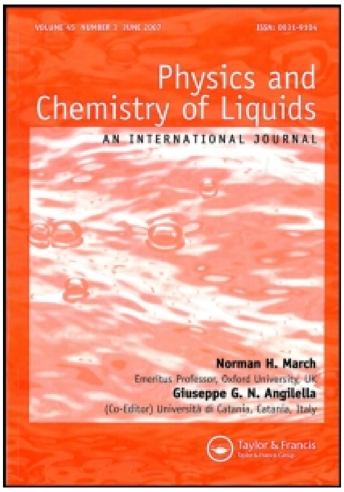

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CHANGES OF REFRACTIVE INDICES OF THE TERNARY MIXTURES CHLOROBENZENE + *n*-HEXANE + (*n*-NONANE OR *n*-DECANE) AT 298.15 K

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The measures of the refractive indices of the ternary mixtures chlorobenzene + *n*-hexane + (*n*-nonane or *n*-decane) have been done at 298.15 K and atmospheric pressure in the whole composition diagram. The composition dependence of the derived magnitude has been compared with the data obtained with several theoretical models. Attending to the accurate results of these models, the equation of state enclosing mixing rules are pointed out as simple procedures for a multicomponent estimation of refractive indices, the corresponding binary parameters could be used to other thermophysical studies.

Keywords: Refractive index; Chlorobencene; Alkanes; Equation of state; Estimation

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 use. The contamination with halogenated aromatic and hydrocarbons of different nature is perhaps one of the most serious problems that mankind faces today. So, the design of an effective remediation strategy for the contamination of air, ground, and surface water with halogenated aromatic compounds of different nature, physical, chemical, and biodegradation potential of each contaminant must be researched. Although pure compounds properties are usually encountered into open literature, a minor availability of mixing properties are disposable. Due to this fact,

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we have conducted in the last few years systematic studies on the thermodynamic properties of mixtures related to industrial processes [1–4], food technology [5, 6], or pharmacological mixtures [7, 8].

The purpose of this work is to continue our labor on the field of thermochemical properties for a better understanding of mixing trend of chemicals related to contamination with chlorobencene and hydrocarbons [9–12]. In this way, the first step is the thermodynamic characterization of the mixtures (physical properties, vapor–liquid equilibria, liquid–liquid equilibria, etc.) involved into the separation problem and then, an engineering study to evaluate, optimize, and design adequate unit operations. From a remediation standpoint, the chlorobenzene is moderately soluble in water, exhibiting a strong tendency to vaporize to ambient air at moderate temperature but these characteristics are strongly dependent on solvents.

Chlorobenzene is used primarily as an organic solvent of different chemicals as *n*-alkanes, as degreasing agent, and chemical intermediate (pesticide formulations, manufacture of diisocyanate or nitrochlorobenzene). Limited information is available on the acute effects, although effects to the central nervous systems in humans are reported in different studies of neurotoxicity. No information is available on the carcinogenic effects. Human exposure to chlorobenzene appears to be primarily occupational and in urban areas, may be released to the ambient air or water during its manufacture and as contaminant of waste water.

In this work, we present new measurements of refractive indices of the ternary mixtures chlorobenzene + *n*-hexane + (*n*-nonane or *n*-decane) that have been measured at 298.15 K and atmospheric pressure in the whole composition diagram, as well as, the corresponding derived changes of refractive index on mixing. Parameters of polynomial equations which represent the molar fraction dependence of the derived property are gathered. Different binary contributions estimative procedures were applied for the derived property, a comparative accuracy being obtained. A real predictive procedure of this magnitude was attempted by different equations of state with simple mixing rules, an interpretation in terms of structure and length of molecular chain of aliphatic alkanes was made from the obtained results, such parameters could be used in the prediction of multicomponent refractive index or different thermodynamic properties by current thermodynamic expressions.

EXPERIMENTAL

Chemicals

The substances employed were supplied by Merck (Lichrosolv quality). Their mole-fraction purities were better than 0.995 for the chemicals used. Values of refractive indices, were in accordance with that published in open literature [13] as is shown in Table I. Molecular sieves (3 or 4 Å) were used to dehydrate solvents and ultrasonic treatment for degassing them. Manipulation procedure of chemicals and applied techniques in our laboratory are commented in a previous paper [14].

Measurement Procedure

The refractive indices were measured by an automatic refractometer ABBEMAT-HP Dr. Kernchen with a precision of ± 0.00001. Thermostation of refractometer was reali-

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

Component	n_D	
	Experimental	*Literature*[a]
Chlorobenzene	1.52378	1.52138
n-Hexane	1.37234	1.37226
n-Nonane	1.40336	1.40311
n-Decane	1.40937	1.40967

[a] Ref. [13].

zed by a controller bath PolyScience model 9510, with a temperature stability of $\pm 10^{-2}$ K. Samples preparation was made by weight using a Mettler AT-261 Delta Range balance with a precision of $\pm 10^{-4}$ g, covering the whole composition range of the ternary mixtures. Before each series of measurements, the instruments were calibrated in accordance with the use instructions, no systematic errors being detected in the measurements. The accuracy for both, changes of refractive indices on mixing and mole fractions, were estimated better than 10^{-4}. A wider explanation of the technical device used in this work could be obtained from open literature or earlier papers [14, 15].

RESULTS AND DISCUSSION

Data Correlation

The refractive indices and changes of refractive indices on mixing are given in Tables II and III, the Eq. (1) being applied to compute the corresponding derived magnitude:

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

In this equation, n_D is the refractive index in the mixture, n_{Di} is the property of pure components, x_i the molar fraction of component i in the mixture, N is the number of components, and δ means the variation of a magnitude. A Redlich–Kister type equation [16] was used to correlate the changes of refractive indices on mixing of the corresponding binary mixtures. This equation is expressed as:

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

where m is the limit of the expansion (Bevington test [17]) and B_p are the fitting parameters. The ternary correlation was realized by means of a Nagata type equation [18] as follows:

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

where δQ_{12}, δQ_{13}, and δQ_{23} are the binary contributions by the Redlich–Kister expression for each binary mixture. Figure 1(a) and (b) shows the derived property against

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

x_1	x_2	n_D	δn_D
0.0480	0.0471	1.4052	– 0.0021
0.0987	0.0963	1.4079	– 0.0040
0.1978	0.0957	1.4155	– 0.0084
0.2949	0.0976	1.4227	– 0.0129
0.4027	0.0963	1.4335	– 0.0152
0.4956	0.0978	1.4438	– 0.0161
0.6039	0.0923	1.4568	– 0.0163
0.6979	0.1003	1.4693	– 0.0149
0.8002	0.0973	1.4851	– 0.0116
0.9025	0.0476	1.5034	– 0.0072
0.0992	0.1920	1.4055	– 0.0035
0.1964	0.1975	1.4136	– 0.0071
0.2957	0.2001	1.4221	– 0.0105
0.4031	0.1995	1.4325	– 0.0131
0.5032	0.1967	1.4438	– 0.0139
0.5995	0.1992	1.4558	– 0.0135
0.7059	0.1941	1.4709	– 0.0114
0.1004	0.2923	1.4031	– 0.0030
0.1996	0.2967	1.4113	– 0.0067
0.2971	0.3019	1.4203	– 0.0093
0.4001	0.2976	1.4305	– 0.0117
0.5004	0.2973	1.4422	– 0.0121
0.5973	0.3014	1.4548	– 0.0111
0.0982	0.3977	1.4009	– 0.0017
0.1987	0.3997	1.4083	– 0.0064
0.2907	0.4046	1.4173	– 0.0083
0.3972	0.3994	1.4288	– 0.0099
0.5005	0.3976	1.4410	– 0.0102
0.0995	0.4962	1.3979	– 0.0019
0.2005	0.4950	1.4065	– 0.0055
0.3000	0.4969	1.4161	– 0.0079
0.3893	0.5097	1.4253	– 0.0090
0.0975	0.6056	1.3948	– 0.0014
0.1964	0.6045	1.4032	– 0.0049
0.2924	0.6090	1.4121	– 0.0075
0.0991	0.7031	1.3919	– 0.0015
0.1951	0.7079	1.4002	– 0.0046
0.0974	0.8036	1.3884	– 0.0017
0.0481	0.9023	1.3801	– 0.0010

molar fraction as well as the curves fitted. In the whole composition diagram, the mixtures show a miscible trend. The correlation was realized taking into account the binary contributions, by the method of least squares with all points weighting equally by means of a routine developed in accordance with Marquard algorithm [19].

No values of these properties for the investigated ternary system has been published in currently available literature. The parameters of Eq. (3) and 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.

$$\sigma = \sqrt{\frac{\sum_i^n \left(z_{\text{exp}} - z_{\text{pred}}\right)^2}{n}} \tag{4}$$

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

x_1	x_2	n_D	δn_D
0.0492	0.0460	1.4108	− 0.0025
0.0999	0.0964	1.4132	− 0.0040
0.1989	0.0971	1.4199	− 0.0087
0.2999	0.0957	1.4272	− 0.0129
0.3982	0.0936	1.4357	− 0.0157
0.5134	0.0749	1.4476	− 0.0178
0.5991	0.0996	1.4569	− 0.0173
0.7050	0.0935	1.4705	− 0.0160
0.7708	0.1326	1.4808	− 0.0119
0.9019	0.0474	1.5030	− 0.0078
0.1002	0.1888	1.4112	− 0.0027
0.1982	0.1970	1.4774	− 0.0072
0.3004	0.1992	1.4253	− 0.0110
0.3979	0.1994	1.4337	− 0.0138
0.4981	0.2026	1.4444	− 0.0144
0.6032	0.1979	1.4568	−0.0142
0.6972	0.2018	1.4697	− 0.0120
0.0995	0.3009	1.4077	− 0.0019
0.2025	0.2987	1.4153	− 0.0061
0.2875	0.3051	1.4217	− 0.0093
0.4164	0.2898	1.4339	− 0.0123
0.5034	0.2965	1.4436	− 0.0123
0.5979	0.3000	1.4552	− 0.0115
0.1008	0.3959	1.4049	− 0.0013
0.2020	0.4020	1.4124	− 0.0052
0.2953	0.4050	1.4199	− 0.0083
0.3956	0.4023	1.4294	− 0.0103
0.4912	0.4065	1.4400	− 0.0105
0.0997	0.4980	1.4018	− 0.0005
0.1990	0.5010	1.4091	− 0.0045
0.2980	0.4992	1.4175	− 0.0074
0.3994	0.5016	1.4277	− 0.0087
0.0992	0.6021	1.3982	− 0.0002
0.1970	0.6034	1.4056	− 0.0040
0.2971	0.6025	1.4140	− 0.0070
0.0977	0.7059	1.3938	− 0.0006
0.1937	0.7068	1.4010	− 0.0043
0.0987	0.8023	1.3897	− 0.0012
0.0480	0.9030	1.3711	− 0.0103

Physical Properties Estimation

The prediction of different thermodynamic properties of multicomponent mixtures have been the subject of study in the last few years, applying different empirical or semiempirical models. In this article, the measured experimental refractive indices were compared with those estimated applying several mixing rules [14] (Lorentz–Lorenz (L–L), Dale–Gladstone (D–G), Arago–Biot (A–B), Eykman (Eyk), Newton (Nw), Oster (Os), and Eyring–John (E–J)). In Table V the root mean square deviations of the estimations are gathered. The best refractive indices estimation are those obtained by D–G, A–B equations for the mixture with *n*-nonane, and L–L, Eyk, and E–J for the mixture with *n*-decane, considering in both cases additivity on mixing.

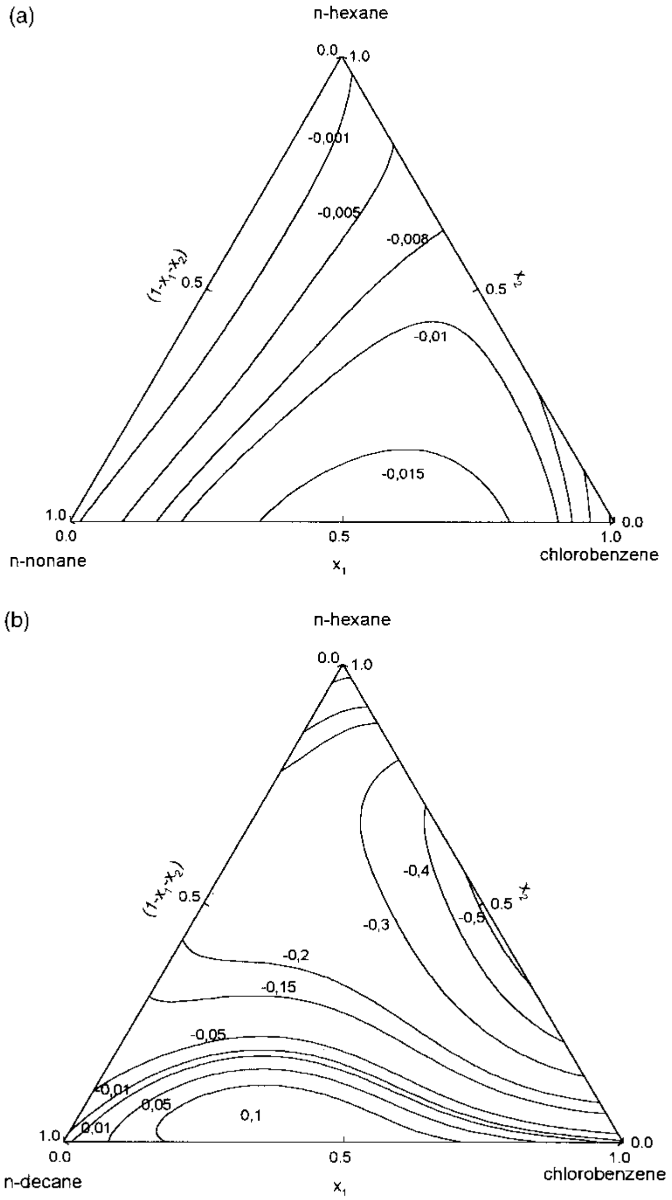

FIGURE 1 Curves of constant changes in refractive indices on mixing at 298.15 K for (a) chlorobenzene + *n*-hexane + *n*-nonane and (b) chlorobenzene + *n*-hexane + *n*-decane.

Binary Contribution Rules for Derived Properties

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

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

TABLE IV Parameters of changes of refractive index by Eq. (3) and the corresponding root mean square deviations (σ) (Eq. (4))

Chlorobenzene + *n*-hexane + *n*-nonane				
δn_D	$B_0 = 1.10 \times 10^{-5}$	$B_1 = 1.39 \times 10^{-4}$	$B_2 = -7.90 \times 10^{-5}$	
	$B_3 = -2.84 \times 10^{-4}$	$B_4 = 3.51 \times 10^{-4}$	$B_5 = -2.53 \times 10^{-4}$	
	$B_6 = 1.23 \times 10^{-4}$	$B_7 = -3.01 \times 10^{-4}$	$B_8 = 3.16 \times 10^{-4}$	$\sigma = 3.0 \times 10^{-4}$
Chlorobenzene + *n*-hexane + *n*-nonane				
δn_D	$B_0 = 3.71 \times 10^{-5}$	$B_1 = -2.48 \times 10^{-5}$	$B_2 = 4.55 \times 10^{-4}$	
	$B_3 = 1.01 \times 10^{-4}$	$B_4 = -1.48 \times 10^{-3}$	$B_5 = -6.31 \times 10^{-5}$	
	$B_6 = -1.79 \times 10^{-4}$	$B_7 = 1.38 \times 10^{-3}$	$B_8 = 9.57 \times 10^{-5}$	$\sigma = 1.7 \times 10^{-3}$

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

L–L	*D–G*	*A–B*	*Eyk*	*Nw*	*Os*	*E–J*
Chlorobenzene + *n*-hexane + *n*-nonane						
0.00099	0.00081	0.00081	0.00070	0.00167	0.00128	0.00070
0.00045*	0.00113*	0.00254*	0.00087*	0.00210*	0.00172*	0.00431*
Chlorobenzene + *n*-hexane + *n*-nonane						
0.00984	0.00972	0.00972	0.00974	0.00971	0.00970	0.00976
0.00979*	0.00974*	0.00999*	0.00975*	0.00978*	0.00976*	0.01065*

*An asterisk indicates non-additivity on mixing.

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 the different individual contribution of one of the binaries, the latter being normally attributed to polar components. In the estimation of changes of refractive indices on mixing, an asymmetric equation of Tsao–Smith, Scatchard, or Toop (chlorobencene as polar component) type shows the lowest deviations with respect to experimental results. Comparative accuracy were obtained when symmetric rules as Kohler, Jacob–Fitzner, or Colinet were applied. In the Fig. 2(a,b), the 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 could be observed as the zone corresponding to approximately equimolar ternary compositions presenting the highest dependence with interactions of the three components in the mixture, the *n*-nonane system being those of highest values. In Table VI the root mean square deviations of each method are gathered.

Predictions by Equations of State

For many practical purposes it is necessary to predict the nonideality of binary or multicomponent liquid mixtures from physical parameters or by means of pure components properties in adequate models. In the last few years, the interest related to work based on equations of state for prediction of excess magnitudes, phase

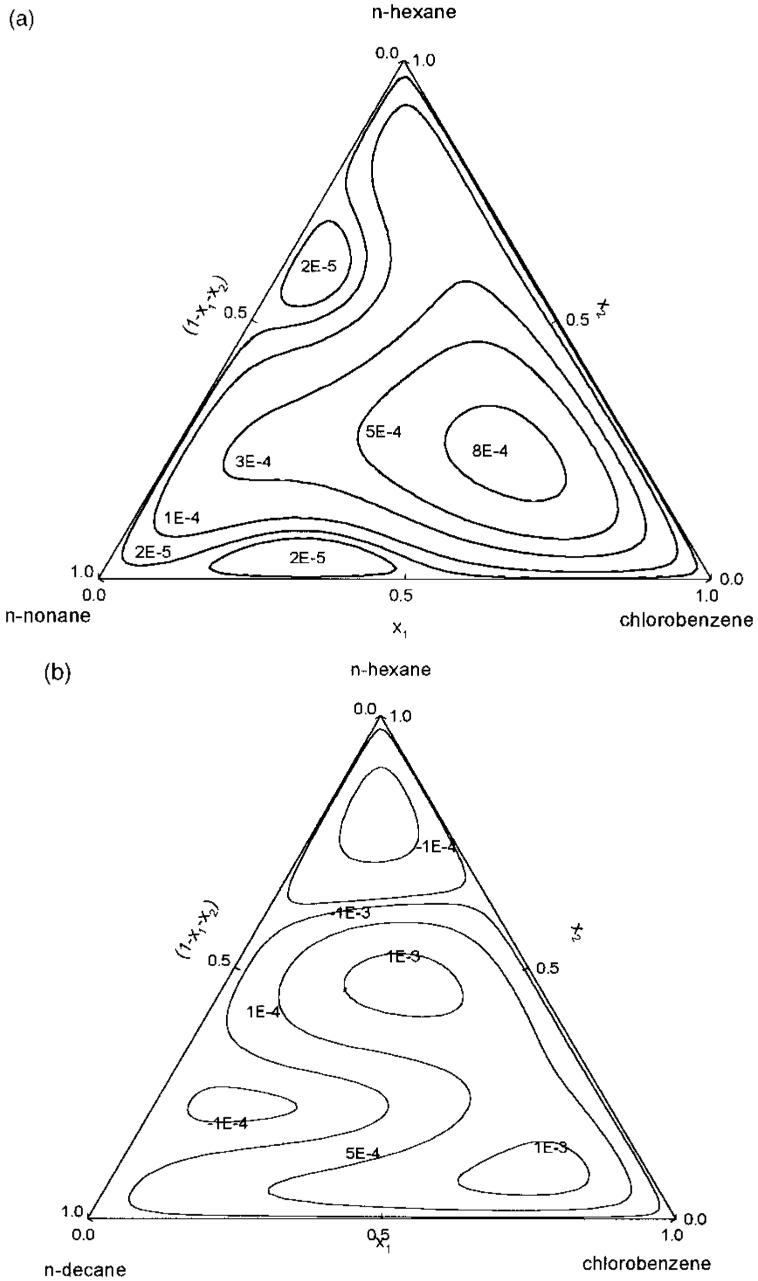

FIGURE 2 Curves of constant ternary contributions of changes of refractive indices at 298.15 K using Eq. (3) without binary contributions for (a) chlorobenzene + *n*-hexane + *n*-nonane and (b) chlorobenzene + *n*-hexane + *n*-decane.

equilibria, and other properties has increased. This fact is due to its high simplicity as a model, 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–

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

	Mixture with n-nonane	*Mixture with n-decane*
Kohler	0.00179	0.01014
Jacob–Fitzner	0.00127	0.01007
Colinet	0.00135	0.01009
Knobeloch	0.00265	0.01071
Lakhanpal	0.00286	0.01102
Tsao–Smith[a]	0.00208	0.00993
Tsao–Smith[b]	0.00427	0.01149
Tsao–Smith[c]	0.00300	0.01068
Scatchard[a]	0.00178	0.00994
Scatchard[b]	0.00198	0.01037
Scatchard[c]	0.00151	0.01005
Toop[a]	0.00179	0.00995
Toop[b]	0.00209	0.01040
Toop[c]	0.00184	0.01010
Mathieson–Tynne[a]	0.01455	0.02645
Mathieson–Tynne[b]	0.00656	0.01158
Mathieson–Tynne[c]	0.02386	0.02762
Hillert[a]	0.00294	0.00995
Hillert[b]	0.00922	0.01546
Hillert[c]	0.00524	0.01139

[a]Chlorobenzene is the asymmetric component in the equation; [b]*n*-hexane is the asymmetric component in the equation; [c]*n*-nonane or *n*-decane is the asymmetric component in the equation.

Redlich–Kwong (S–R–K) [20], and the Peng–Robinson (P–R) [21] equations were selected and applied with combining rules of one or two parameters in the *a* and *b* factors. We have divided this section into three parts; the first one is a brief explanation of the rules and 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 [14] which was tested under different conditions, previously. It has been presented that the mixing rules for refractive indices are functions of the volume fractions of the mixture, since it is possible to generalize them in a function of the density of the mixture and of the pure components [22]:

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

In this equation, w_i is the weight fraction, and f is a mathematical function of the refractive indices of the mixture (n_D), and the refractive index of each component (n_{Di}). Attending to a previously explained substitution, it is possible to obtain an expression for the refractive index as [22]:

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

where *f* has been substituted by the L–L mixing rule [14] and the partial quantities, and the molar volume were computed from the corresponding equation of state, the former being dependent on applied mixing rule, and the latter on the selected equation of state. In accordance to previous Eqs. (6) and (7), a general expression for predicted refractive index on mixing is obtained from the derivation of Eq. (8) where V is the mixture molar volume, n the number of moles in the mixture, and δ_1 and δ_2 a couple of parameters which show the following values: $\delta_1 = 1$, $\delta_2 = 0$ for S–R–K, and $\delta_1 = 1 + \sqrt{2}$, $\delta_2 = 1 - \sqrt{2}$ for P–R. The general equation which must be derived is:

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

Three different combining rules for binary parameters were incorporated to these models, which show different correlation dependence (Eqs. (9)–(11)):

$$\text{Mixing rule } R1: \quad l_{ij} = m_{ij} = 0 \tag{9}$$

$$\text{Mixing rule } R2: \quad l_{ij} = 0 \tag{10}$$

$$\text{Mixing rule } R3: \quad k_{ij}, l_{ij}, m_{ij} \neq 0 \tag{11}$$

these parameters being a constant value over the whole range of composition diagrams for every mixture. The general equations for the applied mixing rules are:

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j (1 - k_{ij} - l_{ij} x_i)(a_i a_j)^{1/2} \tag{12}$$

$$b = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j (1 - m_{ij}) \left(\frac{b_i + b_j}{2} \right) \tag{13}$$

In Table VII, the values of the parameters for each binary mixture (obtained from previously published data [9]) by S–R–K and P–R equations by application of the mixing rules are gathered (σ from experimental values into brackets). It could be observed as similar deviations are obtained for binary correlations by both equations, being the rules R_2 or R_3, those of the lowest deviations.

In order to compute the binary interaction parameters for each mixing rule, a common correlation procedure were applied such as minimize an objective function (Eq. (14)) which means the relative accuracy of predicted and experimental values, and leads to zero.

$$\mathrm{OF} = \frac{\sum_{i=1}^{n} (z_{\mathrm{exp}} - z_{\mathrm{pred}})^2}{z_{\mathrm{exp}}} \tag{14}$$

A Marquard routine were applied to correlate in combination with a Newton–Raphson method the fitting parameters being computed. In what is referred to the capability of correlate experimental data, a good response is obtained for all the binary mixtures, the deviations being close to the accuracy of measurement as it could be observed in

TABLE VII Binary interaction parameters of mixtures rules applied to S–R–K and P–R state equations (σ into brackets)

	Soave–Redlich–Kwong			*Peng–Robinson*		
Mixtures	*R1*	*R2*	*R3*	*R1*	*R2*	*R3*
Chlorobencene + *n*-hexane	0.019789 (0.0106)	0.017018 −0.021688 (0.0104)	0.835105 −0.002744 −0.021688 (0.0110)	−0.906812 0.018638 −0.016584 (0.0072)	0.012530 (0.0150)	0.021590 −0.019616 (0.0104)
Chlorobencene + *n*-nonane	−0.047061 (0.0325)	−0.188283 −0.065228 (0.0208)	−0.054803 −0.000448 −0.065230 (0.0221)	−0.856342 −0.027197 −0.030900 (0.0058)	−0.045984 (0.0326)	−0.193486 −0.065511 (0.0224)
Chlorobencene + *n*-decane	−0.071904 (0.0118)	−0.098679 −0.071308 (0.0019)	0.739307 −0.002811 −0.071308 (0.0020)	−0.981761 −0.028019 −0.057741 (0.0017)	−0.069283 (0.0134)	−0.104975 −0.072284 (0.0019)
n-Hexane + *n*-nonane	0.028800 (0.0653)	−0.001921 −0.010182 (0.0100)	0.003583 −0.000018 −0.010182 (0.0107)	−1.110656 0.038659 −0.018259 (0.0096)	0.026542 (0.0579)	−0.004532 −0.010148 (0.0102)
n-Hexane + *n*-decane	0.034248 (0.0666)	0.008243 −0.017127 (0.0087)	0.693296 −0.002298 −0.017127 (0.0092)	−0.979768 −0.001668 −0.016856 (0.0092)	0.030919 (0.0556)	0.006066 −0.016869 (0.0087)

TABLE VIII Root mean square deviations for ternary refractive indices on mixing from the prediction by the application of the binary interaction parameters on mixing rules of S–R–K and P–R equations, enclosed in Table VII

	Soave–Redlich–Kwong			*Peng–Robinson*		
Mixtures	*R1*	*R2*	*R3*	*R1*	*R2*	*R3*
Chlorobencene + *n*-hexane + *n*-heptane	0.0005	0.0007	0.0006	0.0005	0.0007	0.0006
Chlorobencene + *n*-hexane + *n*-octane	0.0031	0.0030	0.0030	0.0031	0.0030	0.0030
Chlorobencene + *n*-hexane + *n*-nonane	0.0005	0.0007	0.0005	0.0005	0.0007	0.0005
Chlorobencene + *n*-hexane + *n*-decane	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004
Chlorobencene + *n*-hexane + *n*-undecane	0.0004	0.0005	0.0005	0.0005	0.0005	0.0005
Chlorobencene + *n*-hexane + *n*-dodecane	0.0074	0.0074	0.0073	0.0075	0.0074	0.0073

Table VII. The poorest results were obtained for the mixtures where *n*-decane was enclosed. Slight better results were showed by P–R equation but both of them show similar behavior. The capability of ternary prediction was adequate attending to the obtained deviations which are gathered in Table VIII. Both equations show similar deviations, slight differences being obtained by the applied mixing rules. Better results were computed for the mixture chlorobenzene + *n*-hexane + *n*-nonane due to the high local deviation obtained near *n*-hexane in the chlorobenzene + *n*-hexane + *n*-decane mixture where a sigmoidal trend is observed in terms of excess molar volumen.

The changes of refractive indices on mixing mainly depend in these mixtures on two effects: (a) variation of intermolecular forces when two components come into contact and (b) the variation of molecular packing as a consequence of differences in size and shape of chemicals enclosed into 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 magnitude will be obtained.

This usually occurs when the components have polar groups and/or similar molecular characteristics. Linear aliphatic hydrocarbons are nearly nonpolar but the chlorobenzene shows two behavior trends attending 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 among the Cl atoms of the chlorobenzene. This effect is clearly shown in Fig. 2(a) and (b) in terms of the ternary contribution against composition. As polar interactions diminish, the refractive index becomes lower. The experimental results agree with this explanation since all the studied mixtures show excess volumes that are negative in accordance with previously published data [11]. 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 magnitudes from *n*-nonane to *n*-decane. If we compare the minimum values at the two ternary mixtures, the following observations can be made: more negative values correspond to mixtures of more different hydrocarbons in terms of length chain. The results can be interpreted qualitatively as a consequence of the diminution of solubility of hydrocarbons into chlorobenzene environment and then, a slight stronger interaction among polar groups for high concentrations of the aromatic compound.

In conclusion, the computed binary interaction parameters could be used with the prediction of multicomponent refractive index or many other different thermodynamic properties by thermodynamic expressions.

References

[1] G. Marino, B. Orge, M. Iglesias and J. Tojo (2000). *J. Chem. Eng. Data*, **45**, 457.
[2] L.M. Casas, A. Tourniño, G. Marino, M. Iglesias, B. Orge and J. Tojo (2002). *J. Chem. Eng. Data*, **47**, 887.
[3] A. Touriño, M. Iglesias and G. Marino (2002). *J. Solution Chem.*, **31**, 793.
[4] A. Touriño, M. Hervello, V. Moreno, M. Iglesias and G. Marino (2002). *Phys. Chem. Liq.*, **34**, 1.
[5] C. González, M. Iglesias, J. Lanz and J.M. Resa (1999). *Thermochimica Acta*, **328**, 277.
[6] C. González, M. Iglesias, J. Lanz, G. Marino, B. Orge and J.M. Resa (2001). *J. Food Engng.*, **50**, 29.
[7] M.J. Fontao and M. Iglesias (2000). *Phys. Chem. Liq.*, **38**, 623.
[8] M.J. Fontao and M. Iglesias (2002). *Int. J. of Themophys.*, **23**, 513.
[9] A. Touriño, M. Hervello, V. Moreno, M. Iglesias and G. Marino (2003) *Phys. Chem. Liq.*, (in press).
[10] A. Touriño, M. Hervello, V. Moreno, M. Iglesias and G. Marino (2003). *Korean J. Chem. Eng.*, (in press).
[11] A. Touriño, M. Hervello, V. Moreno, M. Iglesias and G. Marino (2003). *J. Solution Chem. Soc.*, (submitted for publication).
[12] A. Touriño, M. Hervello, V. Moreno, M. Iglesias and G. Marino (2003). *J. Serbian Chem. Soc.*, (in press).
[13] *TRC Thermodynamic Tables* (1994). Thermodynamic Research Center, Texas A&M Unviersity, College Station, TX.
[14] M. Iglesias, B. Orge and J. Tojo (1996). *Fluid Phase Equilib.*, **126**, 203.
[15] M. Iglesias, B. Orge and J. Tojo (1996). *J. Chem. Thermodyn.*, **27**, 1161.
[16] O. Redlich and A. Kister (1948). *Ind. Eng. Chem.*, **40**, 345.
[17] P. Bevington (1969). *Data Reduction and Error Analysis for the Physical Sciences.* McGraw-Hill, New York.
[18] I. Nagata and K. Tamura (1990). *J. Chem. Thermodyn.*, **22**, 279.
[19] D.W. Marquardt (1963). *J. Soc. Indust. Appl. Math.*, **2**, 431.
[20] H.G. Rackett (1970). *J. Chem. Eng. Data*, **15**, 514.
[21] C.F. Spencer and R.P. Danner (1972). *J. Chem. Eng. Data*, **17**, 236.
[22] B. Orge, M. Iglesias, G. Marino, B.E. de Cominges, M.M. Piñeiro and J. Vijande (1999). *J. Thermal Anal and Calorimetry*, **56**, 381.