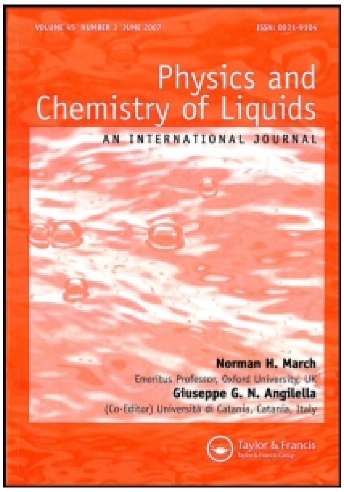

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Touriño, A. , Gayol, A. , Marino, G. and Iglesias, M.(2004) 'Ultrasonic velocity measurements for the ternary mixtures chlorobenzene + *n*-hexane + linear aliphatic alkane (C_7-C_8) at 298.15 K', Physics and Chemistry of Liquids, 42: 4, 323 — 337

To link to this Article: DOI: 10.1080/00319100410001658876

URL: http://dx.doi.org/10.1080/00319100410001658876

Physics and Chemistry of Liquids
Vol. 42, No. 4, August 2004, pp. 323–337

ULTRASONIC VELOCITY MEASUREMENTS FOR THE TERNARY MIXTURES CHLOROBENZENE + *n*-HEXANE + LINEAR ALIPHATIC ALKANE (C_7–C_8) AT 298.15 K

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(Received 10 November 2003)

The ultrasonic velocity of the ternary mixtures chlorobenzene + *n*-hexane + (*n*-heptane or *n*-octane) at 298.15 K and atmospheric pressure, has been measured over the whole concentration range. The corresponding change of isentropic compressibility was computed from the experimental data. The results were fitted by means of the Nagata equation, such parameters being gathered. The experimental ultrasonic velocities have been analyzed by theoretical procedures, an adequate agreement between the experimental and theoretical values both in magnitude and sign being obtained, despite the high nonideal trend of mixtures.

Keywords: Ultrasonic velocities; Isentropic compressibilities; *n*-Alkane; Chlorobenzene

1. INTRODUCTION

Halogenated solvents and their mixtures in hydrocarbons are frequently used for cleaning applications for industrial machinery, aerospace technology and motor vehicle manufacturing. As a consequence of these industrial activities, contamination of ground and surface water with halogenated, aromatic and aliphatic hydrocarbons is one of the different environmental problems mankind faces today. Recent international legislation has resulted in continuously decreasing contaminating emissions, an important amount is still being emitted to the environment. To this aim, an optimal design of separation units and development of freewaste processes and technologies are severely conditioned by a sufficient knowledge of mixing thermodynamics. The estimation models play an important role in the study and simulation of clean alternative unit operations and processes, an important effort has been developed in the last few years, although these prediction techniques cannot replace actual experimentation.

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ISSN 0031-9104 print: ISSN 1029-0451 online
DOI: 10.1080/00319100410001658876

The present work continues our research program on the chemical thermodynamics of mixtures related to pharmacology, food technology or chemical processes [1–5], as well as, in this case the identification and study of alternative separation agents and cosolvents in modified rectification processes. In this way, the first step is the thermodynamic characterization of the mixtures to be separated and those enclosing the entrainer (physical properties, vapor–liquid equilibria, liquid–liquid equilibria, etc.) involved into the industrial separation problem. To this end, we present in this article new measurements of ultrasonic velocities of the ternary mixtures chlorobenzene + *n*-hexane + linear aliphatic alkane (*n*-heptane or *n*-octane) at 298.15 K, and the corresponding changes of isentropic compressibilities, which were correlated by means of a current fitting equation into open literature.

Our purpose is to discuss the dependence of the isentropic compressibility on mixing and other acoustic parameters on the composition and molecular structure, in order to provide a better understanding concerning the factors which contribute to the special behavior in enclosing aromatic polar molecules into *n*-alkane mixtures, where the solvent is of shorter chain and different molecular nature. Due to the importance of theoretical procedures on industrial design, different procedures [6–9] were applied for the isentropic compressibilities, the obtained results being analyzed, and commented upon. We have attempted to explain the physico-chemical behavior of the mixtures indicated above, in order to explore the strength and nature of the interactions between the components by deriving various thermodynamic parameters from the ultrasonic velocity and density data [10]. Various parameters such as intermolecular free length (L_f), van der Waals' constant (b), molecular radius (r), geometrical volume (B), molar surface area (Y), available volume (V_a), volume at absolute zero (V_0), molar sound velocity (R), collision factor (S), specific acoustic impedance (Z), relative association (R_A), and molecular association (M_A) were computed. The analysis of excess acoustic magnitudes pointed out the availability of intense effects among unlike molecules at determined range of concentration (low composition of the heaviest *n*-alkane into the ternary mixture).

2. EXPERIMENTAL

All chemicals used were Merck chromatographic grade and were treated as usual in previous works [3]. Ultrasonic treatment was used for degassing and molecular sieves (type 4a or 3a, 1/16 inch, Aldrich cat. n° 20.860-4 or 20.858-2, respectively) were introduced into the bottles to reduce possible water contents. The gas chromatographic analysis of pure components showed that the major peak area exceeds 99.0% for any solvent. Solution composition were determined gravimetrically, special care being taken during solution preparation to avoid evaporation losses. The ultrasonic velocities were measured with an Anton Paar DSA-48 device with a precision of $\pm 1\,\mathrm{m s^{-1}}$. Calibration of the apparatus was performed periodically, in accordance with technical specifications, using Millipore quality water (resistivity, $18.2\,\mathrm{M\Omega\,cm^{-1}}$) and ambient air. Samples were prepared by mass using a Mettler AT-261 Delta Range balance with an accuracy of $\pm 10^{-4}$ g, covering the whole composition ranges of the mixtures. The accuracy of the mole fractions was estimated better than 10^{-4}. Maximum deviation in the calculation of changes of isentropic compressibility for these mixtures have been estimated better than $1\,\mathrm{TPa^{-1}}$. The values of the pure components, as well as, open

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

Compound	*M* (g mol^{-1})^{a}	*Exptl.* *u* (m s^{-1})	*Literature* *u* (m s^{-1})
Chlorobenzene	112.560	1267.6	1271^{b}
n-Hexane	86.177	1077.0	1076.37^{c}
n-Heptane	100.203	1130.5	1131^{d}
n-Octane	114.230	1172.0	1180^{e}

[a][11]; [b][12]; [c][13]; [d][14]; [e][15].

literature data are given in Table I. Further details about technical procedures or manipulation can be found in earlier works [5].

3. DATA PROCEDURE

Correlation of Derived Magnitudes

The changes of isentropic compressibilities are presented in Table II and were computed from the Eq. (1):

$$\delta Q = Q - \sum_{i=1}^{N} x_i Q_i \qquad (1)$$

In this equation, δQ means the variation of a magnitude Q (κ_S, isentropic compressibilities calculated by the Laplace equation from density and ultrasonic velocity), Q_i is the pure solvent magnitude, x_i is the mole fraction, and N is the number of components into the mixtures. A Redlich–Kister [16] type equation was used to correlate the derived properties of the binary mixtures, by the unweighted least squares method, all experimental points weighting equally:

$$\delta Q_{ij} = x_i \cdot x_j \cdot \sum_{p=0}^{m} B_p \cdot (x_i - x_j)^p \qquad (2)$$

where δQ_{ij} stands for the derived magnitude, B_p are the fitting parameters and M is the degree of the polynomial, determined applying the *F*-test due to Bevington [17]. These binary parameters were collected from previous works [18,19]. The B_p parameters were computed using a nonlinear optimization algorithm due to Marquardt [20]. The ternary derived magnitudes were fitted to the equation:

$$\delta Q_{123} = \delta Q_{12} + \delta Q_{13} + \delta Q_{23} + \Delta_{123} \qquad (3)$$

where the binary magnitudes δQ_{ij} have been correlated to Eq. (2) and Δ_{123} is the ternary contribution fitted by means of the equation of Nagata and Tamura [21]:

$$\Delta_{123} = x_1 x_2 x_3 RT \cdot \left(B_0 - B_1 x_1 - B_2 x_2 - B_3 x_1^2 - B_4 x_2^2 - B_5 x_1 x_2 - B_6 x_1^3 - B_7 x_2^3 - B_8 x_1^2 x_2\right) \qquad (4)$$

TABLE II Ultrasonic velocities, isentropic compressibilities and change of isentropic compressibilities for the ternary mixtures at 298.15 K

x_1	x_2	$u\,(\mathrm{ms^{-1}})$	$\kappa_S\,(\mathrm{TPa^{-1}})$	$\delta\kappa_S\,(\mathrm{TPa^{-1}})$
Chlorobenzene + n-hexane + n-heptane				
0.0484	0.0482	1131.7	1126.4	−4.7
0.0988	0.0952	1132.0	1102.4	−7.0
0.1967	0.0967	1138.6	1042.2	−10.0
0.2953	0.0961	1145.5	983.8	−10.5
0.3903	0.0976	1157.3	922.0	−16.8
0.5001	0.0965	1170.3	854.9	−19.3
0.6027	0.0999	1185.6	791.6	−23.1
0.6974	0.0988	1200.9	735.9	−23.1
0.7981	0.1010	1222.1	671.6	−28.7
0.9030	0.0475	1245.7	614.1	−15.9
0.0992	0.1980	1127.7	1113.4	−12.6
0.1955	0.1972	1134.7	1051.5	−17.9
0.3000	0.1960	1143.8	985.5	−22.5
0.3990	0.1986	1154.7	920.5	−29.8
0.4992	0.1981	1160.6	868.1	−23.4
0.6029	0.1972	1179.4	799.6	−30.9
0.6936	0.2045	1194.4	744.3	−34.3
0.0779	0.3075	1118.3	1147.1	−9.4
0.1954	0.2997	1125.3	1072.1	−14.2
0.3014	0.3040	1135.2	1001.8	−23.1
0.3964	0.3012	1146.9	936.6	−32.2
0.5014	0.2960	1160.2	868.5	−37.8
0.5990	0.2985	1174.1	807.1	−42.3
0.0976	0.3993	1115.2	1145.7	−14.3
0.1978	0.4020	1123.3	1077.4	−24.3
0.3010	0.3993	1131.4	1010.2	−30.6
0.3945	0.4035	1141.0	948.1	−38.5
0.4979	0.3997	1154.6	878.5	−46.9
0.1017	0.4975	1110.2	1157.3	−16.5
0.1911	0.5122	1115.9	1098.1	−25.7
0.3001	0.4959	1126.8	1020.3	−36.9
0.4012	0.4988	1138.9	945.6	−52.8
0.1018	0.6004	1104.6	1172.2	−18.5
0.2016	0.5958	1112.2	1100.5	−30.8
0.2965	0.6019	1121.0	1032.1	−44.6
0.1011	0.6955	1099.2	1188.3	−18.4
0.1971	0.7023	1106.8	1116.6	−34.9
0.1009	0.7975	1094.2	1202.6	−20.9
0.0495	0.9025	1084.1	1262.3	−8.6
Chlorobenzene + n-hexane + n-octane				
0.0492	0.0453	1169.5	1030.7	−0.5
0.0980	0.0953	1165.3	1021.0	−0.5
0.1998	0.0960	1167.5	977.6	4.5
0.2965	0.0979	1172.4	932.0	4.4
0.3996	0.0979	1178.1	883.2	4.7
0.5008	0.0964	1186.4	832.0	2.3
0.6014	0.0941	1196.0	780.7	−0.4
0.7019	0.0931	1208.1	728.0	−5.0
0.8028	0.0975	1223.4	673.3	−12.7
0.9028	0.0467	1244.2	617.7	−6.7
0.0994	0.1950	1157.9	1038.2	−10.0
0.2005	0.1951	1160.9	991.9	−8.1
0.2957	0.1994	1163.8	948.5	−7.3
0.4015	0.1949	1171.8	891.7	−12.4
0.4957	0.2005	1177.2	847.0	−13.7

(*continued*)

TABLE II Continued

x_1	x_2	$u\,(\mathrm{ms}^{-1})$	$\kappa_S\,(\mathrm{TPa}^{-1})$	$\delta\kappa_S\,(\mathrm{TPa}^{-1})$
0.6040	0.1969	1188.4	788.3	−19.7
0.6979	0.1994	1199.9	737.0	−26.9
0.0998	0.2957	1149.4	1058.3	−17.3
0.1969	0.2995	1152.1	1012.2	−18.0
0.2983	0.2957	1155.7	962.9	−18.0
0.3958	0.2960	1162.0	911.3	−23.2
0.4991	0.3000	1169.4	856.3	−30.0
0.6044	0.2964	1180.4	796.9	−38.3
0.1009	0.4143	1138.6	1083.9	−23.6
0.2012	0.3990	1141.2	1033.5	−22.0
0.2961	0.3966	1146.6	981.7	−27.9
0.3981	0.3991	1151.9	927.7	−33.9
0.5012	0.4001	1159.8	870.3	−42.4
0.0971	0.5041	1129.8	1107.5	−26.4
0.1962	0.5010	1132.6	1055.3	−30.4
0.2822	0.5130	1133.7	1013.6	−34.5
0.4012	0.4940	1140.7	946.1	−40.0
0.0981	0.6023	1119.8	1133.3	−27.0
0.1995	0.5984	1123.3	1075.5	−35.4
0.2988	0.6002	1126.9	1021.3	−42.8
0.0980	0.6987	1110.3	1159.4	−27.4
0.2034	0.6962	1112.1	1101.1	−34.7
0.0986	0.8009	1099.0	1190.6	−23.9
0.0488	0.9020	1087.8	1251.9	−14.0

TABLE III Fitting parameters for the isentropic compressibility (TPa^{-1}) by Eqs. (3) and (4) and root mean square deviations (σ) (Eq. (5))

Chlorobenzene + n-hexane + n-heptane			
$B_0 = -1.1302$	$B_1 = -1.5902$	$B_2 = -4.6059$	
$B_3 = -2.7559$	$B_4 = 5.4792$	$B_5 = 5.6862$	
$B_6 = 5.6038$	$B_7 = -0.5180$	$B_8 = 3.5191$	$\sigma = 4.30$
Chlorobenzene + n-hexane + n-octane			
$B_0 = -0.3690$	$B_1 = -2.5487$	$B_2 = 1.3555$	
$B_3 = 0.7893$	$B_4 = -4.4538$	$B_5 = 1.0621$	
$B_6 = 2.0271$	$B_7 = 5.4947$	$B_8 = 8.1974$	$\sigma = 3.23$

where x_i is the molar fraction, R, the universal constant for gases and T, the temperature in Kelvin degrees. The parameters calculated for the Eqs. (3) and (4) and its root means square deviations are enclosed in Table III. The root mean square deviations presented were computed using the Eq. (5), where z is the value of the derived magnitude, and n_{DAT} is the number of experimental data:

$$\sigma = \left(\frac{\sum_{i=1}^{n_{\mathrm{DAT}}} \left(z_{\exp} - z_{\mathrm{pred}} \right)^2}{n_{\mathrm{DAT}}} \right)^{1/2} \tag{5}$$

No previously published data have been found at the studied conditions for both ternary mixtures. Curves of constant changes of isentropic compressibility for the ternary mixtures chlorobenzene + *n*-hexane + (*n*-heptane or *n*-octane), have been plotted in Fig. 1(a) and (b), where a clear contractive tendency is shown for both the mixtures, due to the slight dispersive (methylene groups) and polar/inducted

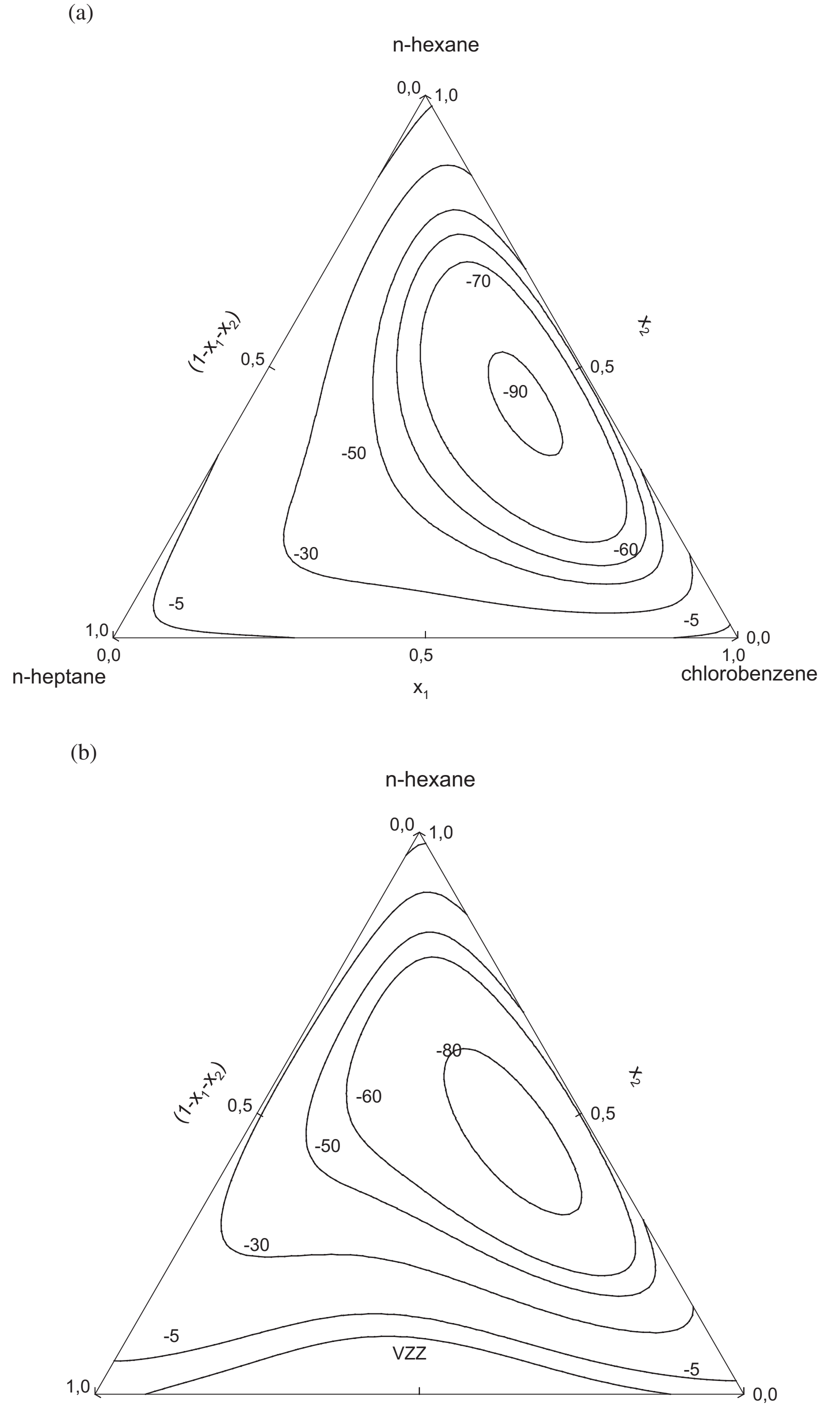


FIGURE 1 Curves of changes of isentropic compressibility for (a) chlorobenzene + *n*-hexane + *n*-heptane and (b) chlorobenzene + *n*-hexane + *n*-octane at 298.15 K.

interactions (chloride groups) that reaches a maximum effect for approximately equimolar mixtures chlorobenzene + *n*-alkane mixtures. At this point, the mixtures show ternary minima, decreasing their negative values as the aliphatic chain is increased. This fact produces a strong negative ternary nonideality at low composition of the highest alkane, the short chain solvents showing a high capability to be enclosed into chlorobenzene structure. As an exception providing the tendence, the mixture chlorobenzene +*n*-hexane + *n*-octane shows a negligible tendence (minor than $9 \times 10^{-3}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$) of slight expansion at large dilution of *n*-octane [22], which is not detected in terms of changes of isentropic compressibility. In Fig. 2(a) and (b) the ternary contribution to the derived property (Δ_{123}), expressed in terms of the Nagata equation, with strong negative values at almost any composition (for the two ternary mixtures) is observed. At any case the ternary contribution is considerable (30% for chlorobenzene + *n*-hexane + *n*-heptane and 50% for chlorobenzene + *n*-hexane + *n*-octane) attending to the strong interactions and steric hindrance among three different molecules.

Acoustic Parameters

We have attempted to explain the physico-chemical behavior of the mixtures indicated above, in order to explore the strength and nature of the interactions between the components by deriving various thermodynamic parameters from the ultrasonic velocity and density data. The parameters derived from the experimental measured data were intermolecular free length (L_f), the van der Waals' constant (b), molecular radius (r), geometrical volume (B), molar surface area (Y), available volume (V_a), volume at absolute zero (V_0), molar sound velocity (R), collision factor (S), specific acoustic impedance (Z), relative association (R_A), and molecular association (M_A), attending to the following set of equations:

$$L_f = \left(\frac{K}{u \cdot \rho^{1/2}}\right) \tag{6}$$

$$b = \left(\frac{M}{\rho}\right) - \left(\frac{RT}{\rho \cdot u^2}\right) \cdot \left(\left[1 + \frac{M \cdot u^2}{3RT}\right]^{1/2} - 1\right) \tag{7}$$

$$r = \left(\frac{3b}{16\Pi N}\right)^{1/3} \tag{8}$$

$$B = \left(\frac{4}{3}\right)\Pi r^3 N \tag{9}$$

$$Y = \left(36\Pi N B^2\right)^{1/3} \tag{10}$$

$$V_a = V\left(1 - \left(\frac{u}{u_\infty}\right)\right) \tag{11}$$

$$V_0 = V - V_a \tag{12}$$

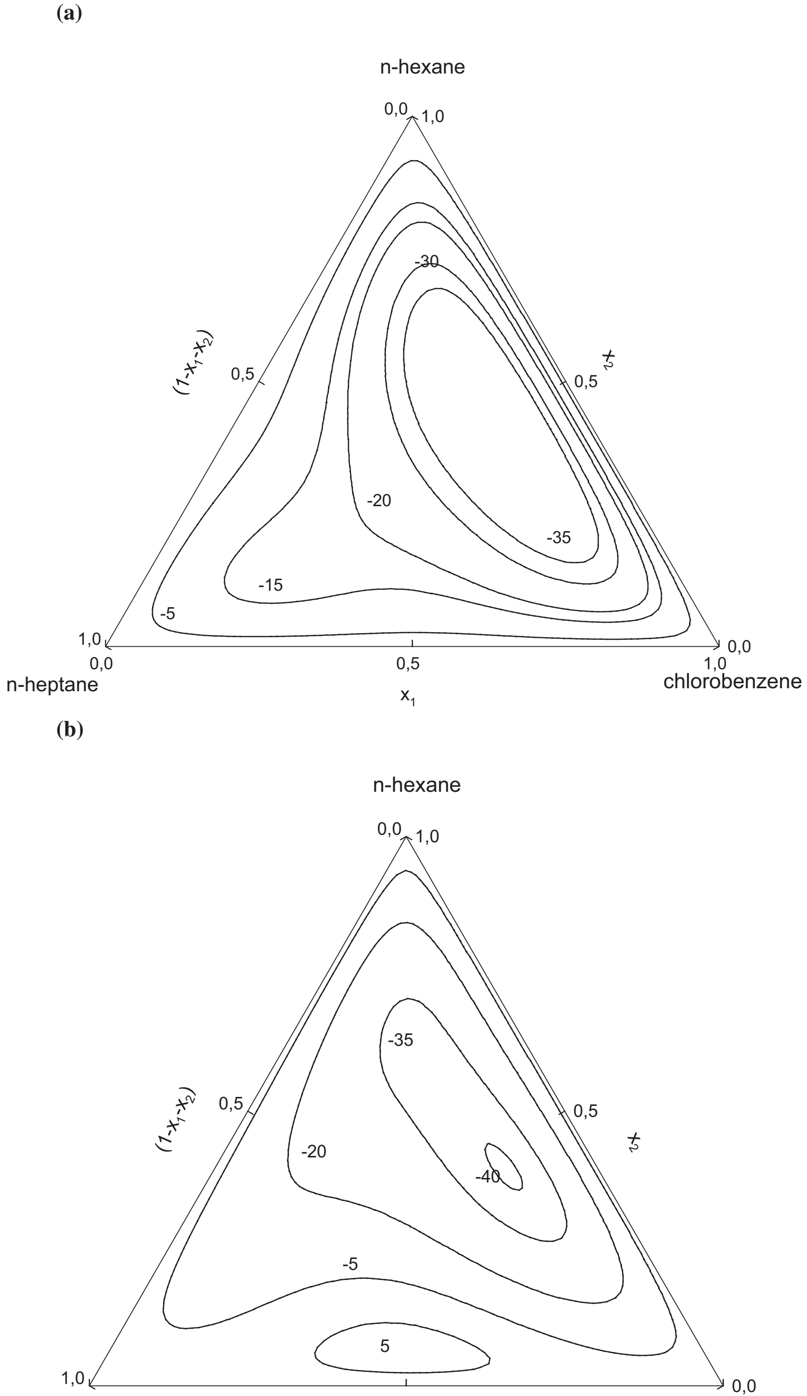


FIGURE 2 Curves of ternary contribution of the changes of isentropic compressibility for (a) chlorobenzene + *n*-hexane + *n*-heptane and (b) chlorobenzene + *n*-hexane + *n*-octane at 298.15 K.

TABLE IV Acoustic parameters for the pure compounds enclosed in the studied mixtures at 298.15 K

	L_f (Å)	$b \times 10^6$ (m^3)	r (nm)	$B \times 10^6$ ($m^3\,mol^{-1}$)	$Y \times 10^{-6}$ (m^2)	$V_a \times 10^6$ ($m^3\,mol^{-1}$)	$R \times 10^3$ ($m^3\,mol^{-1}$) $\cdot$ $(m\,s^{-1})^{1/3}$	S	R_A	$Z \times 10^{-3}$ $kg\,m^{-2}\,s^{-1}$
Chlorobenzene	0.489	96.58	0.212	24.14	0.341	21.24	1.11	3.35	1	1395.67
n-Hexane	0.746	122.41	0.230	30.60	0.400	43.00	1.35	2.89	0.628	705.54
n-Heptane	0.698	138.16	0.239	43.28	0.433	43.28	1.54	3.02	0.641	768.06
n-Octane	0.664	153.97	0.248	43.74	0.466	43.74	1.72	3.11	0.651	818.68

$$R = \frac{M \cdot u^{1/3}}{\rho} \tag{13}$$

$$S = \frac{u \cdot V}{B \cdot u_\infty} \tag{14}$$

$$Z = u \cdot \rho \tag{15}$$

$$R_A = \left(\frac{\rho_{\text{mix}}}{\rho}\right) \cdot \left(\frac{u}{u_{\text{mix}}}\right)^{1/3} \tag{16}$$

$$M_A = \left[\left(\frac{u_{\text{mix}}}{\sum_i x_i u_i}\right)^2 - 1\right] \tag{17}$$

where L_f is the free length of ideal mixing, K is a temperature dependent constant ($K = (93.875 + 0.375 \cdot T) \cdot 10^{-8}$), u_∞ is taken as $1600\,ms^{-1}$ [22], and R and Π are common universal constants. These parameters are gathered in Table IV for the pure compounds. The variation of the magnitudes L_f and Z (by means of Eq. (1)) for the ternary mixtures are shown in Figs. 3 and 4, respectively, showing these magnitudes as a function of $z = \prod_{i=1}^{N} x_i$, where x_i stands for the same meaning as indicated above. These figures let to difference pseudobinary (low values of z) and equimolar ternary compositions (high values of z) trends. In accordance to the contractive trend observed for other ternary mixtures which are being studied in our laboratory, extreme values are gathered at low concentration of the heaviest alkane.

Estimation Models

Due to the strong dependence of design, and optimization of chemical processes on computer calculations, the availability of accurate, simple, and tested methods, as well as related parameters is of increasing relevance. The estimation of different thermodynamic properties of binary or multicomponent mixtures have been the subject of study in recent years, applying different empirical or semiempirical models due to their interest to optimize industrial equipment and to understand the mixing liquids trend. Despite the effort on experimental and theoretical thermodynamics in the last few years, the knowledge of models and general applications for processes design is far away from actual requirements. In this field, the ultrasonic velocity measurements are scarce for multicomponent mixtures in open literature and the accuracy of theoretical procedures for calculation are not tested in a wide range. Experimental data for the isentropic compressibility of the mixtures were compared with values

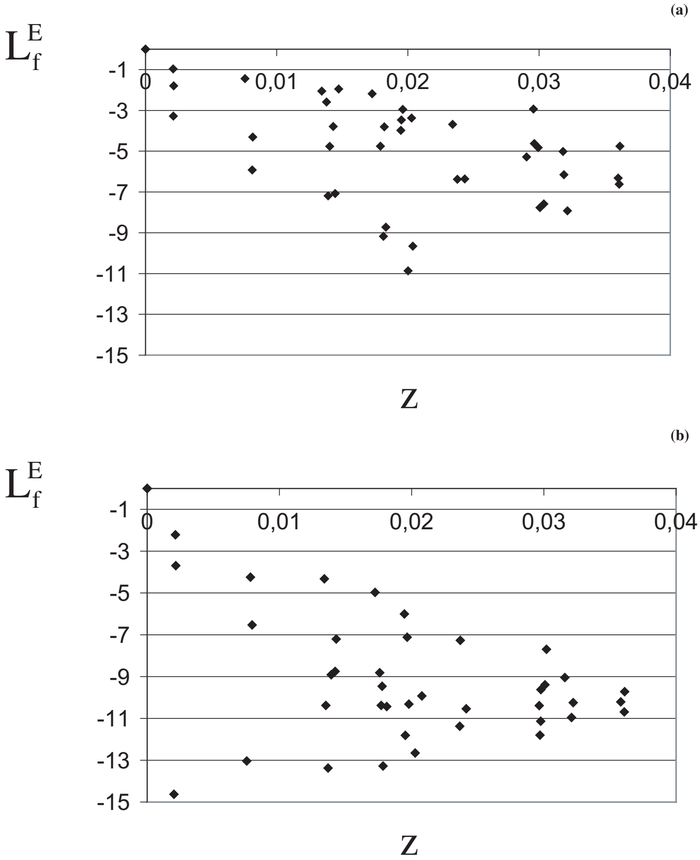


FIGURE 3 Curves of excess intermolecular free length for (a) chlorobenzene + *n*-hexane + *n*-heptane and (b) chlorobenzene + *n*-hexane + *n*-octane at 298.15 K as a function of $z = \prod_{i=1}^{N} x_i$.

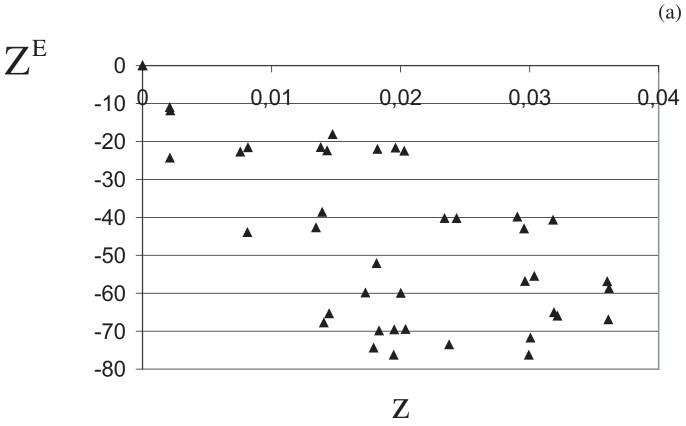
determined by different mixing procedures. The models of Danusso and Nomoto (Eqs. (18) and (19)) [6, 7]:

$$\kappa_S = \left(\frac{1}{M \cdot \rho}\right) \cdot \left(\sum_{i=1}^{N} \frac{n_i M_i}{\rho_i^2 u_i^2}\right) \tag{18}$$

$$\kappa_S = \left(\frac{1}{\rho}\right) \cdot \left(\frac{\sum_i^N n_i R_i}{\sum_i^N n_i u_i}\right)^{-6} \tag{19}$$

where $R = u^{1/3} \cdot \sum_i^N n_i V_i$ and Collision Factor Theory (CFT) [8,9], (Eq. (20)) for the isentropic compressibilities were applied:

$$\kappa_S = \left(\frac{1}{\rho^3}\right) \cdot \left(\frac{M}{u_\infty \cdot \sum_i^N x_i S_s \cdot \sum_i^N x_i B_s}\right)^2 \tag{20}$$



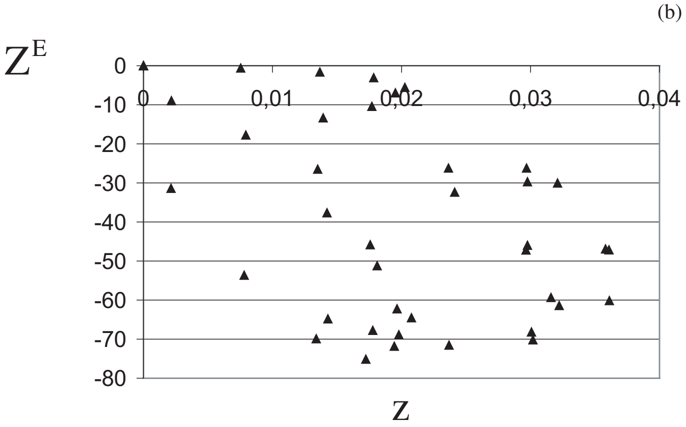


FIGURE 4 Curves of excess specific acoustic impedance for (a) chlorobenzene + n-hexane + n-heptane and (b) chlorobenzene + n-hexane + n-octane at 298.15 K as a function of $z = \prod_{i=1}^{N} x_i$.

The Collision Factor Theory (CFT) is dependent on the collision factors among molecules as a function of temperature into pure solvent or mixture. The pertinent relations in these calculations and its theoretical basis were described by the literature cited above. The collision factors (S) and the characteristic molecular volumes (B) of the pure solvents used in the CFT calculations were estimated by using the experimental ultrasonic velocities, enclosed in this article, and the corresponding molar volumes [10]. These values could be also evaluated by means of the group contribution method proposed by Schaffs when no experimental data are disposable [23].

The deviations of each procedure for the ternary mixtures are gathered into Table V, using the pure parameters from Table IV and literature data [12].

4. RESULTS AND CONCLUSIONS

In this work, the ultrasonic velocities of the mixtures chlorobenzene + n-hexane + (n-heptane or n-octane) have been measured at 298.15 K, the changes of isentropic

TABLE V Root mean square deviations for estimated isentropic compressibilities from experimental data for the ternary mixtures at 298.15 K

Mixture	*Danusso* (Eq. (19))	*Nomoto* (Eq. (20))	*CFT* (Eq. (21))
Chlorobenzene + *n*-hexane + *n*-heptane	81.01	40.11	43.55
Chlorobenzene + *n*-hexane + *n*-octane	90.85	45.85	26.29

compressibilities being calculated. These data were correlated by polynomial expressions which fitted the data well. Not surprisingly, the systems exhibited a strong contractive tendence attending to the solvent (*n*-heptane or *n*-octane) composition, but with a weakening effect as the aliphatic chain increases. This trend is showed in terms of negative change of isentropic compressibility though the composition diagram and a sharp ternary minimum. No values for the ternary mixtures were found in the open literature as far as we know. It is well known that when nonpolar or slight polar + nonpolar compounds are mixed, moderate variations in the intermolecular interactions take place. The new specific dispersive interactions that appear should be suitably measured by vibrational, optical, calorimetric or rheological techniques. Usually, these kind of mixtures show a nonideal behavior, which is severely conditioned by the difference in molecular volume and structure among the components into mixture. In this case, the steric hindrance is the most important factor in mixing thermodynamics due to the globular structure and the slight polarity in the halogenated compound and the quasi-linear chain of *n*-alkane. Disruption of polar interaction among chlorobenzene molecules deals progressively from negative to positive values through the aliphatic homologous series of *n*-alkanes [18] when molecular weight is increased. In the mixture chlorobenzene + *n*-hexane + (*n*-heptane or *n*-octane), chloride and methylene groups are contained and the tendence in changes of isentropic compressibility could be explained attending to the following factors; first, steric hindrance between phenyl group and aliphatic chain, that makes the molecular packing difficult by induction and polar interaction far away from equimolar composition. In the binary chlorobenzene + (*n*-heptane or *n*-octane), an important change of tendence could be observed at equimolar composition; the second factor is the partial activation of halogen atom that occurs at an adequate composition. In Fig. 1, the changes of isentropic compressibilities at each ternary mixture are showed as a function of solvent molar fraction, where the influence of the methylene group contribution difference can be observed. Another factor to take into account is the ternary contribution to the changes of isentropic compressibility (the final term at right side of Eq. (3)), which shows, strong negative trend at low composition of *n*-heptane or *n*-octane into the ternary mixture. This contribution is high enough in these mixtures to decide the final value (30–50% at each case) (Fig. 2).

In Fig. 1, the changes of isentropic compressibilities at each ternary mixture are showed as a function of solvent molar fraction, where the influence of the methylene group contribution difference can be observed. In what is referred to *n*-alkanes, the functional variation decreases the negative change of isentropic compressibility from *n*-hexane to *n*-nonane, progressively, as observed in our studies [18] and recent ternary experiments in our laboratory [10, 24, 25]. As it is observed in Figs. 3 and 4, and Table IV, all the acoustic parameters decrease with increasing mole fraction of chlorobenzene. Only L_f increases at any system in the present investigations which indicate slight interaction among solute and solvent molecules for infinite dilution and a reinforcement of solvent–solvent interaction. From these measurements three factors must be derived; first, the highest interaction was observed for any case at equimolar composition, which is related with an adequate number of molecules that build the first coordination sphere around chlorobenzene. Second, the minimum value was obtained always for the shortest *n*-alkane. This effect is due to the disruption that long aliphatic chains produce into the chlorobenzene packing. Third, the whole mixtures present lower values of compressibility than ideality. The last fact is a consequence of the molecular characteristics of the chlorobenzene, a small molar volume, molar surface area and similar dispersive interactions among aliphatic ends, that permit the creation of a more structured packing of molecules under mixing conditions. The addition of solvents to chlorobenzene tends to cause breaking of interactions and the creation of better packed clusters increasing isentropic compressibility and contractive trend as observed previously. This important change of chemical environment is noted by a high and progressive modification of each acoustic parameter at infinite dilution of chlorobenzene. In the present investigation, relative association R_A, is found to decrease with mole fraction of both alkanes. Relative high values signifies that unlike interactions are relatively strong compared to like interactions. Great values were observed for M_A in all systems, this magnitude being decreased with increasing chain length. Due to ultrasonic velocities that diminish with increasing molar fractions at each system, the liquid structure looses rigidity. The observed negative values of change of isentropic compressibility mean that the mixing structure is less compressible than the ideal mixture.

As shown in Fig. 3, all the systems present negative values for the excess intermolecular free length, which may be attributed to the presence of strong molecular interactions between unlike molecules. These negative values indicate that sound wave covers shorter distance due to a decrease in intermolecular free length as a result of the increment of packing mixture. As commented above, this effect reaches a maximum at equimolar fraction of solvent, approximately. All the systems exhibit positive values for the excess acoustic impedance at all concentrations of the mixtures, which reinforce our view that significant interactions are present among unlike compounds (Fig. 4).

In what is referred to theoretical estimation, as it could be observed in the Table V, similar results are computed for the different mixtures by each procedure. The accuracy achieved was quantitative by Danusso, Nomoto and CFT, an overestimation of the experimental data being obtained at the whole cases for high molar fractions in solvents.

The results of the comparison of predicted values with experimental data appear resumed in this table. Since Danusso's model assumes additivity of the molar volume, this equation more accurately predicts values for mixtures that show ideal behavior (no excess volume). This fact explains the highest deviations found for the mixtures with high excess volumes.

Attending to the deviation computed data, we arrive at the conclusion that the application of the CFT produces close agreement with the experimental data reported in this article, showing this procedure as an accuracy tool for isentropic compressibility data in high nonideal systems (Fig. 5a and b).

The obtained results gather the strong interaction of chlorobenzene and short chains of inert alkanes and the need of thermodynamic knowledge on cosolvents into modified

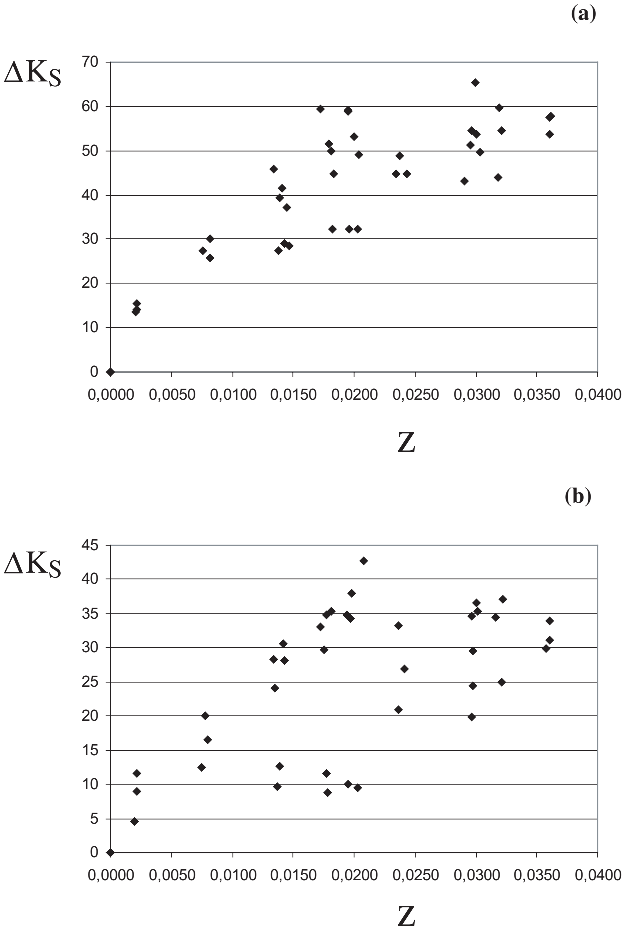


FIGURE 5 Curves of deviation from experimental data of the estimation by CFT for (a) chlorobenzene + *n*-hexane + *n*-heptane and (b) chlorobenzene + *n*-hexane + *n*-octane at 298.15 K as a function of $z = \prod_{i=1}^{N} x_i$.

processes to weaken these interactions in multicomponent separation by liquid entrainers.

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