

## Temperature Dependence of Isentropic Compressibilities for the Ternary Mixture: Acetone + Methanol + *n*-Hexane

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Received 25 May 2018, Accepted 12 September 2018

### Abstract

In this work, the applicability of Free Length and Collision Factor theories to predict multicomponent isentropic compressibilities is analyzed and compared. To this end, appropriate expansions for ternary mixtures were derived from the original works, and then applied to a mixture containing dislike compounds in terms of functional molecular groups. Excess molar volumes from open literature and new experimental ultrasonic velocities of the mixture acetone+methanol+n-hexane were used to compute the corresponding isentropic compressibilities. A good accuracy was obtained when ternary prediction is attempted in this partially soluble mixture at different temperatures by the Collision Factor theory. These results show the versatility of this model for estimation studies in complex multicomponent mixtures enclosing phase splitting.

**Keywords.** *Ultrasonic velocity; isentropic compressibility; acetone; methanol; n-hexane; theoretical model*

### 1. Introduction

In the last few years, nonintrusive automatic ultrasonic techniques has been used for a wide range of applications such as related physico-chemical magnitudes estimation, phase equilibria boundaries studies, critical micelles concentration analysis and mixtures compositions calculation. Although the amount of disposable ultrasonic data has increased in recent years, in what is referred to complex mixtures, the scarce of information is still important, thus the use of mathematical models is essential for both theoretical studies and industrial technology. Into open literature, different methods are available with varying degrees of success (semi empirical mixing rules, associative equilibrium models, equations of state with mixing rules, or statistical mechanical theories) [1-19] although in a whole part, such studies and predictions are related to binary mixtures. Usually, large deviations for predictions of ultrasonic properties are observed when biochemical, polar or selfassociative molecules are involved in multicomponent or partial miscible mixtures, due to the considerable non-ideal behaviour and special aggregation into these complex systems, indeed these facts pose significant challenges. Clearly, for mixtures with complex molecular interactions and/or association phenomena among components, simple mixing rules for ultrasonic velocity cannot be expected to give high precision agreement with experimental data, even when the calculations are supported by experimental data for pure components. Models which predict both association phenomena and complex molecular interactions by means internal parameters are therefore required.

In order to analyze this term, in this work, we present new measurements as a function of temperature of ultrasonic velocity for the ternary mixture

acetone+methanol+n-hexane, different acoustic parameters being derived from these new data as intermolecular free length, collision factor, specific acoustic impedance, or compressibility solvation numbers, due to their importance in terms of theoretical models and understanding internal cohesion into liquid environment. An attempt was made to analyse as Free Length and Collision Factor theories work in prediction of ternary systems where complex interactions exist, as that studied here, as well as the effect of temperature in their estimation capability.

### 2. Experimental

Merck Lichrosolv quality was employed for all chemicals in the preparation of samples. The pure components were stored in inert argon atmosphere (N-55, weaker than 3 ppm in water), degassed with ultrasound technique and stored over molecular sieves type 4a or 3a, 1/16 inch (Aldrich cat. n° 20,860-4 or 20,858-2, respectively) to remove trace amounts of water. The ultrasonic velocity measured experimentally for each component was compared with literature values in Table 1 [20-30]. Precautions were taken, such as cooling chemicals to reduce vapour pressure, before the samples preparation. Vapour space was limited to a minimum into the vessels to avoid preferential evaporation which would lead to composition errors. GLC tests of the solvents showed higher purities than those found in technical specifications supplied by Merck. Their mole fraction purities were better than 0.995 for n-hexane and 0.998 for the other chemicals. A PolyScience controller bath model 9510, ensuring a temperature stability of  $\pm 10^{-2}$  K was used to thermostat the samples. The samples were prepared by mass using a Mettler AE-240 balance with a precision of  $\pm 10^{-4}$  g, which made the maximum error in mole fraction

determination to be  $10^{-4}$ . The ultrasonic velocity of the mixtures and pure chemicals were measured with an Anton Paar DSA-48 device with a precision of  $\pm 1 \text{ ms}^{-1}$ . Calibration of the employed device was performed periodically, using a double fluid reference (Millipore quality water and ambient air). Accuracy in the calculation of changes of isentropic compressibilities was evaluated to be better than  $1 \text{ TPa}^{-1}$ . The immiscibility region was estimated by tie lines correlation, the liquid-liquid study being enclosed in an earlier work [31]. Table 1 shows the experimental data, literature data and other relevant information of the studied pure compounds.

Table 1. Comparison of experimental and literature data for the used pure liquids at 298.15 K.

component	$M^a$ (kg/kmol)	$\rho$ /(gcm <sup>-3</sup> )		$u$ /(ms <sup>-1</sup> )	
		exptl.	lit.	exptl.	lit.
Acetone	58.080	0.7844	0.78440 <sup>b</sup>	1161.0	1162 <sup>e</sup>
			0.78547 <sup>c</sup>		1165 <sup>i</sup>
Methanol	32.042	0.7866	0.78664 <sup>c</sup>	1102.1	1109 <sup>f</sup>
			0.78653 <sup>f</sup>		1104 <sup>j</sup>
n-Hexane	86.178	0.6551	0.65484 <sup>c</sup>	1077.0	1078 <sup>h</sup>
			0.654843 <sup>h</sup>		1076 <sup>k</sup>

References a) 20, b) 21, c) 22, d) 23, e) 24, f) 25, g) 26, h) 27, i) 28, j) 29, k) 30

### 3. Data correlation

The ultrasonic velocity, isentropic compressibility, as well as, the fitting parameters corresponding to the binary mixtures enclosed into the studied ternary mixture were gathered in earlier papers [32-34]. Changes of isentropic compressibility for the ternary mixture at the studied temperatures, as shown in Table 2, were computed applying the following equation:

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

where Q stands for the isentropic compressibility of the mixture and  $Q_i$  is the isentropic compressibility of pure chemicals at the same temperature,  $x_i$  is the molar fraction and N the number of components. The relation between ultrasonic velocity and isentropic compressibility is defined by the Newton-Laplace equation. The necessary data of density of the ternary mixture were taken from literature [35]. The changes of isentropic compressibilities were fitted to a Redlich-Kister type expression for every binary mixture, in accordance to:

$$\delta Q_{ij} = x_i x_j \sum_{p=0}^M \left( \sum_{i=0}^2 (A_{pi} \cdot T^i) \right) \cdot (x_i - x_j)^p \quad (2)$$

where  $\delta Q_{ij}$  stands for the binary derived magnitude,  $A_p$  are the fitting parameters, and M is the degree of the polynomial, established applying the F-test. The  $A_p$  parameters were computed using a non-linear optimization algorithm, each point weighting equally.

The ternary derived magnitudes were fitted to Eq. 3:

$$\delta Q_{123} = \delta Q_{12} + \delta Q_{13} + \delta Q_{23} + \delta Q_{ter} \quad (3)$$

Table 2. Ultrasonic velocity, isentropic compressibilities and changes of isentropic compressibilities for acetone+methanol+n-hexane at 278.15-298.15 K.

T=278.15 K				
$x_1$	$x_2$	$u$ (ms <sup>-1</sup> )	$\kappa_s$ (TPa <sup>-1</sup> )	$\delta\kappa_s$ (TPa <sup>-1</sup> )
0.7981	0.1025	1218.8	861.2	27
0.6909	0.1020	1194.6	924.0	58
0.7410	0.2076	1229.3	833.2	1
0.5821	0.1193	1179.6	969.5	74
0.5986	0.1943	1190.4	931.9	55
0.6072	0.2850	1208.0	879.8	22
0.5002	0.1065	1169.9	1005.2	83
0.4923	0.2085	1175.1	978.8	73
0.4970	0.2864	1183.2	947.5	57
0.5068	0.3858	1201.3	890.6	21
0.4045	0.1005	1162.7	1036.7	85
0.4122	0.1855	1165.6	1016.5	83
0.3993	0.2967	1169.4	992.1	75
0.3967	0.4014	1177.9	954.9	56
0.3970	0.4958	1192.8	905.2	23
0.3064	0.1197	1158.3	1058.8	82
0.3094	0.1935	1158.6	1047.4	85
0.3026	0.2963	1159.6	1030.7	85
0.2960	0.4019	1162.5	1007.0	78
0.2996	0.5008	1169.8	971.0	61
0.2978	0.5975	1183.7	920.6	28
0.2004	0.1215	1155.5	1080.2	72
0.2148	0.2043	1154.6	1070.1	81
0.2054	0.3018	1153.7	1060.1	86
0.2093	0.3941	1154.2	1043.5	87
0.2031	0.4931	1155.5	1023.7	84
0.2122	0.5863	1161.5	988.5	68
0.2046	0.6924	1173.7	938.6	35
0.1014	0.1315	1155.0	1094.0	58
0.1215	0.2108	1152.6	1087.9	72
0.1216	0.2967	1150.9	1081.1	81
0.1056	0.7884	1158.8	968.2	53
0.6432	0.1959	1199.9	905.2	42
0.0689	0.0906	1157.1	1097.3	44
0.0560	0.8929	1162.0	943.2	32
0.0733	0.8219	1153.7	978.0	59
0.1517	0.5954	1152.6	1019.6	83
0.1618	0.4920	1151.6	1040.8	88
0.1415	0.4064	1150.4	1062.6	88
0.1167	0.7002	1151.8	1004.5	76

T=288.15 K				
$x_1$	$x_2$	$u$ (ms <sup>-1</sup> )	$\kappa_s$ (TPa <sup>-1</sup> )	$\delta\kappa_s$ (TPa <sup>-1</sup> )
0.7905	0.1086	1174.1	941.3	32
0.6820	0.1136	1150.4	1009.7	66
0.6870	0.2054	1169.1	951.7	30
0.5779	0.1244	1135.0	1061.6	86
0.5947	0.1998	1146.7	1018.0	64
0.5929	0.2955	1163.5	962.7	29
0.5017	0.1057	1125.0	1102.0	97
0.4888	0.2146	1131.2	1070.6	85
0.4968	0.2952	1141.0	1030.6	66
0.4930	0.3950	1157.4	974.1	30
0.3884	0.1187	1116.9	1139.3	100
0.4000	0.1994	1120.3	1116.0	98
0.3933	0.2996	1125.0	1087.6	89
0.3872	0.4166	1135.2	1040.9	66
0.3987	0.4939	1151.5	984.3	30
0.2982	0.1185	1112.4	1165.5	97
0.2890	0.2073	1112.5	1153.9	101
0.3090	0.2836	1115.3	1130.6	101
0.2992	0.4038	1119.6	1099.3	93
0.2967	0.5037	1127.7	1058.8	73
0.2899	0.6013	1141.9	1004.0	38
0.2027	0.1086	1110.2	1187.6	85
0.2151	0.2046	1109.4	1175.0	98
0.1971	0.3043	1108.5	1165.5	104
0.2147	0.3875	1110.4	1143.0	105
0.2063	0.4968	1112.9	1116.7	100
0.2111	0.5876	1119.8	1077.7	83
0.2046	0.6929	1134.4	1017.5	43
0.1146	0.1246	1109.4	1200.8	73
0.1039	0.2176	1106.8	1198.2	87

0.1191	0.2614	1106.2	1191.7	95
0.0986	0.6965	1107.4	1109.2	101
0.1061	0.7854	1120.2	1050.3	64
0.0558	0.8934	1125.7	1017.1	37
0.0705	0.7333	1104.2	1114.4	105
0.0654	0.0844	1111.6	1206.2	53
0.1042	0.4224	1103.7	1176.2	110
0.1150	0.4912	1104.1	1160.5	113
0.1207	0.5520	1105.1	1144.3	112
0.1098	0.3137	1105.0	1188.9	101
0.0969	0.6465	1104.6	1129.6	110

T=298.15 K				
$x_1$	$x_2$	$u$ (ms <sup>-1</sup> )	$\kappa_S$ (TPa <sup>-1</sup> )	$\delta\kappa_S$ (TPa <sup>-1</sup> )
0.7885	0.1120	1129.9	1030.7	37
0.6875	0.1181	1107.4	1102.8	73
0.6782	0.2225	1127.2	1035.7	31
0.5764	0.1252	1089.8	1168.5	100
0.5939	0.2076	1103.4	1113.4	73
0.6119	0.2845	1123.4	1044.5	32
0.5031	0.1044	1079.6	1214.2	112
0.4866	0.2195	1086.9	1176.1	99
0.5025	0.2964	1098.9	1124.9	75
0.4937	0.4045	1117.9	1055.5	31
0.3837	0.1319	1071.8	1254.2	116
0.3955	0.2074	1075.7	1227.4	114
0.3901	0.3095	1081.6	1192.1	104
0.3857	0.4213	1093.5	1136.6	77
0.3975	0.5039	1113.0	1064.8	32
0.2942	0.1180	1067.2	1285.9	111
0.2953	0.1995	1068.0	1270.2	117
0.3076	0.3203	1072.9	1231.9	116
0.2903	0.4185	1076.9	1204.0	108
0.2910	0.5137	1086.6	1155.0	85
0.2913	0.6107	1105.1	1082.1	38
0.1918	0.1201	1064.7	1310.2	97
0.2007	0.2086	1064.1	1297.8	112
0.1922	0.3147	1064.0	1282.4	122
0.2012	0.3971	1066.1	1259.1	125
0.2008	0.5035	1070.4	1224.0	118
0.1966	0.6089	1078.8	1175.4	96
0.2006	0.6999	1096.0	1103.6	50
0.0878	0.1408	1063.7	1327.3	82
0.1003	0.2186	1061.8	1320.9	101
0.1018	0.3132	1060.5	1310.9	117
0.0943	0.4145	1059.5	1298.5	129
0.0974	0.5081	1059.9	1278.2	135
0.1003	0.6065	1062.5	1247.3	132
0.1019	0.7014	1068.8	1203.4	114
0.0531	0.7053	1059.8	1241.9	136
0.0537	0.5977	1057.1	1277.0	142
0.0547	0.4057	1057.8	1313.1	127
0.1973	0.7005	1095.3	1105.9	52
0.0995	0.7909	1081.7	1141.1	75

where the binary magnitudes were fitted to Eq. 2, and the ternary contribution ( $\delta Q_{ter}$ ) by the Nagata equation [36]:

$$\delta Q_{ter} = x_1 x_2 x_3 RT \cdot (B_0 - B_1 x_1 - B_2 x_2 - B_3 x_1^2 \dots \dots - B_4 x_2^2 - B_5 x_1 x_2 - B_6 x_1^3 - B_7 x_2^3 - B_8 x_1^2 x_2) \quad (4)$$

Figures 1a, b, and c show curves of constant ternary changes of isentropic compressibilities by application of Eqs. 3 and 4, for the three studied temperatures. In Table 3, the fitting parameters corresponding to these equations are enclosed. The root mean square deviations gathered were computed using the Eq. 5. In this equation,  $z$  is the value of the derived property, and  $n_{DAT}$  is the number of experimental data:

$$\sigma = \sqrt{\frac{\sum_i^{n_{DAT}} (z_{EXP} - z_{PRED})^2}{n_{DAT}}} \quad (5)$$

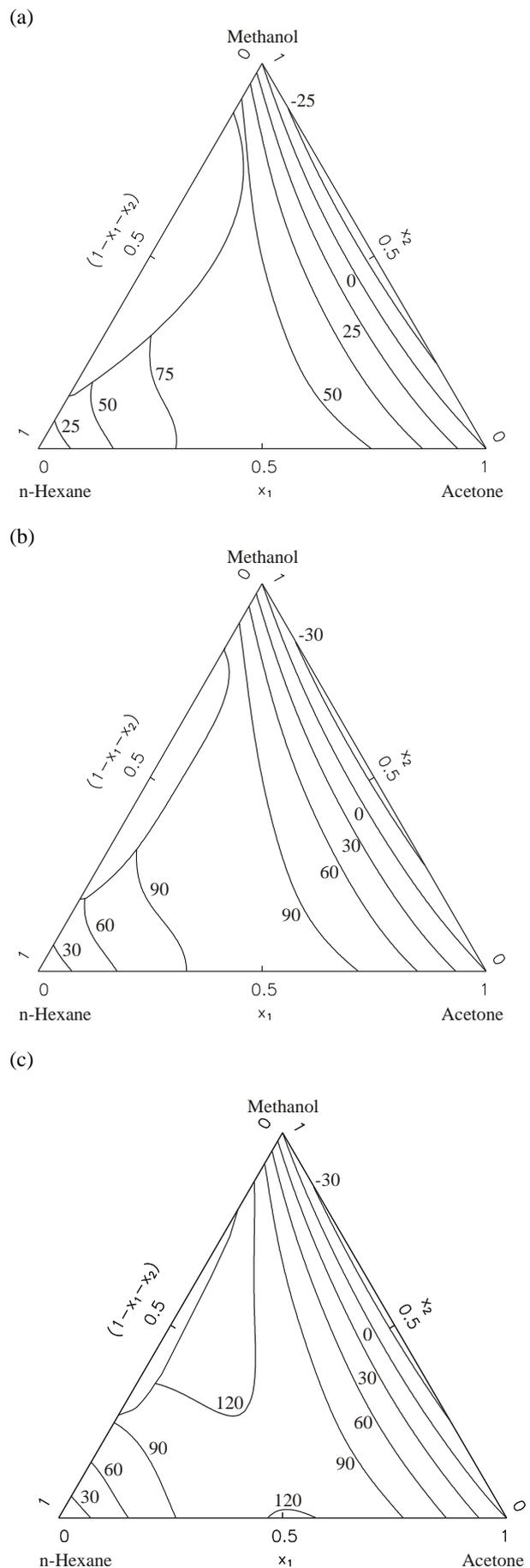


Figure 1. Constant value lines of ternary changes of isentropic compressibilities using Eqs. 3 and 4 at (a) 278.15 K, (b) 288.15 K and (c) 298.15 K.

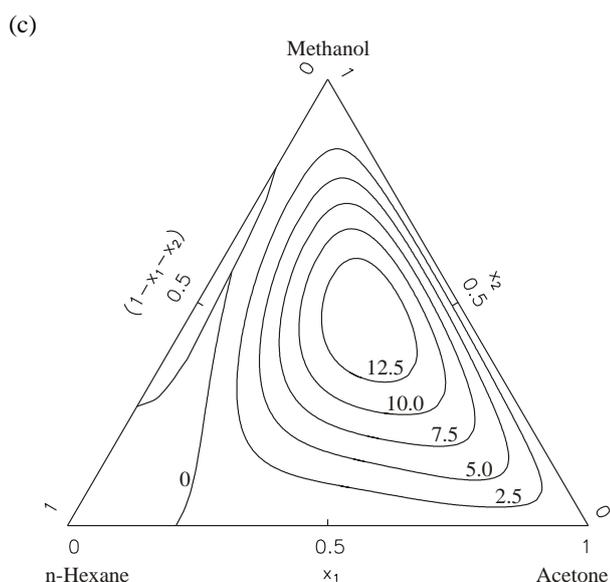
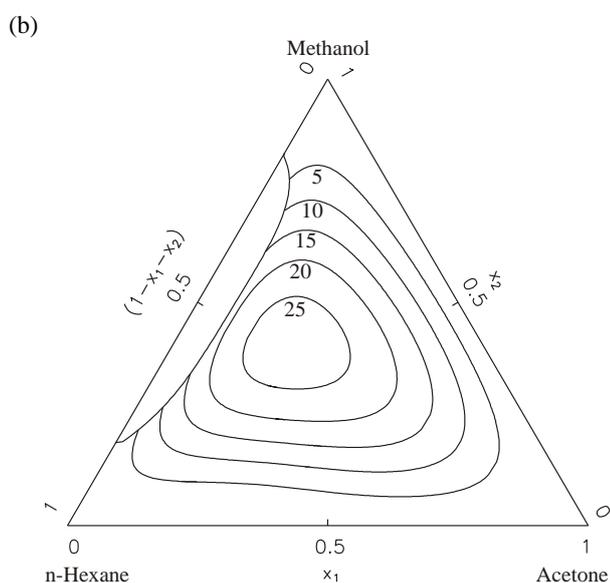
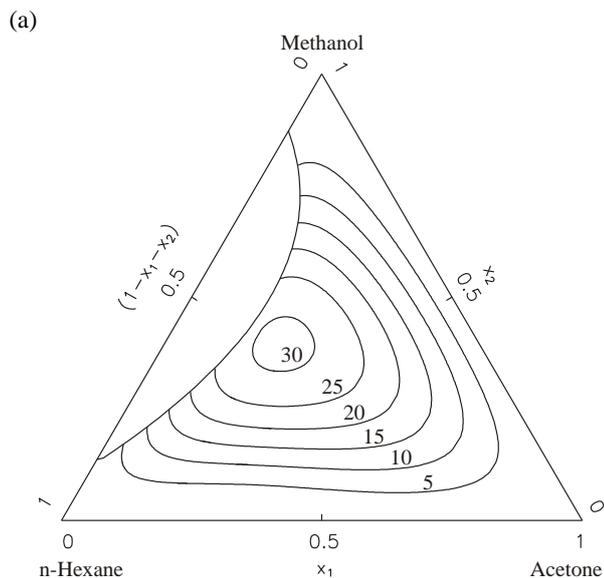


Figure 2. Constant value lines of ternary contribution ( $\delta Q_{\text{ter}}$ ) to the changes of isentropic compressibilities in accordance with Eq. 4 at (a) 278.15 K, (b) 288.15 K and (c) 298.15 K.

Table 3. Parameters of Eqs. 3 and 4 and root mean square deviations ( $\sigma$ ) in accordance to Eq. 5.

T=278.15 K		
$B_0=0.256338$	$B_1=1.806590$	$B_2=-2.024779$
$B_3=-4.001887$	$B_4=2.742504$	$B_5=-0.118894$
$B_6=2.379625$	$B_7=-0.561498$	$B_8=2.171638$
$\sigma=1.05$		
T=288.15 K		
$B_0=0.219148$	$B_1=1.823809$	$B_2=-1.709702$
$B_3=-4.437367$	$B_4=2.095675$	$B_5=-0.155719$
$B_6=2.885180$	$B_7=-0.324732$	$B_8=2.019121$
$\sigma=0.94$		
T=298.15 K		
$B_0=-0.115389$	$B_1=-0.929835$	$B_2=0.195056$
$B_3=2.188979$	$B_4=-0.730483$	$B_5=-0.919766$
$B_6=-1.845800$	$B_7=0.292767$	$B_8=0.178095$
$\sigma=1.08$		

Figures 2a, b, and c show curves of constant ternary contribution to the changes of isentropic compressibilities ( $\delta Q_{\text{ter}}$ ) in accordance to the Eq. 4, for the studied temperatures.

## 4. Derived properties

### 4.1 Acoustic parameters

We have attempted to explain the physico-chemical behaviour of the studied ternary mixture, in order to explore the strength and nature of the interactions between the components by deriving various thermodynamic parameters from the new collection of ultrasonic velocity and open literature 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 ( $Ra$ ), collision factor ( $S$ ), and specific acoustic impedance ( $Z$ ), attending to the following set of equations:

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

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

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

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

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

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

$$V_0 = V - V_a \quad (12)$$

Table 4. Acoustic parameters computed from the measured experimental data for application into Collision Factor theory (CFT) and Free Length theory (FLT) to predict the isentropic compressibilities of the ternary mixture acetone+methanol+n-hexane at different temperatures.

Collision Factor Theory						
	B (characteristic molecular volume, cm <sup>3</sup> )			S (collision factor)		
	278.15 K	288.15 K	298.15 K	278.15 K	288.15 K	298.15 K
Acetone	15.65			3.595	3.515	3.433
Methanol	11.83			2.458	2.414	2.372
n-Hexane	33.20			2.816	2.742	2.667

Free Length Theory						
	Y (liquid internal surface, cm <sup>2</sup> )			L <sub>f</sub> (free length, cm)		
	278.15 K	288.15 K	298.15 K	278.15 K	288.15 K	298.15 K
Acetone	6.030 10 <sup>9</sup>	6.086 10 <sup>9</sup>	6.145 10 <sup>9</sup>	5.053 10 <sup>-9</sup>	5.076 10 <sup>-9</sup>	5.101 10 <sup>-9</sup>
Methanol	4.071 10 <sup>9</sup>	4.102 10 <sup>9</sup>	4.135 10 <sup>9</sup>	4.089 10 <sup>-9</sup>	4.105 10 <sup>-9</sup>	4.121 10 <sup>-9</sup>
n-Hexane	8.854 10 <sup>9</sup>	8.927 10 <sup>9</sup>	9.013 10 <sup>9</sup>	6.131 10 <sup>-9</sup>	6.156 10 <sup>-9</sup>	6.186 10 <sup>-9</sup>

$$Ra = \frac{M \cdot u^{1/3}}{\rho} \quad (13)$$

$$S = \frac{u \cdot V}{B \cdot u_{\infty}} \quad (14)$$

$$Z = u \cdot \rho \quad (15)$$

where  $u_{\infty}$  is a constant taken as 1600 ms<sup>-1</sup>, K is a temperature polynomial dependent parameter expressed as  $K = (93.875 + 0.375 \cdot T) \cdot 10^{-8}$ , and R and  $\Pi$  are common universal constants.

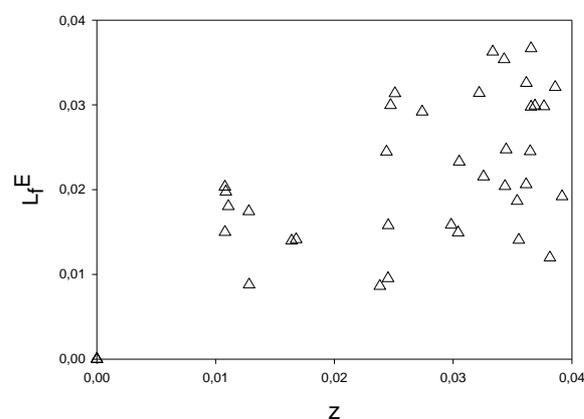
Several parameters of the pure compounds are gathered in Table 4, for application into calculations of the Collision Factor and Free Length theories. For example, the variation of the magnitudes  $L_f$  and Z (by means of Eq. 1) for the ternary mixtures are shown in the Figures 3a and 3b, respectively, 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. This procedure is a simple way to visualise in a 2 dimension diagram, ternary plots, the lowest values of z corresponding to pseudobinary compositions and the largest values of the abscise value (z magnitude) corresponding to equimolar compositions (the centre of the Gibbs composition triangle).

As observed, excess free length increases from pseudobinary region towards bulk ternary compositions which is coincident with the expansive trend of this mixture, as previously reported [35]. Specific acoustic impedance is a measure of the opposition that a mixture presents to the acoustic flow resulting of an acoustic pressure applied to the system, thus is a quantity which depends on the molecular packing of the mixture. The negative values of excess specific acoustic impedance are in accordance with the presence of weak interactions between the components into mixture, as previously commented. The tendency of the excess specific acoustic impedance should be explained in a similar way, a progressive diminution of this excess magnitude is observed towards more complex mixture (higher values of z and then, far away of pseudobinary conditions) which reflects weaker interactions than those observed close to the binary compositions.

(a)



(b)

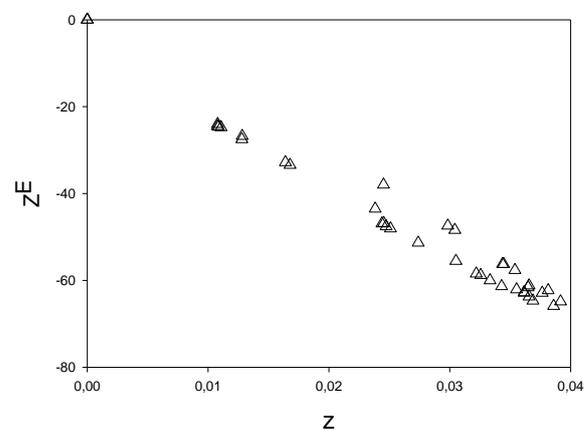


Figure 3. (a) Excess free length ( $\text{\AA}$ ) and (b) excess specific acoustic impedance ( $\text{gcm}^{-3}\text{ms}^{-1}$ ) for the ternary mixture acetone+methanol+n-hexane at 298.15 K

#### 4.2 Compressibility solvation numbers

Despite solvation numbers of covalent molecules into aqueous solution are key parameters necessary when discussing intermolecular interactions or interfacial phenomena, these data are extremely scarce and dispersed into open literature. If the search for these data was related to other solvent than water, the situation is still worse. Solvation numbers are based on isentropic compressibilities, a parameter easily derived from acoustic measurements, as previously commented. The connexion between compressibility solvation numbers and isentropic

compressibility is almost intuitive, solvation process involves a strong force field around solute molecule, acting as pressure, being clear that compressibility decreases with pressure due to decreasing intermolecular distances produces a progressive rising in terms of intermolecular forces of repulsion.

The compressibility solvation numbers are calculated using the following equation, attending to usual expressions [34]:

$$n_s = \left( \frac{n_{\text{solvent}}}{n_{\text{solute}}} \right) \cdot \left( 1 - \frac{\kappa_s}{\kappa_{s0}} \right) \quad (16)$$

where  $n_{\text{solvent}}$  and  $n_{\text{solute}}$  are the mol number of solvent and solute into a binary mixture, respectively.

The equation used for computing compressibility solvation numbers assumes that the solvation layer around the corresponding solute molecule is incompressible, which is not the case. Despite this, it provides an acceptable approximation of the extent of interaction of the solute with solvent. These parameters are derived from isentropic compressibility measurements and therefore, account for the first two layers of solvent around the solute.

For example, Figures 4a and 4b show the evolution of the compressibility solvation numbers for the binary mixtures acetone+n-hexane as a function of temperature (278.15 K, 288.15 K and 298.15 K) and the enclosed mixtures into ternary system, acetone+methanol, acetone+n-hexane and methanol+n-hexane at 298.15 K, respectively. As observed, only a slight effect is produced by variation of temperature at the studied range (Figure 4a). The binary systems acetone+n-hexane and methanol+n-hexane show negative compressibility solvation numbers (Figure 4b). When the temperature is increased from 278.15 to 298.15 K, there is a corresponding decrease in the ultrasonic velocity and then, an increment of entropy of the system, the strongest values of solvation numbers being observed for low temperatures. The negative solvation numbers reflect strong interactions; this effect could be ascribed to longer lifetimes hydrogen bonds or polar interactions.

## 5. Ultrasonic velocity modelling

In this case, consideration was given to the Jacobson (Free Length Theory) [16] and Schaffs-Nutsch-kuhnkies (Collision Factor Theory) [17-19] methods to estimate the isentropic compressibility for the ternary mixture.

The Free Length Theory (FLT) estimates the isentropic compressibility of a mixture attending to the free displacement of molecules ( $L_f$ ) as a main function of temperature (Eq. 17).

$$\kappa_s = \left( \frac{L_f^2}{K^2} \right) \quad (17)$$

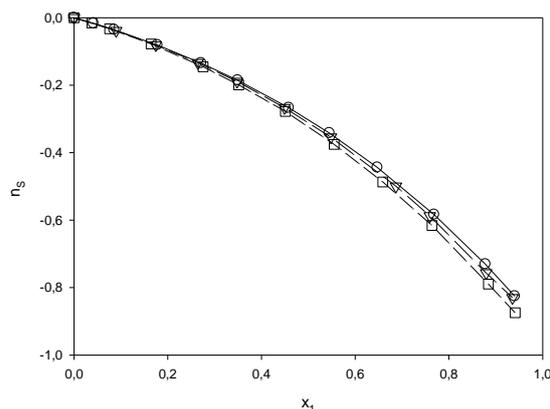
The Collision Factor theory (CFT) is dependent on the collision factors among molecules as a function of temperature into pure solvent or mixture (Eq. 18). The pertinent relations in these calculations and its theoretical basis were described at the literature cited.

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 paper, and the corresponding molar volumes from open literature [35]. These values could be also evaluated by means a group contribution method, when no experimental ones are disposable [37].

$$\kappa_s = \left( \frac{1}{\rho^3} \right) \cdot \left( \frac{M}{u_\infty \cdot \sum_i x_i S_i \cdot \sum_i x_i B_i} \right)^2 \quad (18)$$

(a)



(b)

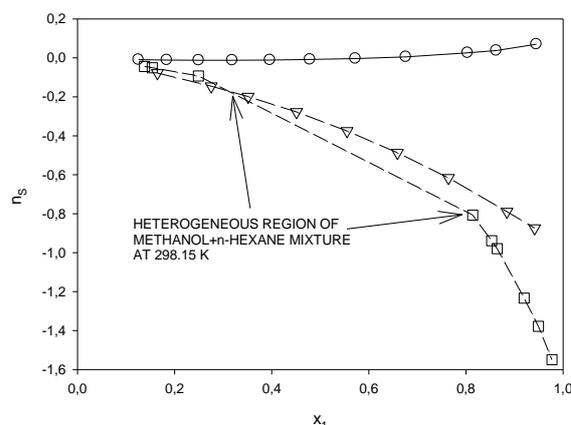


Figure 4. Compressibility solvation number for the binary mixtures (a) acetone+n-hexane as a function of temperature (O, 278.15 K;  $\nabla$ , 288.15 K;  $\square$ , 298.15 K) and (b) acetone+methanol (O), acetone+n-hexane ( $\nabla$ ) and methanol+n-hexane ( $\square$ ) at 298.15 K [32-34].

In Table 4, the models' parameters are gathered. The application of Collision Factor theory (CFT) presents lower deviation values when predicting the isentropic compressibilities in the ternary mixture (Figure 5). These values are closer to those experimental at the neighbouring of binaries (low z values).

These figures show the excess magnitude as a function of  $z = \prod_i x_i$ , where  $x_i$  is the molar fraction, as previously explained. These estimations by CFT are accuracy with mean deviations better than 5 %, as could be observed in Table 5. The FLT over predicts values of isentropic compressibility and this fact is increased with temperature (Figure 6). Errors higher than 10 % are encountered for

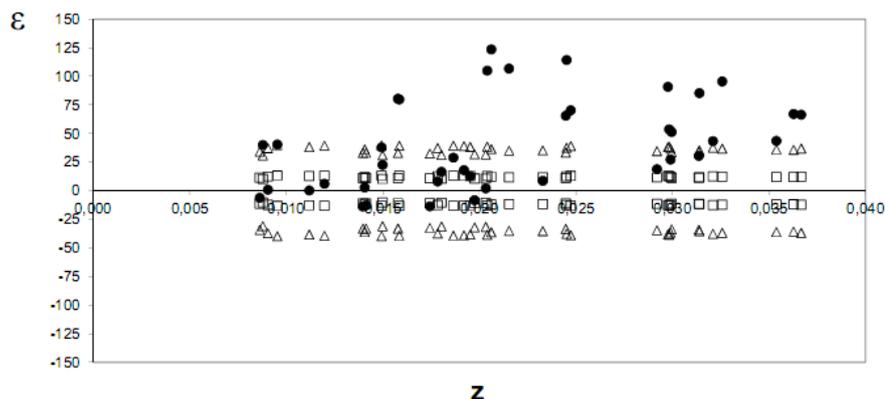


FIGURE 5. Deviations ( $TPa^{-1}$ ) ( $\Delta\kappa_S = \kappa_{S,exp} - \kappa_{S,CFT}$ , ( $\square$ )  $\pm 1\%$ ; ( $\Delta$ )  $\pm 3\%$ ) from experimental isentropic compressibilities ( $\epsilon$ ) for the ternary mixture acetone+methanol+n-hexane at 298.15 K for the Collision Factor theory (CFT). The experimental values of the measured mixture are shown through the solid line of zero value.

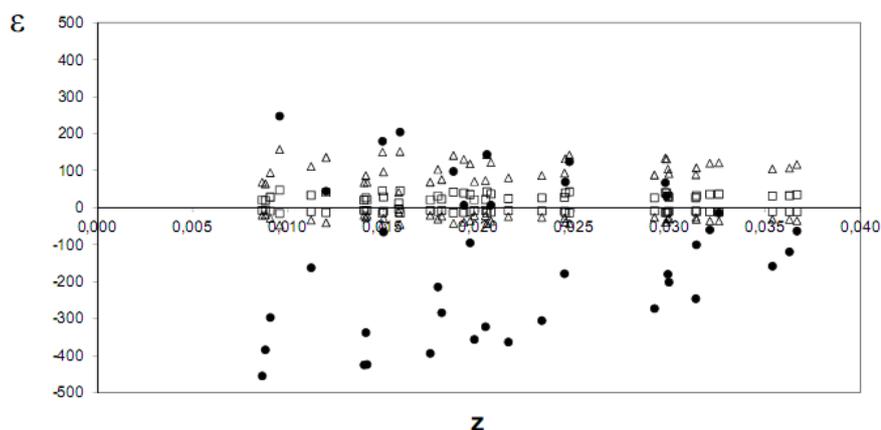


FIGURE 6. Deviations ( $TPa^{-1}$ ) ( $\Delta\kappa_S = \kappa_{S,exp} - \kappa_{S,FLT}$ , ( $\square$ )  $\pm 1\%$ ; ( $\Delta$ )  $\pm 3\%$ ) from experimental isentropic compressibilities ( $\epsilon$ ) for the ternary mixture acetone+methanol+n-hexane at 298.15 K for the Free Length theory (FLT). The experimental values of the measured mixture are shown through the solid line of zero value.

ternary estimations at 298.15 K. This model does not show an adequate tendency at equimolar compositions where high interactions are observed, as showed at high ternary compositions.

Table 5. Root mean square deviations ( $TPa^{-1}$ ) from experimental data for the estimation of isentropic compressibilities by Free Length theory (FLT) and Collision Factor theory (CFT) for acetone+methanol+n-hexane at 278.15-298.15 K

Free Length Theory		
278.15 K	288.15 K	298.15 K
0.235	0.226	0.231
Collision Factor Theory		
278.15 K	288.15 K	298.15 K
0.045	0.024	0.025

## 6. Results and Discussion

In this work, we present new measurements of ultrasonic velocity for the ternary mixture acetone+methanol+n-hexane. Attending to the complex interaction and the temperature dependence of phase splitting, this partially miscible mixture was selected to test the ability of different models to predict multicomponent isentropic compressibilities.

As it could be expected, attending to the molecular structure of solvents into this mixture, three different trends could be observed: a hydrogen bond interaction domains acetone+methanol mixture yielding to negative

values (negative deviation from ideality) of the derived property into the corresponding binary mixture and neighbouring ternary compositions (see right side of Figure 1). A phase splitting occurs in methanol+n-hexane mixtures when neither methanol nor n-hexane is the most abundant component. The acetone+n-hexane mixture shows expansive trend with a maximum of derived property located at equimolar composition, due to the disruption of the polar interaction among ketone molecules by the inert diluent. This behaviour is extrapolated to near ternary compositions such predominant interaction being attenuated by the rising composition of the third solvent. The auto associative behaviour of methanol is the cause of contractive tendency with acetone (slight polar carbonyl group) and partial immiscibility with n-hexane (inert aliphatic molecule). Acetone and n-hexane mixtures show high expansive trend but the polar difference is weak enough for phase splitting at ambient temperature, although liquid-liquid equilibria has been experimentally determined at lower conditions [38].

Attending to this trend, it is not surprising to observe a symmetric attenuation forwards diluted ternary compositions (Figure 1).

The mathematical structure of Eq. 3 leads to analyze the ternary contribution  $\delta Q_{ter}$  (simultaneous interactions among all compounds into mixture) in terms of Eq. 4, in what is referred to shape and sign (Figures 2a, b and c).

This contribution shows two pointing out questions: firstly, the considerable contribution to the derived

property by ternary molecular interactions, although its a decreasing factor for higher temperatures (from 30% to 10% of the total value); second, the approximately equimolecular maximum in ternary contribution with only negative values for the highest studied temperature at rich n-hexane composition (see left side of Figure 2c).

Such trend is normal due to the evolution of the physical property as a function of molar fraction. The rupture of alcohol+ketone structure when the aliphatic hydrocarbon is introduced is reflected in the isentropic compressibility by a strong and continuous decreasing trend. The solvation layer around the n-hexane is dissolved faster as temperature rises which may also be true for the whole set of aliphatic linear hydrocarbons. A global weakening of intermolecular interactions is observed which could be used to account for the isentropic compressibilities. n-Hexane is a non-polar linear aliphatic molecule and only van der Waals interactions occur while H-bond or polar interactions are observed into methanol or acetone environment. In methanol+n-hexane mixtures, the alcohol molecules associate forming clusters into apolar medium. Molecular association is an important factor for observed deviations of theoretical models, it is not taken into account in these procedures and they are inadequate for a properly description of the mixing process of complex systems.

An attempt was made to analyse as Free Length and Collision Factor theories work in prediction of this ternary system where complex interactions exist, as well as the effect of temperature.

The Collision Factor theory considers that the elastic nature of the molecules enclosed into mixture is responsible for the molecular interaction, while the Free Length theory assumes that molecules are rigid with no interaction and the later hypothesis is not valid in the present mixture. The predictive abilities of these ultrasonic theories depend upon the strength of the interactions prevailing throughout the composition space in this ternary system. These theories generally fail to predict accurately the sonic trend where strong effects as H-bonds or polar interactions exist, but attending to the obtained deviations for both methods, CFT shows better agreement than the other procedure at the studied temperatures.

Both models are, at least, of qualitative accuracy to predict ternary values of isentropic compressibility (Figures 5 and 6), showing CFT a lower deviation for the whole composition range. Deviations yielded for the estimated ternary magnitude also show dependence with the temperature (Table 5), and can be considered as a satisfactory result for this model, supporting its validity as predictive tool, having in mind the high non-ideality of the tested ternary mixture, where both associative and phase splitting phenomenon occurs.

## 7. Conclusions

Ultrasonic velocity has been a subject of core interest during the recent past years due to measurements of this magnitude in solutions formed by liquid components show the degree of deviation from ideality behaviour. These deviations have been used to gain insight into nature and degree of interactions among the enclosed molecules into the studied systems. Accurate data of ultrasonic velocity as a function of composition and temperature/pressure helped

to understand the nature of molecular interactions in complex systems and extreme operational conditions.

## Acknowledgments

The authors would like to thank CAPES (Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior) for the financial support for developing this research.

## Nomenclature

$A_{ip}$  – fitting parameters  
 $b$  – van der Waals' constant ( $\text{cm}^3\text{mol}^{-1}$ )  
 $B$  – geometrical volume ( $\text{m}^3$ )  
 $B_0, B_1, B_2, B_3, B_4, B_5, B_6, B_7, B_8$  – Fitting parameters of Eq. 4  
 $L_f$  – Intermolecular free length (cm)  
 $M$  – molar mass ( $\text{gmol}^{-1}$ )  
 $n$  – number of experimental data  
 $n_S$  – solvation number  
 $n_{\text{solvent}}$  – solvent mole number  
 $n_{\text{solute}}$  – solute mole number  
 $N$  – Avogadro number  
 $Q$  – mixing thermodynamic magnitude  $Q$   
 $Q_i$  – thermodynamic magnitude  $Q$  of a component  $i$   
 $r$  – molecular radius (cm)  
 $R$  – Universal constant of gases ( $\text{Jmol}^{-1}\text{K}^{-1}$ )  
 $R_a$  – molar sound velocity ( $\text{cm}^3\text{mol}^{-1}(\text{ms}^{-1})^{1/3}$ )  
 $S$  – collision factor  
 $T$  – temperature (K)  
 $u$  – ultrasonic velocity ( $\text{ms}^{-1}$ )  
 $u_{\infty}$  – ultrasonic velocity constant ( $1600 \text{ms}^{-1}$ )  
 $V_a$  – available volumen ( $\text{cm}^3$ )  
 $V$  – molar volume ( $\text{cm}^3\text{mol}^{-1}$ )  
 $V_0$  – volume at absolute zero ( $\text{cm}^3$ )  
 $x_i$  – molar fraction of  $i$  compound  
 $x_j$  – molar fraction of  $j$  compound  
 $Y$  – molar surface area ( $\text{cm}^2$ )  
 $z$  – value of a variable  
 $Z$  – specific acoustic impedance ( $\text{gcm}^{-3}\text{ms}^{-1}$ )  
 $\delta Q$  – change of a thermodynamic magnitude  $Q$  for a mixture  
 $\delta Q_{ij}$  – change of a thermodynamic magnitude  $Q$  for a binary mixture of compounds  $i$  and  $j$   
 $\delta Q_{123}$  – change of a thermodynamic magnitude  $Q$  for a ternary mixture of compounds 1, 2 and 3  
 $\delta Q_{12}$  – change of a thermodynamic magnitude  $Q$  for a binary mixture of compounds 1 and 2  
 $\delta Q_{13}$  – change of a thermodynamic magnitude  $Q$  for a binary mixture of compounds 1 and 3  
 $\delta Q_{23}$  – change of a thermodynamic magnitude  $Q$  for a binary mixture of compounds 2 and 3  
 $\delta Q_{\text{ter}}$  – ternary contribution for a change of a thermodynamic magnitude  $Q$   
 $\kappa_S$  – isentropic compressibility of a mixture ( $\text{TPa}^{-1}$ )  
 $\kappa_{S0}$  – isentropic compressibility of a solvent into a binary mixture ( $\text{TPa}^{-1}$ )  
 $\Pi$  – pi number  
 $\rho$  – density of a mixture ( $\text{gcm}^{-3}$ )  
 $\sigma$  – root mean square deviation

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