square deviations (Eq. (4)) are gathered in Table IV. In this expression the value of the property and the number of experimental data are represented by  $z$  and  $n$ , respectively.

$$\sigma = \sqrt{\frac{\sum_i^n (z_{\text{exp}} - z_{\text{cal}})^2}{n}} \quad (4)$$

TABLE IV. Parameters of Eq. (3) and root mean square deviations ( $\sigma$ )

Chlorobenzene + <i>n</i> -hexane + <i>n</i> -heptane			
$B_0 = 6.22 \times 10^{-5}$	$B_1 = 2.79 \times 10^{-4}$	$B_2 = 2.23 \times 10^{-4}$	
$B_3 = -5.58 \times 10^{-4}$	$B_4 = -3.65 \times 10^{-4}$	$B_5 = -4.13 \times 10^{-4}$	
$B_6 = 3.04 \times 10^{-4}$	$B_7 = 2.63 \times 10^{-4}$	$B_8 = 4.07 \times 10^{-4}$	$\sigma = 3 \times 10^{-4}$
Chlorobenzene + <i>n</i> -hexane + <i>n</i> -octane			
$B_0 = 2.84 \times 10^{-6}$	$B_1 = 1.53 \times 10^{-5}$	$B_2 = 1.37 \times 10^{-6}$	
$B_3 = -6.85 \times 10^{-5}$	$B_4 = -5.97 \times 10^{-5}$	$B_5 = -1.12 \times 10^{-5}$	
$B_6 = 2.03 \times 10^{-5}$	$B_7 = 8.10 \times 10^{-5}$	$B_8 = 2.28 \times 10^{-5}$	$\sigma = 2 \times 10^{-4}$

#### Physical properties estimation

The prediction of different thermodynamic properties of multicomponent mixtures has been a subject of study during the last few decades, whereby different empirical or semi-empirical models were applied. In this paper, the measured experimental refractive indices were compared to those estimated by application of several mixing rules<sup>17</sup> (Lorentz-Lorenz, (L-L), a Dale - Gladstone (D-G), Arago-Biot (A-B), Eykman (Ey), Newton (Nw), Oster (Os), and Eyring-John (E-J). The root mean square deviations of the estimations are gathered in Table V. The best refractive indices estimation are those obtained by the D-G, A-B equations for the mixture with *n*-heptane, and the L-L, Ey and E-J for the mixture with *n*-octane, considering in both cases non-additivity on mixing.

TABLE V. Root mean square deviations of the experimental refractive indices from the estimated results using the Lorentz–Lorenz (L–L), Dale–Gladstone (D–G), Arago–Biot (A–B), Eykman (Ey), Newton (Nw), Oster (Os) and Eyring–John (E–J) equations

Chlorobenzene + <i>n</i> -hexane + <i>n</i> -heptane						
L–L	D–G	A–B	Ey	Nw	Os	E–J
0.00156	0.00052	0.00052	0.00075	0.00121	0.00076	0.00095
0.00074*	0.00145*	0.00493*	0.00120*	0.00242*	0.00205*	0.00945*
Chlorobenzene + <i>n</i> -hexane + <i>n</i> -heptane						
L–L	D–G	A–B	Ey	Nw	Os	E–J
0.00323	0.00329	0.00329	0.00322	0.00374	0.00351	0.00321
0.00326*	0.00359*	0.00487*	0.00346*	0.00416*	0.00392*	0.00688*

\* An asterisk indicates non-additivity on mixing

#### *Binary contribution rules for derived properties*

The ternary excess properties of mixtures may be estimated from binary values applying Eq. (5):

$$\delta Q_{ijk} = \sum_{i < j} (x_i x_j / x'_i x'_j) \delta Q_{ij}(x'_i, x'_j) \quad (5)$$

For each ternary mixture, the molar fractions  $x'$  may be obtained from a triangular diagram by projecting the point representing the ternary mixture onto the corresponding binary axis, using different symmetric or asymmetric criteria of binary contribution to the ternary value. According to the aforementioned equation, symmetry is understood to be the contribution of the three binaries to the ternary excess, all three of which contribute equally. Asymmetry is understood to indicate different individual contributions of one of the binaries, the latter being normally attributed to polar components. In the estimation of changes of refractive indices on mixing, the b type asymmetric equations of Tsao–Smith, Scatchard or Toop (chlorobenzene as the polar component) show the lowest deviations with respect to the experimental results. Comparative accuracy was obtained when symmetric rules, such as those of the Kohler, Jacob–Fitzner or Colinet, were applied. In Figs. 2a and 2b, isolines corresponding to the ternary contribution of the changes of refractive indices on mixing are shown. This ternary contribution to the derived magnitude is not considered by the binary contribution rules. It can be observed that the zone corresponding to approximately equimolar ternary compositions presents the highest dependence with simultaneous interactions of the three components in the mixture, the *n*-heptane system having the higher values. The root mean square deviations of each empirical equation are gathered in Table VI.



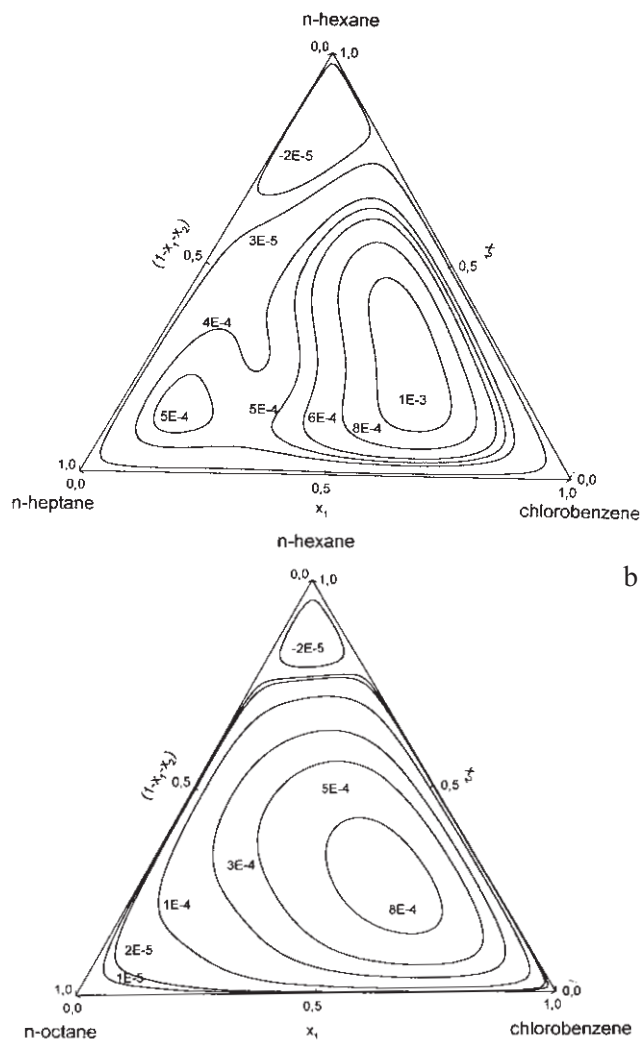


Fig. 2. Curves of constant ternaary contributions of changes of refractive indices at 298.15 K using Eq. (3) without binary contributions for (a) chlorobenzene + *n*-hexane + *n*-heptane and (b) chlorobenzene + *n*-hexane + *n*-octane.

#### Predictions by equations of state

For many practical purposes it is necessary to predict the non-ideality of binary or multicomponent liquid mixtures from physical parameters or by means of the properties of pure components using adequate models. In the last few years, interest related to work based on equations of state for the prediction of excess properties, phase equilibria and other properties has increased. This fact is due to their high simplicity as models, relative accuracy, low information requirements and wide versatility in operation conditions. In order to apply these models to estimate thermodynamic properties of mixtures, the implementation of mixing rules is necessary. In this case the Soave-Redlich-Kwong (SRK), and the Peng-Robinson (PR) equations<sup>17</sup> were selected and applied with combining rules of one or two binary interaction parameters in the *a* and *b*

TABLE VI. Root mean square deviations of the changes of refractive indices on mixing from the results predicted by different empirical equations

	Mixture with <i>n</i> -heptane	Mixture with <i>n</i> -octane
Kohler	0.00198	0.00346
Jacob–Fitzner	0.00149	0.00329
Colinet	0.00160	0.00329
Knobeloch	0.00300	0.00380
Lakhanpal	0.00282	0.00381
Tsao–Smith <sup>a</sup>	0.00137	0.00366
Tsao–Smith <sup>b</sup>	0.00395	0.00474
Tsao–Smith <sup>c</sup>	0.00332	0.00394
Scatchard <sup>a</sup>	0.00135	0.00357
Scatchard <sup>b</sup>	0.00223	0.00340
Scatchard <sup>c</sup>	0.00182	0.00337
Toop <sup>a</sup>	0.00135	0.00357
Toop <sup>b</sup>	0.00238	0.00350
Toop <sup>c</sup>	0.00214	0.00346
Mathieson–Tynne <sup>a</sup>	0.01357	0.01506
Mathieson–Tynne <sup>b</sup>	0.00515	0.00669
Mathieson–Tynne <sup>c</sup>	0.01875	0.02255
Hillert <sup>a</sup>	0.00149	0.00389
Hillert <sup>b</sup>	0.00771	0.00860
Hillert <sup>c</sup>	0.00564	0.00593

<sup>a</sup> Chlorobenzene is the asymmetric component in the equation; <sup>b</sup> *n*-hexane is the asymmetric component in the equation; <sup>c</sup> *n*-heptane or *n*-octane is the asymmetric component in the equation

mixture parameters. This section has been divided into three parts; the first one is a brief explanation of the mixing rules and the development of expressions, the second part presents the correlation procedure of binary values to obtain physical parameters and the third part is the evaluation of the obtained results.

The methods applied to these mixtures relate the refractive indices on mixing based on different applications of the Heller equation and a mixing rule<sup>18</sup> which was previously tested under different conditions. It has been suggested that the mixing rules for refractive indices are functions of the volume fractions of the mixture, since it is possible to generalize them as a function of the density of the mixture and of the pure components:<sup>18</sup>

$$\frac{f(n_D)}{\rho} = \sum_{i=1}^N \frac{w_i f(n_{Di})}{\rho_i} \quad (6)$$

In this equation,  $w_i$  is the mass fraction, and  $f$  is a mathematical function of the refractive indices of the mixture ( $n_D$ ), and the refractive index of each component ( $n_{D_i}$ ). Attaining to a previously explained substitution, it is possible to obtain an expression for the refractive index as:

$$\sum_{i=1}^N \left[ \left( \frac{(n_{D_i}^2 - 1)}{n_{D_i}^2 + 2} - \frac{(n_D^2 - 1)}{n_D^2 + 2} \right) \left( \frac{x_i M_i}{\left( \frac{(n_D^2 - 1)}{(n_D^2 + 2)} \right) \rho_i} \right) \right] = \sum_{i=1}^N x_i \left( \frac{\left( \frac{\partial P}{\partial n_i} \right)_{T,V,n}}{\left( \frac{\partial P}{\partial V_m} \right)_{T,n}} - V_i \right) \quad (7)$$

where  $f$  has been substituted by the Lorentz-Lorenz mixing rule<sup>10</sup> and the partial quantities and the molar volume were computed from the corresponding equation of state, the former also being dependent on the applied mixing rule. In accordance to the previous Eqs. (6) and (7), a general expression for the prediction of the refractive index on mixing is obtained from a derivation of Eq. (8), where  $V$  is the molar volume of the mixture,  $n$  represents the number of moles in the mixture, and  $\delta_1$ , and  $\delta_2$  are two parameters which have the following values:  $\delta_1 = 1$ ,  $\delta_2 = 0$  for the Soave-Redlich-Kwong (SRK), and  $\delta_1 = 1 + \sqrt{2}$ ,  $\delta_2 = 1 - \sqrt{2}$  for the Peng-Robinson (PR) equation.

The general form of a cubic equation of state can be given as:

$$P = \frac{RT}{V - b} - \frac{a}{(V + \delta_1 b)(V + \delta_2 b)} \quad (8)$$

The parameters  $a$  and  $b$  are defined by the following Van der Waals one-fluid mixing rules with two binary interaction parameters ( $k_{ij}$ ,  $l_{ij}$ ) for parameter  $a$ , and with one binary interaction parameters ( $m_{ij}$ ) for parameter  $b$ :

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j (1 - k_{ij} - l_{ij} \cdot Z) (a_i a_j)^{1/2} \quad (9)$$

$$b = \sum_{i=1}^N \sum_{j=1}^N x_i x_j (1 - m_{ij}) \left( \frac{b_i + b_j}{2} \right) \quad (10)$$

Four different combining rules for the binary interaction parameters were incorporated into these mixing rules, as follows:

$$\text{Mixing rule R1:} \quad l_{ij} = m_{ij} = 0 \quad Z = x_i - x_j \quad (11)$$

$$\text{Mixing rule R2:} \quad l_{ij} = 0 \quad Z = x_i - x_j \quad (12)$$

$$\text{Mixing rule R3:} \quad k_{ij}, l_{ij}, m_{ij} \neq 0 \quad Z = x_i - x_j \quad (13)$$

$$\text{Mixing rule R4:} \quad k_{ij}, l_{ij}, m_{ij} \neq 0 \quad Z = T \quad (14)$$

giving these parameters a constant value over the whole range of composition diagrams for every mixture.

TABLE VII. Binary interaction parameters of mixing rules applied to the SRK and PR state equations ( $\sigma$  in brackets)

Mixtures	Soave-Redlich-Kwong				Peng-Robinson			
	R1	R2	R3	R4	R1	R2	R3	R4
Chlorobenzene			0.835105	-0.906812			0.880353	-0.892833
+	0.019789	0.017018	-0.002744	0.018638	0.012530	0.021590	-0.002880	0.020255
<i>n</i> -hexane	(0.0106)	(0.0104)	(0.0110)	(0.0072)	(0.0150)	(0.0104)	(0.0110)	(0.0072)
Chlorobenzene			-0.005688	-1.007432			0.213498	-1.003113
+	-0.002951	0.055436	0.000205	-0.023046	-0.006690	0.064771	-0.000499	-0.026222
<i>n</i> -heptane	(0.0421)	(0.0091)	(0.00586)	(0.014893)	(0.0453)	(0.0097)	(0.003683)	(0.013976)
			(0.0096)	(0.0049)			(0.0103)	(0.0049)
<i>n</i> -Hexane			0.819167	-0.993562			0.875219	-0.996176
+	0.012146	0.001672	-0.002742	-0.000433	0.009903	0.001351	-0.002931	-0.000158
<i>n</i> -heptane	(0.0082)	(0.0016)	(0.002475)	(0.002194)	(0.0058)	(1.9 $\times 10^{-5}$ )	(2.1 $\times 10^{-5}$ )	(8.18 $\times 10^{-6}$ )
			(0.0017)	(0.0017)				
<i>n</i> -Hexane			0.003573	-1.062546			-0.038636	-1.059465
+	0.018857	0.002980	-0.000002	0.017919	0.017421	0.002162	0.000137	0.016799
<i>n</i> -octane	(0.0262)	(0.0132)	(0.003554)	(0.009242)	(0.0231)	(0.0132)	(0.003408)	(0.008598)
			(0.0140)	(0.0133)			(0.0140)	(0.0135)

In order to compute the binary interaction parameters for each mixing rule, a common correlation procedure was applied by minimizing an objective function (Eq. (15)) which means the relative deviation of the calculated, and the experimental values and leads to zero

$$OF = \frac{\sum_{i=1}^n (z_{\text{exp}} - z_{\text{cal}})^2}{z_{\text{exp}}} \quad (15)$$

A Marquard routine in combination with the Newton–Raphson method was applied to generate the interaction parameters, the fitting parameters being computed.

Table VII summarizes the binary interaction parameters of the applied mixing rules of the SRK and PR equations for each binary mixture ( $\sigma$  from experimental values in brackets). It can be observed that similar deviations are obtained for binary correlations by both equations using the mixing rules R<sub>2</sub> or R<sub>3</sub>, giving the lowest deviations.

In what is referred to as the capability to correlate experimental data, a good response is obtained for all the binary mixtures, the deviations being close to the accuracy of measurement as can be observed in Table VII. The poorest results were obtained for the mixture where *n*-octane was present. Slightly better results were reached by the PR equation but both equations used exhibited similar behaviour. The capability of ternary prediction was adequate attending to the obtained deviations which are gathered in Table VIII. Both equations show similar deviations, although small differences are obtained depending on the applied mixing rules. Better results were computed for the mixture chlorobenzene + *n*-hexane + *n*-heptane due to the high local deviation obtained near *n*-hexane in the chlorobenzene + *n*-hexane + *n*-octane mixture, where a sigmoidal trend is observed.

TABLE VIII. Root mean square deviations of ternary refractive indices on mixing from the prediction by the application of the binary interaction parameters of mixing rules using the SRK and PR equations, enclosed in Table VII

Mixture	Soave–Redlich–Kwong				Peng–Robinson			
	R1	R2	R3	R4	R1	R2	R3	R4
Chlorobenzene + <i>n</i> -hexane + <i>n</i> -heptane	0.0005	0.0007	0.0007	0.0006	0.0005	0.0007	0.0007	0.0006
Chlorobenzene + <i>n</i> -hexane + <i>n</i> -octane	0.0031	0.0030	0.0030	0.0030	0.0031	0.0030	0.0030	0.0030

The changes of refractive indices on mixing in these mixtures mainly depend on two effects: a) variation of the intermolecular forces when two components come into contact and b) variation of the molecular packing as a consequence of the differences in size and shape of the molecules present in the mixture. If the interactions between the molecules of two mixed components are stronger than in the pure component, the effect

will be a contraction and then, a greater value of the physical property will be obtained. This usually occurs when the components have polar groups and/or similar molecular characteristics. Linear aliphatic hydrocarbons are nearly non-polar but chlorobenzene shows two specific types of behaviour attaining to its special structure: an aromatic ring and a polar atom on the ring structure (flat geometry). When the pure compounds are mixed, the chlorobenzene molecules intersperse among the hydrocarbon molecules, resulting in a decreased interaction between the C1 atoms of the chlorobenzene. This effect is clearly shown in Figs. 2a and b in terms of the ternary contribution against composition. As the polar interactions diminish, the excess volume becomes less negative. The experimental results agree with this explanation since all the studied mixtures show negative. The experimental results agree with this explanation since all the studied mixtures show negative excess volumes in accordance with previously published data.<sup>8</sup> This fact shows that the packing caused by geometrical effects is higher than the change of intermolecular forces. This causes the differences of the derived property between *n*-heptane and *n*-octane. If the minimum values of the two ternary mixtures are compared, the following observation can be made: more negative values correspond to mixtures of hydrocarbons more different in terms of chain length. The results can be interpreted qualitatively as being a consequence of the diminution of the dilution of the hydrocarbons in the chlorobenzene environment and then, a slightly stronger interaction among the polar groups at high concentrations of the aromatic compound.

In conclusion, the cubic equations of state coupled with the corresponding mixing rules could be used with appropriate accuracy for the prediction of multicomponent refractive indices as can other different thermodynamic properties using current thermodynamic models.

#### ИЗВОД

#### ПРОМЕНА ИНДЕКСА РЕФРАКЦИЈЕ ТЕРНЕРНИХ СМЕША САЧИЊЕНИХ ОД ХЛОРОБЕНЗЕНА + *n*-ХЕКСАНА + (*n*-ХЕПТАНА ИЛИ *n*-ОКТАНА) НА 298,15 К

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Измерени су индекси рефракције смеша хлоробензен + *n*-хексан + (*n*-хептан или *n*-октан) на 298,15 К при атмосферском притиску у целој области концентрације дијаграма стања. Одређени су параметри полиномских једначина које повезују састав и мерене физичке и изведене величине. Индекси рефракције и изведене тернерне особине упоређени су са подацима добијеним коришћењем неколико полуемпиријских модела предвиђања одговарајућих особина. Упоређењем мерених вредности и вредности добијених коришћењем Soave–Redlich–Kwong (SRK) и Peng–Robinson (PR) кубне једначине стања уз коришћење Van der Waals-овог правила мешања за један флуид, које укључује различита правила комбиновања за предвиђање индекса рефракције мешања, добијена су добра слагања.

(Примљено 11. августа, ревидирано 5. децембра 2003)

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