Hydroxylic molecular interaction by measurement of ultrasonic velocity as a function of temperature: Ethanol+water+1-pentanol

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Abstract−An analysis of different thermodynamic properties as a function of temperature provides valuable information about their characteristics. The ultrasonic velocity of the ternary mixtures ethanol+water+1-pentanol at the range 288.15-323.15 K and atmospheric pressure, has been measured over the whole concentration range. The experimental ultrasonic velocities have been analysed in terms of different theoretical models, an adequate agreement between the experimental and predicted values both in magnitude and sign being obtained, despite the high non-ideal trend and partial miscibility of the ternary mixture studied in this work. The obtained experimental values indicate varying extent of interstitial accommodation among unlike molecules as a function of steric hindrance attending to 1-pentanol as key component and as a function of hydrogen bond and temperature attending to ethanol as key component.

Key words: Ultrasonic Velocities, Isentropic Compressibility, Estimation, Ethanol, Water, 1-Pentanol, Temperature

INTRODUCTION

Knowledge of thermodynamic properties of ethanol, water and the different flavour components in distillated alcoholic beverages is of practical interest to the food industry to obtain a quality final product since industrial procedures applied are close related on their temperature and pressure dependence. Nowadays, the use of physics methods to mixture analysis yield better results than current chemistry procedures showing higher accuracy and on-line application capability to study liquid phase characteristics and mixing phenomena. Thermodynamics studies provide the additional advantage of an interesting trend of analysis of microscale interaction for understanding macroscale behaviour of gases and liquids on mixing condition. In accordance to that, in the last few years, a considerable effort has been developed in the field of thermodynamic properties although a great scarce of data is observed in open literature for mixtures enclosed into commercial alcoholic beverages. Such properties are strongly dependent on hydrogen-bond potency of hydroxyl groups, chain length, isomeric structures, and molecular packages. In what is referred to as ultrasonic data the situation is worse. Attending to the different origin of grapes, thermal conditions of fermentation reactions and the complexity of composition and molecular chains of components, currently a considerable lack of accuracy or thermodynamic consistency can be observed in the scarce disposable open literature data. In what is referred to as multicomponent mixtures, the scarcity of data references is greater, due to the relatively important non-ideality, as well as the complexity of a wide study and the time-consuming experimental procedures. Simulation and optimization are not used in the right way in this field, an overestimation of equipment or high energy-consuming conditions being usually applied due to inaccurate calculations. The dif-

ficulties of simulation in these types of processes have been commented upon previously [Gaiser et al., 2002]. As a continuation of previous works related to alcoholic beverage components [Resa et al., 2003, b], we present in this paper the temperature dependence of the isentropic compressibilities of the mixture ethanol+water+1-pentanol at the range 288.15-323.15 K and atmospheric pressure, as a function of molar fraction. From the experimental values, the corresponding changes of isentropic compressibility were computed, a temperature-dependent Cibulka type polynomial being fitted to the results [Cibulka, 1990]. Due to the expense of the experimental measurement of such data and current processes design is strongly computer oriented, consideration was also given to how accurate theoretical models work. Despite the importance of computation in chemical processes, the theoretical procedures published in scientific journals are far from being accurate and of wide application. 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 behaviour in enclosing slight polar molecules into hydroxylic environment. Different procedures [Danusso, 1951; Nomoto, 1968; Nutschkuhnkies, 1965; Schaffs, 1975; Jacobson, 1952] were applied for the isentropic compressibility, the obtained results being analysed, and commented upon. Attending to the deviation of computed data, we arrive at the conclusion that the application of the FLT model produces the theoretically closest results, despite the high non-ideal trend of mixture and partial miscibility and partial miscibility.

EXPERIMENTAL

All chemical solvents used in the preparation of samples were of Merck quality with richness better than 99.5 mol. The pure components were stored in sun light protected form and constant humidity and temperature. In order to reduce fraction molar errors, the

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Table 1. Comparison of experimental speed of sound (m·s⁻¹) with literature data for chemicals at the studied temperatures

Component	Molecular weight [12]	288.15 K	290.65 K	293.15 K	295.65 K	298.15 K	300.65 K	303.15 K	305.65 K	308.15 K	310.65 K	313.15 K	315.65 K	318.15 K	320.65 K	323.15 K	lit. (298.15 K)
Ethanol	46.1	1178.2	1169.1	1160.3	1151.6	1143.1	1134.6	1126.2	1117.8	1109.4	1101	1092.7	1084.3	1075.9	1067.5	1058.8	1142.6 [13]
Water	18.0	1466.4	1474.7	1482.5	1489.9	1496.9	1503.4	1509.5	1515.1	1520.3	1525.0	1529.3	1533.2	1536.6	1539.6	1542.1	1498 [14]
1-Pentanol	88.1	1307.8	1299.1	1290.4	1281.8	1273.3	1264.9	1256.6	1248.3	1240.0	1231.7	1223.4	1215.2	1206.8	1198.5	1190.1	1276 [15] 1277 [16]

vapour space into the vessels was minimized during samples preparation. Mixtures were prepared by mass using a Salter ER-182A balance, the whole composition range of the ternary mixture being covered. The accuracy in molar fractions was obtained as higher than $\pm 5 \times 10^{-4}$. The ultrasonic velocities were measured with an Anton Paar DSA-48 device with a precision of ± 1 m·s⁻¹. Calibration of the apparatus was performed periodically, in accordance with technical specifications, using Millipore quality water (resistivity, 18.2 MΩ·cm) and ambient air. Maximum deviation in the calculation of changes of isentropic compressibility for these mixtures have been estimated better than 1 TPa⁻¹. The values of the pure components, as well as, open literature data are in Table 1. More details about techniques and procedure in our laboratory can be obtained from previously published works [Resa et al., 2003a].

DATA PROCEDURE

1. Correlation of Derived Magnitudes

The changes of isentropic compressibility are presented in Table 2 and were computed from the Eq. (1):

$$\delta Q = Q - \sum_{i=1}^{N} x_i Q_i \tag{1}$$

In this equation, δQ means the variation of a magnitude Q (κ_S, isentropic compressibility calculated by the Laplace-Newton 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 [Redlich and Kister, 1948] type equation was used to correlate the derived properties of the binary mixtures, by the unweighted least squares method, all experimental points weighting equally:

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

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, 1969]. These binary parameters were collected from previous works [Gayol et al., 2005; Resa, 2003b]. The B_p parameters were computed by using a non-linear optimization algorithm due to Marquardt [1963]. The ternary derived magnitudes were fitted to the equation:

$$\delta Q_{123} = \delta Q_{12} + \delta Q_{13} + \delta Q_{23} + \Delta_{123} \tag{3}$$

where the binary magnitudes δQ_{ij} have been correlated to Eq. (2) and Δ_{123} is the ternary contribution fitted by means of a modified Cibulka equation [Resa et al., 2003a]:

$$\Delta_{123} = x_1 x_2 x_3 RT \cdot (B_0 + B_1 x_1 + B_2 x_2) \tag{4}$$

Table 2. Ultrasonic velocities. isentropic compressibility and change of isentropic compressibility for ternary mixture at range of 288.15-323.15 K

x_1	x_2	$u/(\text{m·s}^{-1})$	$\kappa_S/(\text{TPa}^{-1})$	$\delta\kappa_S/(\text{TPa}^{-1})$	x_1	x_2	$u/(\text{m·s}^{-1})$	$\kappa_S/(\text{TPa}^{-1})$	$\delta\kappa_S/(\text{TPa}^{-1})$
				323.15 K					
0.8981	0.0523	1085.7	1099.2	−15.8	0.3000	0.3014	1193.2	873.9	40.2
0.0498	0.0458	1189.5	891.1	7.4	0.2871	0.4241	1212.6	833.9	60.9
0.8037	0.0947	1108.3	1045.9	−23.2	0.2992	0.4993	1230.4	799.6	58.2
0.6996	0.2006	1154.0	948.0	−43.0	0.3007	0.6001	1273.8	727.9	33.1
0.6014	0.2984	1171.0	909.3	−9.1	0.2009	0.0988	1181.6	903.3	2.6
0.5974	0.1010	1139.6	981.0	−28.3	0.2008	0.1996	1190.0	884.9	31.2
0.5014	0.3983	1202.7	848.1	3.8	0.2031	0.3003	1199.4	864.5	57.0
0.5005	0.3000	1178.0	898.1	8.3	0.1995	0.4009	1212.4	837.2	77.5
0.4983	0.2017	1163.2	931.1	−3.9	0.2003	0.5006	1229.4	803.0	89.6
0.5012	0.0963	1151.0	959.2	−25.6	0.1999	0.7001	1310.4	672.7	52.3
0.4010	0.0955	1162.0	938.6	−18.9	0.1004	0.1029	1190.6	887.4	16.4
0.4002	0.1992	1172.7	914.4	5.4	0.1032	0.2046	1197.1	873.3	48.8
0.3986	0.3022	1186.1	885.0	24.3	0.0986	0.3001	1205.9	854.5	75.8
0.4010	0.3988	1204.2	847.6	31.3	0.0994	0.3996	1216.5	832.1	99.5
0.4005	0.4981	1236.8	787.8	17.9	0.1479	0.0469	1175.1	915.1	4.8
0.3026	0.0958	1172.1	920.2	−10.0	0.2520	0.0482	1168.7	927.2	−11.1
0.2968	0.2023	1182.3	897.8	18.8	0.1500	0.8005	1391.3	575.4	15.5

Table 2. Continued

x_1	x_2	$u/(m \cdot s^{-1})$	$\kappa_S/(TPa^{-1})$	$\delta\kappa_S/(TPa^{-1})$	x_1	x_2	$u/(m \cdot s^{-1})$	$\kappa_S/(TPa^{-1})$	$\delta\kappa_S/(TPa^{-1})$
				320.65 K					
0.8981	0.0523	1094.2	1079.1	−15.4	0.3000	0.3014	1201.7	859.4	37.8
0.0498	0.0458	1198.1	876.3	6.9	0.2871	0.4241	1220.8	820.7	57.8
0.8037	0.0947	1116.8	1027.1	−22.9	0.2992	0.4993	1238.4	787.3	55.0
0.6996	0.2006	1162.7	931.5	−42.9	0.3007	0.6001	1281.4	717.5	30.2
0.6014	0.2984	1179.6	893.7	−10.2	0.2009	0.0988	1190.1	888.2	2.0
0.5974	0.1010	1148.2	963.8	−28.0	0.2008	0.1996	1198.5	870.4	29.6
0.5014	0.3983	1211.3	834.0	1.9	0.2031	0.3003	1207.8	850.5	54.4
0.5005	0.3000	1186.6	882.8	6.7	0.1995	0.4009	1220.6	823.9	74.1
0.4983	0.2017	1171.8	915.0	−4.7	0.2003	0.5006	1237.3	790.9	85.8
0.5012	0.0963	1159.5	942.8	−25.2	0.1999	0.7001	1317.4	664.1	48.9
0.4010	0.0955	1170.6	922.5	−18.9	0.1004	0.1029	1199.1	872.8	15.5
0.4002	0.1992	1181.3	898.9	4.4	0.1032	0.2046	1205.6	859.0	46.7
0.3986	0.3022	1194.7	870.1	22.4	0.0986	0.3001	1214.3	840.7	72.6
0.4010	0.3988	1212.4	833.9	29.0	0.0994	0.3996	1224.6	819.1	95.6
0.4005	0.4981	1244.9	775.6	15.6	0.1479	0.0469	1184.2	898.9	3.6
0.3026	0.0958	1180.7	904.7	−10.1	0.2520	0.0482	1177.4	911.4	−11.3
0.2968	0.2023	1190.9	882.8	17.4	0.1500	0.8005	1397.6	569.1	12.5
				318.15 K					
0.8981	0.0523	1102.7	1059.4	−15.3	0.3000	0.3014	1209.9	845.5	35.5
0.0498	0.0458	1206.5	861.9	6.3	0.2871	0.4241	1228.8	807.9	54.6
0.8037	0.0947	1125.4	1008.6	−23.0	0.2992	0.4993	1246.3	775.5	51.7
0.6996	0.2006	1171.1	915.4	−42.9	0.3007	0.6001	1288.9	707.3	27.1
0.6014	0.2984	1188.0	878.6	−11.5	0.2009	0.0988	1198.6	873.5	1.4
0.5974	0.1010	1156.7	947.2	−27.8	0.2008	0.1996	1207.0	855.9	27.6
0.5014	0.3983	1219.4	820.7	0.1	0.2031	0.3003	1216.1	836.6	51.5
0.5005	0.3000	1194.9	868.3	5.2	0.1995	0.4009	1228.7	811.0	70.6
0.4983	0.2017	1180.3	899.5	−5.6	0.2003	0.5006	1245.1	779.1	81.9
0.5012	0.0963	1168.0	926.5	−25.2	0.1999	0.7001	1324.3	655.7	45.3
0.4010	0.0955	1179.0	907.0	−18.9	0.1004	0.1029	1207.5	858.5	14.4
0.4002	0.1992	1189.7	883.8	3.2	0.1032	0.2046	1214.0	844.9	44.4
0.3986	0.3022	1202.9	855.9	20.5	0.0986	0.3001	1222.6	827.2	69.4
0.4010	0.3988	1220.6	820.5	26.5	0.0994	0.3996	1232.7	806.4	91.6
0.4005	0.4981	1252.8	763.8	13.1	0.1479	0.0469	1193.0	883.5	2.6
0.3026	0.0958	1189.2	889.5	−10.5	0.2520	0.0482	1186.1	895.7	−11.8
0.2968	0.2023	1199.3	868.1	16.0	0.1500	0.8005	1403.5	563.1	9.4
				315.65 K					
0.8981	0.0523	1111.3	1040.3	−15.4	0.3000	0.3014	1218.3	831.8	33.1
0.0498	0.0458	1215.0	848.0	5.8	0.2871	0.4241	1236.9	795.4	51.4
0.8037	0.0947	1133.9	990.9	−23.0	0.2992	0.4993	1254.0	764.0	48.5
0.6996	0.2006	1179.6	900.0	−42.9	0.3007	0.6001	1296.5	697.5	23.9
0.6014	0.2984	1196.5	863.9	−12.9	0.2009	0.0988	1207.0	859.4	0.9
0.5974	0.1010	1165.2	931.0	−27.6	0.2008	0.1996	1215.3	842.2	26.0
0.5014	0.3983	1227.6	807.6	−1.9	0.2031	0.3003	1224.4	823.4	48.9
0.5005	0.3000	1203.4	853.7	3.3	0.1995	0.4009	1236.7	798.5	67.2
0.4983	0.2017	1188.9	884.3	−6.8	0.2003	0.5006	1252.8	767.7	78.0
0.5012	0.0963	1176.5	910.9	−25.1	0.1999	0.7001	1331.1	647.5	41.6
0.4010	0.0955	1187.5	891.9	−19.0	0.1004	0.1029	1216.0	844.5	13.4
0.4002	0.1992	1198.2	869.3	2.1	0.1032	0.2046	1222.5	831.3	42.1
0.3986	0.3022	1211.3	842.1	18.5	0.0986	0.3001	1230.9	814.2	66.2
0.4010	0.3988	1228.7	807.7	24.1	0.0994	0.3996	1240.7	794.1	87.8

Table 2. Continued

x_1	x_2	$u/(\mathrm{m \cdot s^{-1}})$	$\kappa_S/(\mathrm{TPa^{-1}})$	$\delta\kappa_S/(\mathrm{TPa^{-1}})$	x_1	x_2	$u/(\mathrm{m \cdot s^{-1}})$	$\kappa_S/(\mathrm{TPa^{-1}})$	$\delta\kappa_S/(\mathrm{TPa^{-1}})$
				315.65 K					
0.4005	0.4981	1260.8	752.3	10.4	0.1479	0.0469	1202.0	868.3	1.5
0.3026	0.0958	1197.5	875.0	−10.6	0.2520	0.0482	1194.9	880.5	−12.2
0.2968	0.2023	1207.7	853.9	14.5	0.1500	0.8005	1409.5	557.2	6.1
				313.15 K					
0.8981	0.0523	1119.7	1021.9	−15.3	0.3000	0.3014	1226.4	818.8	30.8
0.0498	0.0458	1223.3	834.5	5.3	0.2871	0.4241	1244.8	783.4	48.2
0.8037	0.0947	1142.3	973.7	−23.0	0.2992	0.4993	1261.8	752.8	45.0
0.6996	0.2006	1188.0	884.9	−43.0	0.3007	0.6001	1303.7	688.1	20.8
0.6014	0.2984	1204.7	849.8	−14.2	0.2009	0.0988	1215.3	845.5	0.1
0.5974	0.1010	1173.6	915.3	−27.6	0.2008	0.1996	1223.6	828.7	24.2
0.5014	0.3983	1235.7	795.0	−3.8	0.2031	0.3003	1232.5	810.5	46.2
0.5005	0.3000	1211.6	839.9	1.6	0.1995	0.4009	1244.7	786.4	63.6
0.4983	0.2017	1197.2	869.8	−7.7	0.2003	0.5006	1260.4	756.5	73.9
0.5012	0.0963	1184.9	895.7	−25.2	0.1999	0.7001	1337.7	639.7	37.8
0.4010	0.0955	1195.9	877.2	−19.1	0.1004	0.1029	1224.4	831.0	12.3
0.4002	0.1992	1206.6	855.0	0.8	0.1032	0.2046	1230.6	818.3	40.1
0.3986	0.3022	1219.6	828.5	16.3	0.0986	0.3001	1238.9	801.7	63.2
0.4010	0.3988	1236.7	795.3	21.6	0.0994	0.3996	1248.6	782.2	83.7
0.4005	0.4981	1268.4	741.3	8.0	0.1479	0.0469	1210.9	853.5	0.3
0.3026	0.0958	1206.0	860.7	−11.1	0.2520	0.0482	1203.4	866.0	−12.5
0.2968	0.2023	1216.0	840.2	12.9	0.1500	0.8005	1415.3	551.5	2.7
				310.65 K					
0.8981	0.0523	1128.2	1003.7	−15.6	0.3000	0.3014	1234.6	806.0	28.4
0.0498	0.0458	1231.7	821.2	4.7	0.2871	0.4241	1252.6	771.6	45.0
0.8037	0.0947	1150.7	956.8	−23.2	0.2992	0.4993	1269.3	742.0	41.7
0.6996	0.2006	1196.4	870.2	−43.4	0.3007	0.6001	1310.9	678.9	17.5
0.6014	0.2984	1213.1	835.8	−15.8	0.2009	0.0988	1223.7	831.9	-0.5
0.5974	0.1010	1182.1	899.8	−27.8	0.2008	0.1996	1231.9	815.6	22.4
0.5014	0.3983	1243.8	782.6	−6.0	0.2031	0.3003	1240.7	797.9	43.4
0.5005	0.3000	1219.7	826.6	0.0	0.1995	0.4009	1252.5	774.7	60.3
0.4983	0.2017	1205.5	855.5	−8.8	0.2003	0.5006	1268.0	745.7	69.8
0.5012	0.0963	1193.2	881.0	−25.1	0.1999	0.7001	1344.2	632.0	34.0
0.4010	0.0955	1204.2	863.0	−19.2	0.1004	0.1029	1232.6	817.9	11.4
0.4002	0.1992	1214.9	841.1	−0.5	0.1032	0.2046	1238.9	805.4	37.8
0.3986	0.3022	1227.6	815.5	14.4	0.0986	0.3001	1247.0	789.3	60.0
0.4010	0.3988	1244.7	783.0	18.9	0.0994	0.3996	1256.3	770.7	80.0
0.4005	0.4981	1276.1	730.6	5.3	0.1479	0.0469	1219.6	839.3	−0.5
0.3026	0.0958	1214.2	846.9	−11.3	0.2520	0.0482	1212.1	851.5	−13.0
0.2968	0.2023	1224.3	826.8	11.5	0.1500	0.8005	1420.9	546.0	−0.9
				308.15 K					
0.8981	0.0523	1136.5	986.4	−15.4	0.3000	0.3014	1242.8	793.4	26.0
0.0498	0.0458	1239.9	808.4	4.4	0.2871	0.4241	1260.5	760.2	41.7
0.8037	0.0947	1159.2	940.3	−23.3	0.2992	0.4993	1276.9	731.4	38.2
0.6996	0.2006	1204.7	856.0	−43.4	0.3007	0.6001	1318.1	669.8	14.0
0.6014	0.2984	1221.4	822.3	−17.3	0.2009	0.0988	1232.2	818.5	−1.3
0.5974	0.1010	1190.4	885.0	−27.6	0.2008	0.1996	1240.2	802.7	20.6
0.5014	0.3983	1251.8	770.5	−8.2	0.2031	0.3003	1248.8	785.6	40.7
0.5005	0.3000	1228.0	813.3	−1.9	0.1995	0.4009	1260.5	763.0	56.6
0.4983	0.2017	1213.9	841.7	−9.8	0.2003	0.5006	1275.5	735.2	65.9

Table 2. Continued

x_1	x_2	$u/(m \cdot s^{-1})$	$\kappa_S/(TPa^{-1})$	$\delta\kappa_S/(TPa^{-1})$	x_1	x_2	$u/(m \cdot s^{-1})$	$\kappa_S/(TPa^{-1})$	$\delta\kappa_S/(TPa^{-1})$
				308.15 K					
0.5012	0.0963	1201.6	866.6	−25.0	0.1999	0.7001	1350.7	624.6	30.0
0.4010	0.0955	1212.6	848.9	−19.4	0.1004	0.1029	1241.0	805.0	10.4
0.4002	0.1992	1223.2	827.6	−1.7	0.1032	0.2046	1247.2	792.8	35.6
0.3986	0.3022	1235.9	802.6	12.2	0.0986	0.3001	1255.2	777.3	56.9
0.4010	0.3988	1252.7	771.1	16.3	0.0994	0.3996	1264.2	759.3	76.0
0.4005	0.4981	1283.8	720.0	2.5	0.1479	0.0469	1228.4	825.4	−1.4
0.3026	0.0958	1222.6	833.2	−11.7	0.2520	0.0482	1220.6	837.7	−13.1
0.2968	0.2023	1232.6	813.6	9.9	0.1500	0.8005	1426.5	540.7	−4.6
				305.65 K					
0.8981	0.0523	1144.9	969.2	−15.5	0.3000	0.3014	1250.9	781.2	23.5
0.0498	0.0458	1248.3	795.8	3.9	0.2871	0.4241	1268.3	749.0	38.4
0.8037	0.0947	1167.6	924.3	−23.5	0.2992	0.4993	1284.5	721.0	34.5
0.6996	0.2006	1213.0	842.1	−43.7	0.3007	0.6001	1325.3	661.1	10.5
0.6014	0.2984	1229.6	809.3	−18.8	0.2009	0.0988	1240.5	805.7	−1.9
0.5974	0.1010	1198.8	870.4	−27.7	0.2008	0.1996	1248.5	790.2	18.8
0.5014	0.3983	1259.8	758.9	−10.4	0.2031	0.3003	1257.0	773.6	37.8
0.5005	0.3000	1236.3	800.5	−3.8	0.1995	0.4009	1268.3	751.9	53.1
0.4983	0.2017	1222.2	828.1	−11.0	0.2003	0.5006	1283.0	724.9	61.7
0.5012	0.0963	1210.0	852.4	−25.2	0.1999	0.7001	1357.2	617.3	25.8
0.4010	0.0955	1221.0	835.2	−19.6	0.1004	0.1029	1249.4	792.3	9.3
0.4002	0.1992	1231.6	814.4	−3.0	0.1032	0.2046	1255.5	780.5	33.4
0.3986	0.3022	1244.1	790.1	10.0	0.0986	0.3001	1263.3	765.5	53.7
0.4010	0.3988	1260.6	759.6	13.6	0.0994	0.3996	1272.1	748.1	71.9
0.4005	0.4981	1291.4	709.8	−0.4	0.1479	0.0469	1237.1	811.9	−2.2
0.3026	0.0958	1231.0	820.0	−12.1	0.2520	0.0482	1229.0	824.2	−13.3
0.2968	0.2023	1240.9	800.8	8.4	0.1500	0.8005	1431.9	535.5	−8.4
				303.15 K					
0.8981	0.0523	1153.3	952.5	−15.4	0.3000	0.3014	1259.1	769.2	21.0
0.0498	0.0458	1256.7	783.3	3.4	0.2871	0.4241	1276.1	738.0	34.9
0.8037	0.0947	1176.1	908.5	−23.6	0.2992	0.4993	1292.1	710.8	30.8
0.6996	0.2006	1221.4	828.4	−44.0	0.3007	0.6001	1332.4	652.4	6.8
0.6014	0.2984	1237.9	796.3	−20.5	0.2009	0.0988	1248.9	792.9	−2.6
0.5974	0.1010	1207.3	856.0	−27.7	0.2008	0.1996	1256.9	777.8	16.9
0.5014	0.3983	1267.8	747.4	−12.7	0.2031	0.3003	1265.1	761.8	35.0
0.5005	0.3000	1244.5	787.8	−5.8	0.1995	0.4009	1276.2	740.8	49.4
0.4983	0.2017	1230.6	814.7	−12.1	0.2003	0.5006	1290.6	714.8	57.4
0.5012	0.0963	1218.4	838.5	−25.2	0.1999	0.7001	1363.6	610.2	21.5
0.4010	0.0955	1229.4	821.8	−19.8	0.1004	0.1029	1257.7	779.9	8.3
0.4002	0.1992	1239.9	801.5	−4.3	0.1032	0.2046	1263.8	768.4	31.1
0.3986	0.3022	1252.2	777.8	7.8	0.0986	0.3001	1271.4	753.9	50.5
0.4010	0.3988	1268.6	748.1	10.8	0.0994	0.3996	1280.0	737.2	67.8
0.4005	0.4981	1299.1	699.7	−3.4	0.1479	0.0469	1245.7	798.8	−2.7
0.3026	0.0958	1239.4	806.9	−12.5	0.2520	0.0482	1237.6	810.8	−13.6
0.2968	0.2023	1249.2	788.2	6.7	0.1500	0.8005	1437.3	530.5	−12.5
				300.65 K					
0.8981	0.0523	1161.7	936.3	−15.4	0.3000	0.3014	1267.2	757.5	18.4
0.0498	0.0458	1265.0	771.3	2.9	0.2871	0.4241	1283.9	727.3	31.4
0.8037	0.0947	1184.5	893.2	−23.9	0.2992	0.4993	1299.6	701.0	27.0
0.6996	0.2006	1229.6	815.2	−44.3	0.3007	0.6001	1339.4	644.1	3.0

Table 2. Continued

x_1	x_2	$u/(m·s^{-1})$	$\kappa_S/(TPa^{-1})$	$\delta\kappa_S/(TPa^{-1})$	x_1	x_2	$u/(m·s^{-1})$	$\kappa_S/(TPa^{-1})$	$\delta\kappa_S/(TPa^{-1})$
				300.65 K					
0.6014	0.2984	1246.1	783.8	−22.2	0.2009	0.0988	1257.2	780.6	−3.3
0.5974	0.1010	1215.6	842.1	−27.8	0.2008	0.1996	1265.1	765.9	15.0
0.5014	0.3983	1275.7	736.3	−15.0	0.2031	0.3003	1273.2	750.3	32.1
0.5005	0.3000	1252.7	775.6	−7.7	0.1995	0.4009	1284.0	730.1	45.7
0.4983	0.2017	1239.0	801.7	−13.4	0.2003	0.5006	1298.1	704.9	53.0
0.5012	0.0963	1226.8	825.0	−25.4	0.1999	0.7001	1369.9	603.3	17.0
0.4010	0.0955	1237.8	808.7	−20.1	0.1004	0.1029	1266.1	767.9	7.2
0.4002	0.1992	1248.2	788.9	−5.7	0.1032	0.2046	1272.1	756.6	28.8
0.3986	0.3022	1260.4	765.9	5.5	0.0986	0.3001	1279.5	742.7	47.2
0.4010	0.3988	1276.4	737.1	8.0	0.0994	0.3996	1287.7	726.7	63.7
0.4005	0.4981	1306.6	690.0	−6.5	0.1479	0.0469	1254.3	786.1	−3.3
0.3026	0.0958	1247.8	794.2	−13.0	0.2520	0.0482	1246.2	797.8	−13.9
0.2968	0.2023	1257.5	776.0	5.1	0.1500	0.8005	1442.6	525.6	−16.7
				298.15 K					
0.8981	0.0523	1170.3	920.2	−15.5	0.3000	0.3014	1275.4	746.0	15.8
0.0498	0.0458	1273.4	759.3	2.4	0.2871	0.4241	1291.8	716.8	27.7
0.8037	0.0947	1193.0	878.3	−24.0	0.2992	0.4993	1307.1	691.3	23.2
0.6996	0.2006	1238.0	802.2	−44.8	0.3007	0.6001	1346.5	635.9	−1.0
0.6014	0.2984	1254.4	771.4	−23.9	0.2009	0.0988	1265.7	768.4	−4.1
0.5974	0.1010	1224.1	828.5	−27.9	0.2008	0.1996	1273.5	754.0	13.1
0.5014	0.3983	1283.7	725.3	−17.6	0.2031	0.3003	1281.4	739.0	29.1
0.5005	0.3000	1260.9	763.6	−9.8	0.1995	0.4009	1291.9	719.5	41.9
0.4983	0.2017	1247.3	789.1	−14.6	0.2003	0.5006	1305.6	695.2	48.5
0.5012	0.0963	1235.3	811.8	−25.5	0.1999	0.7001	1376.2	596.5	12.4
0.4010	0.0955	1246.2	795.9	−20.3	0.1004	0.1029	1274.6	755.9	6.1
0.4002	0.1992	1256.6	776.5	−7.1	0.1032	0.2046	1280.5	745.0	26.4
0.3986	0.3022	1268.6	754.2	3.2	0.0986	0.3001	1287.6	731.6	43.9
0.4010	0.3988	1284.4	726.3	5.0	0.0994	0.3996	1295.6	716.2	59.5
0.4005	0.4981	1314.2	680.4	−9.7	0.1479	0.0469	1262.9	773.5	−3.9
0.3026	0.0958	1256.2	781.7	−13.4	0.2520	0.0482	1254.7	785.2	−14.1
0.2968	0.2023	1265.9	763.9	3.4	0.1500	0.8005	1447.8	520.8	−21.2
				295.65 K					
0.8981	0.0523	1178.8	904.5	−15.6	0.3000	0.3014	1283.6	734.7	13.1
0.0498	0.0458	1282.0	747.5	1.9	0.2871	0.4241	1299.6	706.5	24.0
0.8037	0.0947	1201.5	863.6	−24.3	0.2992	0.4993	1314.7	681.7	19.1
0.6996	0.2006	1246.4	789.3	−45.3	0.3007	0.6001	1353.6	627.8	−5.2
0.6014	0.2984	1262.7	759.5	−25.7	0.2009	0.0988	1274.1	756.4	−4.8
0.5974	0.1010	1232.6	815.0	−28.1	0.2008	0.1996	1281.9	742.4	11.1
0.5014	0.3983	1291.7	714.5	−20.2	0.2031	0.3003	1289.6	727.9	26.1
0.5005	0.3000	1269.2	751.7	−12.0	0.1995	0.4009	1299.8	709.1	38.0
0.4983	0.2017	1255.8	776.5	−16.0	0.2003	0.5006	1313.2	685.6	43.9
0.5012	0.0963	1243.8	798.7	−25.7	0.1999	0.7001	1382.6	589.8	7.5
0.4010	0.0955	1254.8	783.1	−20.7	0.1004	0.1029	1283.0	744.2	5.1
0.4002	0.1992	1265.1	764.3	−8.6	0.1032	0.2046	1288.8	733.7	24.2
0.3986	0.3022	1276.9	742.6	0.7	0.0986	0.3001	1295.9	720.7	40.5
0.4010	0.3988	1292.4	715.5	1.9	0.0994	0.3996	1303.6	705.9	55.2
0.4005	0.4981	1321.8	670.9	−13.1	0.1479	0.0469	1271.7	761.1	−4.6
0.3026	0.0958	1264.8	769.4	−13.9	0.2520	0.0482	1263.4	772.6	−14.3
0.2968	0.2023	1274.3	752.0	1.6	0.1500	0.8005	1453.1	516.1	−25.9

Table 2. Continued

x_1	x_2	$u/(\text{m}\cdot\text{s}^{-1})$	$\kappa_S/(\text{TPa}^{-1})$	$\delta\kappa_S/(\text{TPa}^{-1})$	x_1	x_2	$u/(\text{m}\cdot\text{s}^{-1})$	$\kappa_S/(\text{TPa}^{-1})$	$\delta\kappa_S/(\text{TPa}^{-1})$
				293.15 K					
0.8981	0.0523	1187.5	888.8	−15.8	0.3000	0.3014	1292.0	723.5	10.2
0.0498	0.0458	1290.7	735.7	1.3	0.2871	0.4241	1307.7	696.2	20.1
0.8037	0.0947	1210.3	848.9	−24.6	0.2992	0.4993	1322.5	672.2	14.8
0.6996	0.2006	1255.0	776.7	−45.9	0.3007	0.6001	1360.9	619.7	−9.6
0.6014	0.2984	1271.1	747.5	−27.7	0.2009	0.0988	1282.9	744.4	−5.7
0.5974	0.1010	1241.3	801.6	−28.4	0.2008	0.1996	1290.5	730.8	9.0
0.5014	0.3983	1299.9	703.8	−23.1	0.2031	0.3003	1298.1	716.8	22.9
0.5005	0.3000	1277.7	740.0	−14.3	0.1995	0.4009	1307.9	698.7	33.9
0.4983	0.2017	1264.4	764.1	−17.4	0.2003	0.5006	1321.0	676.0	39.0
0.5012	0.0963	1252.6	785.7	−26.1	0.1999	0.7001	1389.1	583.1	2.4
0.4010	0.0955	1263.5	770.5	−21.1	0.1004	0.1029	1291.8	732.5	3.9
0.4002	0.1992	1273.7	752.1	−10.2	0.1032	0.2046	1297.5	722.2	21.6
0.3986	0.3022	1285.2	731.2	−1.8	0.0986	0.3001	1304.3	709.7	37.0
0.4010	0.3988	1300.5	704.9	−1.4	0.0994	0.3996	1311.7	695.5	50.6
0.4005	0.4981	1329.6	661.5	−16.7	0.1479	0.0469	1280.8	748.6	−5.4
0.3026	0.0958	1273.5	757.1	−14.5	0.2520	0.0482	1272.4	759.9	−14.8
0.2968	0.2023	1283.0	740.2	−0.3	0.1500	0.8005	1458.4	511.4	−31.0
				290.65 K					
0.8981	0.0523	1196.3	873.5	−15.9	0.3000	0.3014	1300.5	712.4	7.3
0.0498	0.0458	1299.5	724.2	0.7	0.2871	0.4241	1315.7	686.0	16.1
0.8037	0.0947	1219.1	834.5	−24.9	0.2992	0.4993	1330.2	662.8	10.4
0.6996	0.2006	1263.5	764.2	−46.5	0.3007	0.6001	1368.1	611.8	−14.2
0.6014	0.2984	1279.6	735.7	−29.7	0.2009	0.0988	1291.7	732.7	−6.6
0.5974	0.1010	1250.1	788.4	−28.7	0.2008	0.1996	1299.2	719.3	6.8
0.5014	0.3983	1308.1	693.3	−25.9	0.2031	0.3003	1306.6	705.8	19.5
0.5005	0.3000	1286.2	728.5	−16.6	0.1995	0.4009	1316.0	688.6	29.8
0.4983	0.2017	1273.2	751.8	−18.9	0.2003	0.5006	1328.7	666.6	34.1
0.5012	0.0963	1261.3	772.9	−26.3	0.1999	0.7001	1395.5	576.5	−3.0
0.4010	0.0955	1272.2	758.2	−21.5	0.1004	0.1029	1300.5	721.0	2.7
0.4002	0.1992	1282.4	740.2	−11.8	0.1032	0.2046	1306.1	711.1	19.2
0.3986	0.3022	1293.7	719.9	−4.4	0.0986	0.3001	1312.7	699.1	33.5
0.4010	0.3988	1308.7	694.4	−4.8	0.0994	0.3996	1319.8	685.6	46.2
0.4005	0.4981	1337.4	652.3	−20.5	0.1479	0.0469	1289.9	736.5	−6.1
0.3026	0.0958	1282.2	745.0	−15.1	0.2520	0.0482	1281.5	747.5	−15.3
0.2968	0.2023	1291.7	728.4	−2.3	0.1500	0.8005	1463.8	506.7	−36.3
				288.15 K					
0.8981	0.0523	1204.9	858.2	−16.0	0.3000	0.3014	1308.8	701.2	4.0
0.0498	0.0458	1308.0	712.6	−0.2	0.2871	0.4241	1323.6	675.8	11.7
0.8037	0.0947	1227.7	820.0	−25.5	0.2992	0.4993	1337.9	653.2	5.5
0.6996	0.2006	1271.8	751.9	−47.2	0.3007	0.6001	1375.1	603.8	−19.1
0.6014	0.2984	1287.8	724.0	−31.8	0.2009	0.0988	1300.2	720.9	−7.8
0.5974	0.1010	1258.6	775.2	−29.1	0.2008	0.1996	1307.5	708.0	4.5
0.5014	0.3983	1316.0	682.8	−29.0	0.2031	0.3003	1314.7	694.9	16.1
0.5005	0.3000	1294.4	716.9	−19.2	0.1995	0.4009	1324.0	678.2	25.1
0.4983	0.2017	1281.6	739.5	−20.7	0.2003	0.5006	1336.3	657.1	28.7
0.5012	0.0963	1269.8	760.2	−26.8	0.1999	0.7001	1401.9	569.7	−8.9
0.4010	0.0955	1280.8	745.7	−22.2	0.1004	0.1029	1309.0	709.5	1.2
0.4002	0.1992	1290.9	728.1	−13.8	0.1032	0.2046	1314.5	699.9	16.4
0.3986	0.3022	1301.9	708.6	−7.4	0.0986	0.3001	1320.9	688.3	29.5
0.4010	0.3988	1316.6	684.0	−8.3	0.0994	0.3996	1327.7	675.3	41.2
0.4005	0.4981	1344.9	643.0	−24.5	0.1479	0.0469	1298.9	723.9	−7.5
0.3026	0.0958	1290.8	732.9	−16.0	0.2520	0.0482	1290.7	734.5	−16.5
0.2968	0.2023	1299.9	717.0	−4.3	0.1500	0.8005	1468.9	502.0	−42.0

where x_i is the molar fraction, R, the universal constant for gases and T, the temperature in Kelvin degrees. The B_i parameters are

temperature dependent as follows:

$$B_i = \sum_{j=0}^{3} B_{ij} \cdot T^j \qquad (5)$$

The B_{ij} parameters were computed and enclosed with their root means square deviations in Table 3. The root mean square deviations presented were computed by using Eq. (6), where z is the value of the derived magnitude, and n_{DAT} is the number of experimental data:
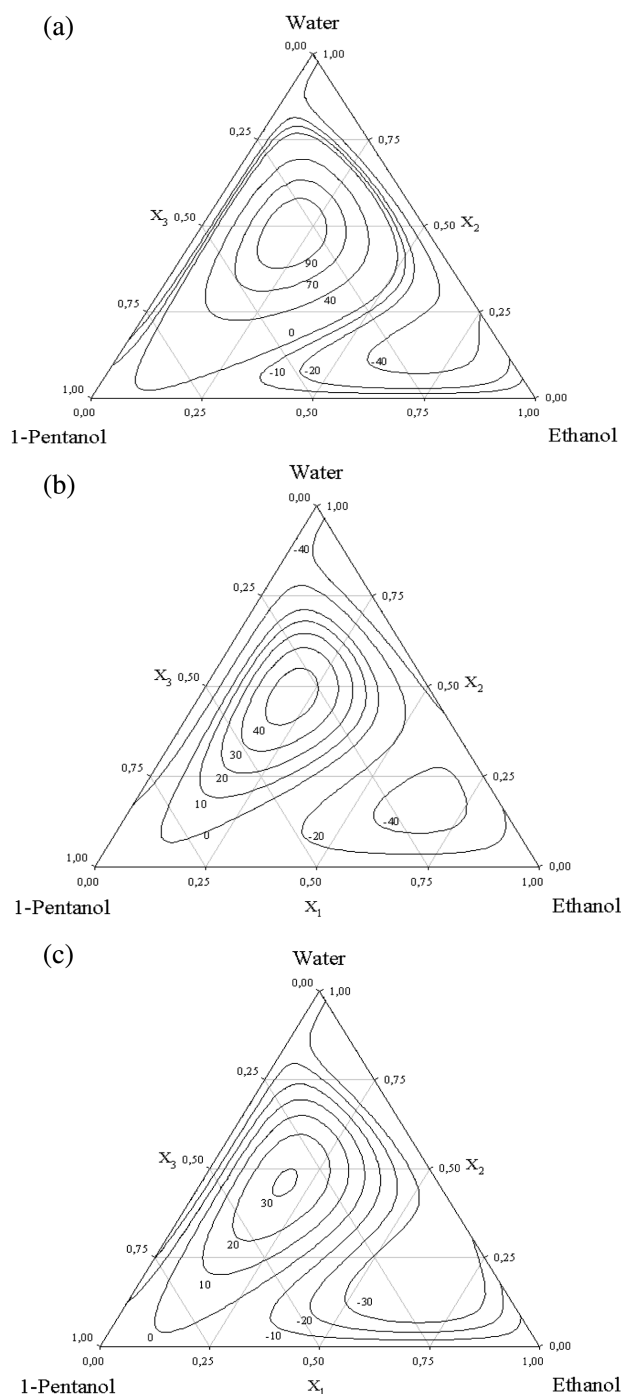
Table 3. Parameters of Eq. (5) in the range 288.15-323.15 K and σ in accordance to Eq. (6)

$C_{00}=103057.5$	$C_{01}=-1057.4$	$C_{02}=3.6$	$C_{03}=0.0$	
$C_{10}=124925.6$	$C_{11}=-1119.4$	$C_{12}=3.3$	$C_{13}=0.0$	
$C_{20}=78323.2$	$C_{21}=-1001.5$	$C_{22}=3.7$	$C_{23}=0.0$	$\sigma=14.98$

Fig. 1. Curves of changes of isentropic compressibility for ethanol +water+1-pentanol (a) 323.15 K (b) 298.15 K (c) 288.15 K.
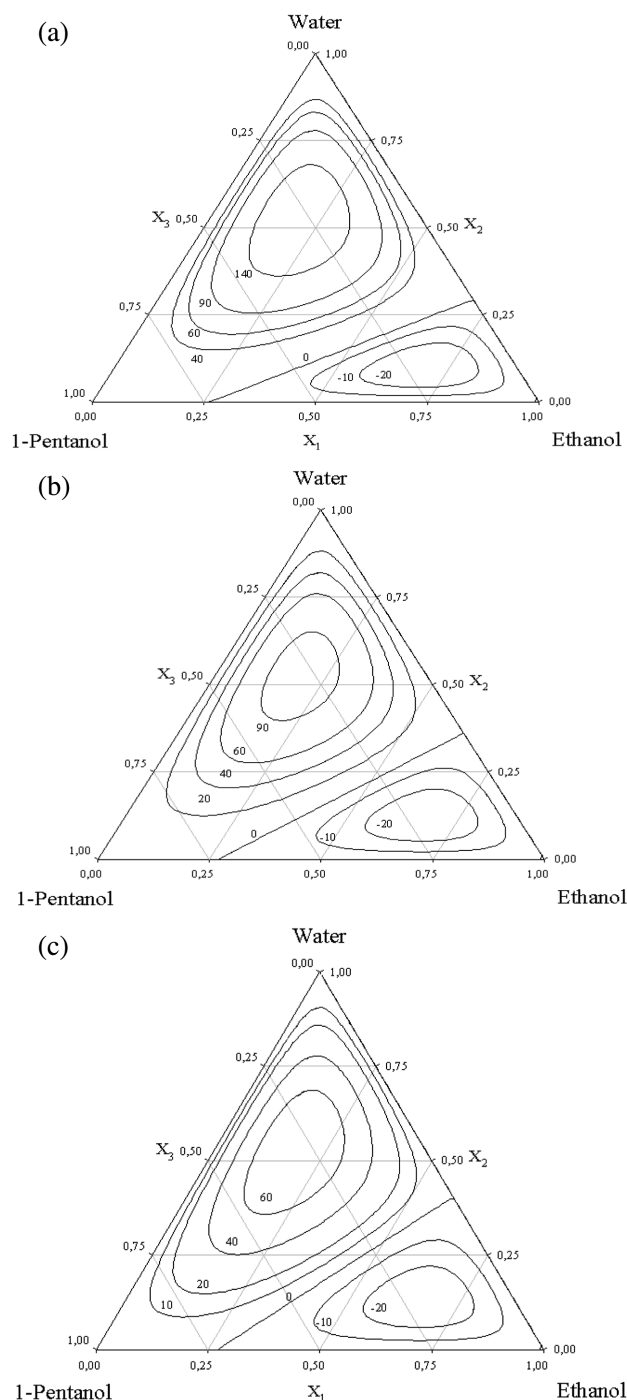
Fig. 2. Curves of ternary contribution of the changes of isentropic compressibility for ethanol+water+1-pentanol (a) 323.15 K (b) 298.15 K (c) 288.15 K.

$$\sigma = \left(\frac{\sum_{i=1}^{n_{DAT}} (Z_{exp} - Z_{pred})^2}{n_{DAT}} \right)^{1/2} \qquad (6)$$

No previously published data have been found at the studied conditions for this ternary mixture. Only a short collection of ultrasonic velocity data for the pure compounds was reported at a few temperatures as shown in Table 1. Curves of constant changes of isentropic compressibility for the ternary mixture ethanol+water+1-pentanol, have been plotted in Figs. 1a, 1b and 1c, at the extreme values of temperature and standard condition. In these figures, a clear contractive tendency is shown for this mixture at the equimolar composition ethanol and water, this effect being attenuated towards 1-pentanol component. In fact, an inversion of trend is produced in the neighbouring of the heavy alcohol. Such effect is reflected in terms of derived value as two different regions: first, a negative zone near ethanol which increases for rising temperatures; second, a positive region exists with a maximum at low concentration of ethanol which is increased for rising temperatures. It is worthwhile to point out the huge ternary contribution for both zones (Figs. 2a, 2b and 2c). As an example, if we compare the values of the change of isentropic compressibility and the corresponding ternary contribution at the same temperature, we may observe that the latter decides the final value and sign of the former. Ternary interactions are then key to quantifying the nonideality of the magnitude and point out the role of each component for diluted mixtures as for alcoholic beverages, where the presence of 1-pentanol is in terms of huge dilution.

2. Acoustic Parameters

We have attempted to explain the physico-chemical behaviour 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 [Resa et al., 2003a]. 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:

$$L_f = \left(\frac{K}{u \cdot \rho^{1/2}} \right) \qquad (7)$$

$$b = \left(\frac{M}{\rho} \right) - \left(\frac{RT}{\rho \cdot u^2} \right) \cdot \left(\left[1 + \frac{M \cdot u^2}{3RT} \right]^{1/2} - 1 \right) \qquad (8)$$

$$r = \left(\frac{3b}{16\Pi N} \right)^{1/3} \qquad (9)$$

$$B = \left(\frac{4}{3} \right) \Pi r^3 N \qquad (10)$$

$$Y = (36 \Pi N B^2)^{1/3} \qquad (11)$$

$$V_a = V \left(1 - \left(\frac{u}{u_\infty} \right) \right) \qquad (12)$$

$$V_0 = V - V_a \qquad (13)$$

$$R = \frac{M \cdot u^{1/3}}{\rho} \qquad (14)$$

$$S = \frac{u \cdot V}{B \cdot u_\infty} \qquad (15)$$

$$Z = u \cdot \rho \qquad (16)$$

$$R_A = \left(\frac{\rho_{mix}}{\rho} \right) \cdot \left(\frac{u}{u_{mix}} \right)^{1/3} \qquad (17)$$

Table 4. Acoustic parameters for the pure compounds enclosed into the studied mixtures

|	L_f	b	$r \cdot 10^{12}$	B	$Y \cdot 10^{-12}$	V_a	R	S	R_A	Z
				323.15 K						
	(Å)	$(m^3 \cdot mol^{-1})$	(m)	$(m^3 \cdot mol^{-1})$	(m^2)	$(m^3 \cdot mol^{-1})$	$(m^3 \cdot mol^{-1}) \cdot (m \cdot s^{-1})^{1/3}$			$(kg \cdot m^{-2} \cdot s^{-1})$
Ethanol	23.237	60.294	3.787	15.073	11.940	20.395	614.596	2.647	1.000	808.966
Water	14.030	18.231	2.542	4.558	5.379	0.659	210.653	3.856	1.141	1523.686
1-Pentanol	20.302	111.258	4.645	27.814	17.962	28.506	1179.088	2.975	0.997	942.846
				298.15 K						
	(Å)	$(m^3 \cdot mol^{-1})$	(m)	$(m^3 \cdot mol^{-1})$	(m^2)	$(m^3 \cdot mol^{-1})$	$(m^3 \cdot mol^{-1}) \cdot (m \cdot s^{-1})^{1/3}$			$(kg \cdot m^{-2} \cdot s^{-1})$
Ethanol	20.297	58.617	3.752	14.654	11.717	16.740	612.942	2.858	1.000	898.363
Water	13.761	18.067	2.534	4.517	5.346	1.164	206.689	3.743	1.160	1492.459
1-Pentanol	17.938	108.699	4.610	27.175	17.686	22.196	1178.210	2.844	1.140	1017.570
				288.15 K						
	(Å)	$(m^3 \cdot mol^{-1})$	(m)	$(m^3 \cdot mol^{-1})$	(m^2)	$(m^3 \cdot mol^{-1})$	$(m^3 \cdot mol^{-1}) \cdot (m \cdot s^{-1})^{1/3}$			$(kg \cdot m^{-2} \cdot s^{-1})$
Ethanol	19.229	57.986	3.738	14.496	11.633	15.288	612.483	2.946	1.000	936.006
Water	13.777	18.029	2.533	4.507	5.339	1.506	204.853	3.666	1.169	1465.084
1-Pentanol	19.229	107.740	4.596	26.935	17.582	19.678	1178.263	3.270	0.995	1069.927
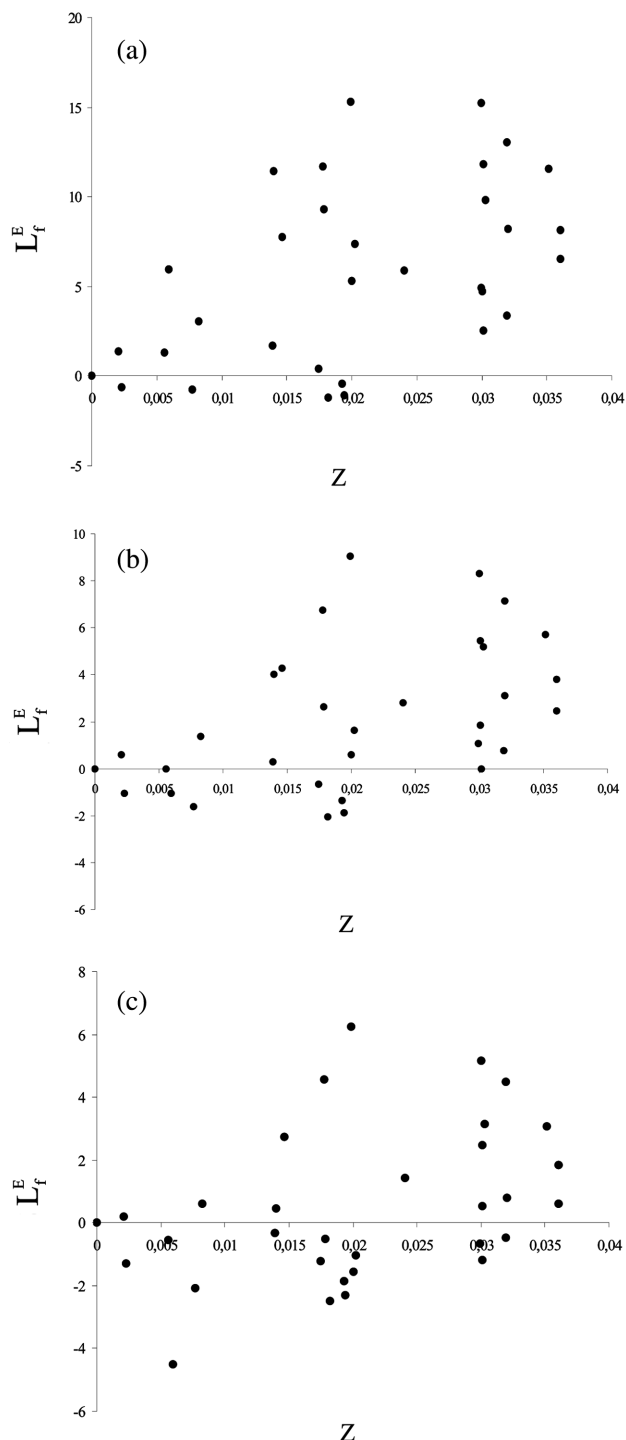
Fig. 3. Curves of excess intermolecular free length for ethanol+ water+1-pentanol (a) 323.15 K (b) 298.15 K (c) 288.15 K versus z.

$$M_A = \left[\left(\frac{u_{mix}}{\sum_i x_i u_i} \right)^2 - 1 \right] \tag{18}$$

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 1,600 ms^{-1} [Schaaffs, 1963], and R and Π are common universal constants. These parameters are gathered in Table 4 for the pure com-
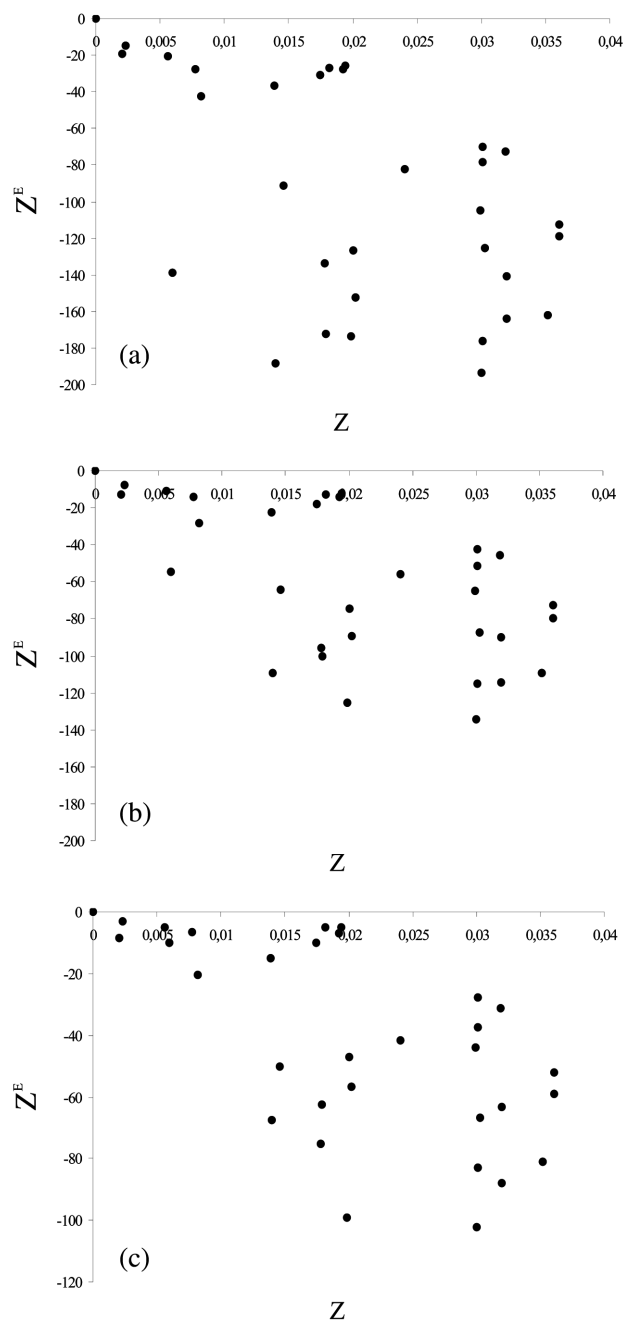
Fig. 4. Curves of excess specific acoustic impedance for ethanol+ water+1-pentanol (a) 323.15 K (b) 298.15 K (c) 288.15 K versus z.

pounds at the same temperatures. The variation of the magnitudes L_f and Z (by means of Eq. (1)) for the ternary mixtures is shown in the Figs. 3 and 4, respectively, showing these magnitudes as a function of $z = \prod_{i=1}^{N} x_i$, where xi stands for the same meaning as indicated above. These figures point out the difference between pseudobinary (low values of z) and ternary compositions (high values of z) trends. In accordance with the contractive trend observed for other ternary mixtures which are being studied in our laboratory, extreme values are gathered at pseudobinaries concentration which reinforce the supposition of the strong disturbation of hydroxylic molecules ac-

commodation by the aliphatic end of 1-pentanol.

The compressibility solvation numbers are calculated by using the following equation, attending to usual expressions [Gonzalez, 1999]:

$$n_S = \left(\frac{n_{solvent}}{n_{solute}}\right) \cdot \left(1 - \frac{\kappa_S}{\kappa_{So}}\right) \tag{18}$$

where $n_{solvent}$ and n_{solute} are mol number of solvent and solute, respectively. The equation used for computing the compressibility solvation numbers assumes that the hydration layer around the ethanol molecule is incompressible, which is not the case. Despite this, it provides an acceptable approximation of the extent of interaction and disturbation of the ethanol with water. These parameters are derived from isentropic compressibility measurements and, therefore, account for the first two layers of solvents around the solute. Falling compressibility hydration numbers indicate that a lower number of molecules of water are displaced by increasing the heavy alcohol in the solution. There is an isoline of zero value where the compressibility of the three components is the same from the ethanol +water to the ethanol+1-pentanol binary mixture. Only at high concentration of ethanol do the negative values change sign and the diagram shows positive values of hydration numbers. The negative hydration numbers reflect strong ternary interactions, this effect could being ascribed to longer lifetimes hydrogen bonds in equimolar ternary mixtures than in ethanol-ethanol o water-water environment. When the temperature is increased from 288.15 to 323.15 K, there is a corresponding rise in the ultrasonic velocity and then an increment of entropy of the system, the strongest values being observed for low temperatures.

3. 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 has been the subject of study in recent years, applying different empirical or semiempirical models due to their interest to optimize industrial equipment and understanding the mixing liquids trend. Experimental data for the isentropic compressibility of the mixtures were compared with values determined by different mixing procedures. The models of Danusso and Nomoto (Eq. (19) and (20)) [Danusso, 1951; Nomoto, 1968]:

$$\kappa_S = \left(\frac{1}{M \cdot \rho}\right) \cdot \left(\sum_{i=1}^{N} \frac{n_i M_i}{\rho_i^2 u_i^2}\right) \tag{19}$$

$$\kappa_S = \left(\frac{1}{\rho}\right) \cdot \left(\frac{\sum_i^N n_i R_i}{\sum_i^N n_i u_i}\right)^{-6} \tag{20}$$

where $R = u^{1/3} \cdot \sum_i^N n_i V_i$, and Collision Factor Theory, (CFT) [Nutschkuhnkies, 1965; Schaffs, 1975] (Eq. (21)) and Free Length Theory (FLT) [Jacobson, 1952] (Eq. (22)) for the isentropic compressibilities were applied:

$$\kappa_S = \left(\frac{1}{\rho^3}\right) \cdot \left(\frac{M}{u_\infty \cdot \sum_i^N x_i S_s \cdot \sum_i^N x_i B_s}\right) \tag{21}$$

$$\kappa_S = \left(\frac{L_f^2}{K^2}\right) \tag{22}$$

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 in 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 paper, and the corresponding molar volumes [Resa et al., 2003a]. These values could be also evaluated by means of the group contribution method proposed by Schaffs, 1963 [Gonzalez et al., 1999] when no experimental data are disposable.

The Free Length Theory estimates the isentropic compressibility of a mixture attending to the free displacement of molecules as a main function of temperature. In the last few years different authors have compared the relative merits of the existent theories with the Free Length Theory (FLT), the FLT results in lower deviations of computed isentropic compressibilities from experimental values. The deviations of each procedure for the studied mixtures are gathered into Table 5 by means of Eq. (5). As expected, they increase as a consequence of rising temperatures. Attending to the deviation computed data, we arrive at the conclusion that the application of the Free Length Theory predicts experimental data extremely well for all the studied mixtures, showing this procedure as an accurate tool for isentropic compressibility data in these kinds of systems.

RESULTS AND DISCUSSION

The mixing properties and behaviour of ethanol vary with the nature of the chemical environment, operation conditions, and then, steric hindrance molecular effects as it was observed in this work. The experimental values of the changes of isentropic compressibility provide information about ethanol+hydroxylic mixtures interactions as the molar fraction of ethanol is changed, as well as the packing efficiency.

It is seen from the measured data that in the three components, an intense effect of temperature is produced. The molecular associ-

Table 5. Root mean square deviations for estimated isentropic compressibility from experimental data for the ternary mixtures at range of 288.15-323.15 K

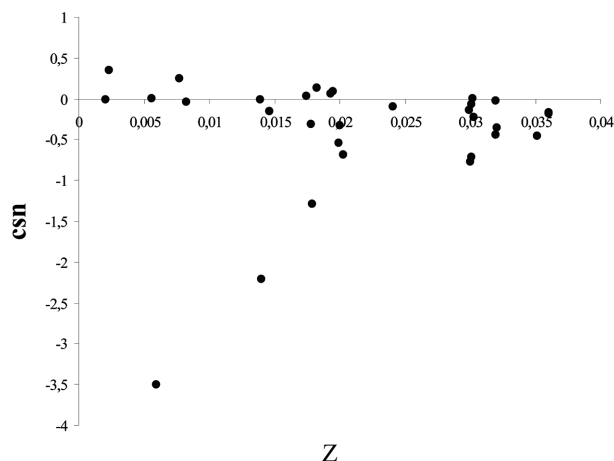| Mixture	Danusso (Eq. (19))	Nomoto (Eq. (20))	CFT (Eq. (21))	FLT (Eq. (22))
Ethanol+water+1-pentanol (323.15 K)	110.26	31.08	75.33	2.61
Ethanol+water+1-pentanol (298.15 K)	91.56	34.88	31.25	1.47
Ethanol+water+1-pentanol (288.15 K)	86.47	37.02	15.99	1.18

Fig. 5. Compressibility hydration numbers for ethanol+water+1-pentanol at 298.15 K.

ation becomes maximum at those composition points (in this case, pure water) where velocity maximum occurs. This may be interpreted due to the formation of strong hydrogen bonding resulting into complex formation producing displacement of electrons and nuclei. The chemical interaction may involve association due to hydrogen bonding; due to the dipole-dipole interaction or due to the formation of charge-transfer complexes, all of them may lead to strong interaction of forces. The occurrence of maximum velocity is for pure water at any temperature, and then a subsequent decrease of velocity with further increase in concentration may be explained by an increment in entropy and a diminution of hydroxyl interaction power by steric hindrance. New molecules of ethanol and 1-pentanol may be accommodated in the liquid matrix, and this fact produces liquid phase separation when low concentrations of ethanol are enclosed. The awakening of the intermolecular forces is probably the reason for the strong decrease in ultrasonic velocity and partial miscibility. Furthermore, it may be seen from Fig. 1a, 1b and 1c where the change of isentropic compressibility is showed. As it could be expected, attending to the molecular structure of solvents, three different trends of interaction could be observed: a hydrogen bond interaction domains the ethanol+water mixture yielding to intense contractive trend in the corresponding pseudobinary mixture. Second, a phase splitting occurs in water+1-pentanol mixtures when neither water nor 1-pentanol is the most abundant component. And third, a slight expansion occurs for almost equimolar compositions in the neighbourhood of the binary ethanol+water (maxima of change of isentropic compressibility).

Steric hindrance awakens hydrogen bonding between oxygen and protons, resulting in the formation of short mean life hydrogen bonds and less rigid mixtures at any specific temperature.

The excess intermolecular free length (Figs. 3a, 3b and 3c) reflects the progressive increment of negative values when temperature decreases. Intermolecular free length is a predominant factor in determining the variation of ultrasonic velocity in solutions.

Table 4 indicates the variation of the acoustic parameters at the extreme and standard temperatures. About the obtained values for the excess acoustic impedance at all concentrations of the mixtures, they are negative at any composition, decreasing their negative values as temperature diminishes.
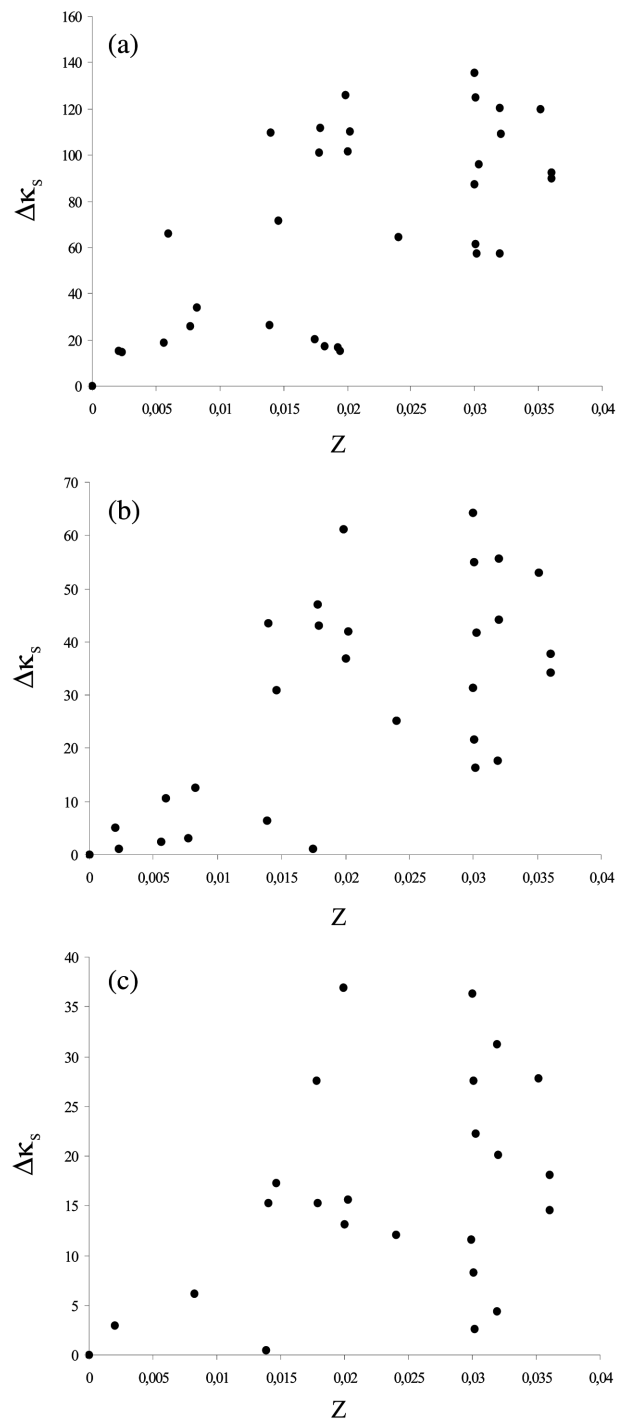
Fig. 6. Curves of deviation from experimental data of the estimation by CFT for ethanol+water+1-pentanol (a) 323.15 K (b) 298.15 K (c) 288.15 K.

In what is referred to as theoretical estimation, as it could be observed in the Table 5, the better deviations are shown for the FLT model, a slight overestimation being observed when the temperature is high.

CONCLUSIONS

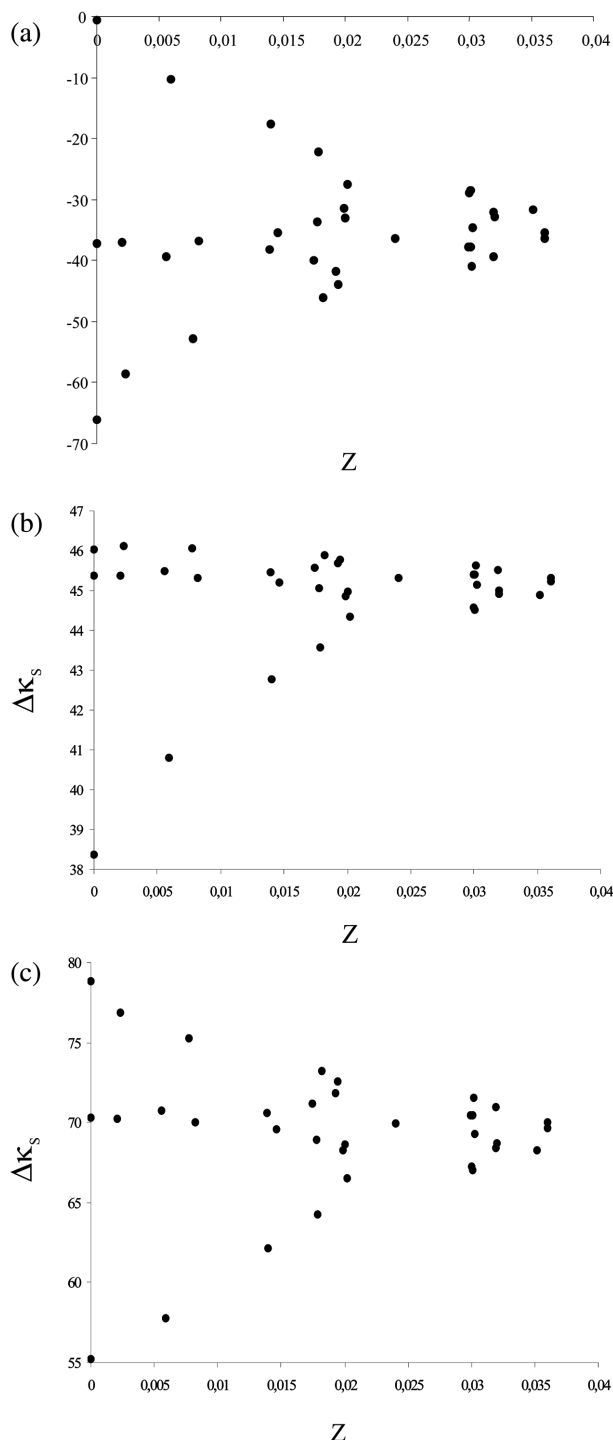Expansive equimolar behaviour is conditioned mainly by the steric

Fig. 7. Curves of deviation from experimental data of the estimation by FLT for ethanol+water+1-pentanol (a) 323.15 K (b) 298.15 K (c) 288.15 K.

hindrance over the aliphatic end of the heavy alcohol into the extremely ordered hydroxylic structure in such a way that diminution or increment of 1-pentanol composition notably affects the contractive tendency and then in the sign and magnitude of change of isentropic compressibility.

Temperature is a fact that in this work deals towards diminution of maxima of change of isentropic compressibility, probably due to

an increasing difficulty of accommodation of the aliphatic end of the heavy alcohol by molecular kinetics.

The special structure is specially sensitive to globular molecules with polar or slight polar groups (as 1-pentanol) and inert solvents, which are difficultly enclosed. The pentyl group (-C5H11) is much bulkier than ethyl group (-C2H5) attached with hydroxyl group. Due to that, the short molecules in mixture experience greater steric hindrance as compared to the pure solvent situation or single interaction short solvent+1-pentanol.

The auto associative behaviour of ethanol is the cause of contractive tendency with water (polar hydroxyl group) and slight polar-dispersive interaction with the aliphatic end of 1-pentanol. Water+1-pentanol mixtures show partial expansive trend due to the polar difference is strong enough for phase splitting at the studied temperatures.

The ternary contribution DQ shows two questions to be pointed out: first, the considerable contribution to the derived property by ternary molecular interactions, although it's a decreasing factor for higher temperatures; second, the different sign of this contribution attending to ethanol composition. Such trend is normal due to the evolution of the physical property as a function of molar fraction.

Intermolecular free length shows an analogous behaviour as reflected by isentropic compressibility for this mixture. The decreased compressibility brings the molecules to a closer packing resulting in a decrease of intermolecular free length.

The decrease in the values of isentropic compressibility and intermolecular free length with increase in ultrasonic velocity indicates that there is a significant interaction among molecules due to which structural arrangement is considerably affected.

The whole models are, at least, of qualitative accuracy to predict ternary values of isentropic compressibility, showing the FLT a lower deviation for the whole composition range. Deviations yielded for the estimated ternary magnitude also show dependence with the temperature. They 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 ternary mixture, where both an associative and a phase splitting phenomenon occurs.

ACKNOWLEDGMENTS

NOMENCLATURE

δQ : means the variation of a magnitude
κ_S : isentropic compressibility
B : geometrical volume
b : van der Waals' constant
B_p : fitting parameters
K : temperature dependent constant
L_f : intermolecular free length
M : degree of the polynomial
M_A : molecular association
N : number of components into mixtures
n_{DAT} : number of experimental data

n_{solute} : mol number of solute
$n_{solvent}$: mol number of solvent
Q   : magnitude
Q_i : pure solvent magnitude
R   : molar sound velocity
r   : molecular radius
R_A : relative association
S   : collision factor
V_0 : volume at absolute zero
V_a : available volume
x_i : mole fraction
Y   : molar surface area
Z   : specific acoustic impedance

REFERENCES

Bevington. P., *Data reduction and error analysis for the physical sciences*, McGraw-Hill, New York (1969).

Cibulka, I., "A relation between excess volume and the form of the dependence of density on composition for binary-liquid mixtures," *Coll. Czech. Chem. Comm.*, **55**(7), 1653 (1990).

Danusso, F., "Ultrasonic velocity and adiabatic compressibility of liquid mixtures," *Atti Accad. Nazl. Lince.i*, **10**, 235 (1951).

Eyring, H. and Kincaid, J. F., "The activate complex in chemical reactions," *J. Chem. Phys., (USA)*, **6**, 620 (1938).

Gaiser, M., Bell, G. M., Lim, A. W., Roberts, N. A., Faraday, D. B. F., Schultz, R. A. and Grob, R., "Computer simulation of a continuous whisky still," *J. Food Eng.*, **51**, 27 (2002).

Gayol, A., Iglesias, M., Concha, C. G, Goenaga, J. M., Gonzalez, C. and Resa, J. M., "Effect of temperature on thermophysicalmagnitudes of (ethanol+aliphatic elcohols (c4-c5)) mixtures," *J. M. Phys. Chem. Liq.* (2005) (submitted for publication).

Gonzalez, C., Iglesias, M., Lanz, J. and Resa, J. M., "Temperature dependence of excess molar volumes in (n-alkane (C-6-C-9) or alcohol (C-2-C-4)) plus olive oil mixtures," *Thermochimica Acta.*, **328**, 277 (1999).

Jacobson, B., "Intermolecular free lengths in the liquid state. 1. Adiabatic and isothermal compressibilities," *Acta Chemica Scandinavica*, **6**, 1485 (1952).

Marquardt, D. W., "An algorithm for least-squares estimation of non-linear parameters," *J. Soc. Indust. Appl., Math* **2**, 431 (1963).

Nomoto, O., "Empirical formula for sound velocity in liquid mixtures," *J. Phys. Soc. Japan*, **13**, 1528 (1968).

Nutsch-kuhnkies, R., "Sound characteristics in binary mixtures and solutions," *Acustica*, **15**, 383 (1965).

Orge, B., Iglesias, M., Marino, G, Dominguez, M., Piñeiro, M. and Tojo, J., "Mixing properties of benzene+2-methyl-2-butanol+1-pentanol at 298.15 K. Experimental results and comparison between ERAS model and cubic EOS estimations for excess molar volumes," *J. Fluid Phase Eq.*, **170**, 151 (2000).

Orge, B., Iglesias, M., Rodriguez, A., Canosa, J. M. and Tojo, J., "Mixing properties of (methanol, ethanol, or 1-propanol) with (n-pentane, n-hexane, n-heptane and n-octane) at 298.15 K," *Fluid Phase Eq.*, **133**, 213 (1997).

Redlich, O. and Kister, A. T., "Algebraic representation of thermodynamic properties and the classification of solutions," *Ind. Eng. Chem.*, **40**, 345 (1948).

Resa, J. M., Gonzalez, C., Goenaga, J. M. and Iglesias, M., "Temperature dependence of excess molar volumes of ethanol plus water plus ethyl acetate," *J. Solution Chem.*, **33**(2), 169 (2004).

Schaaffs, W., *Molekularakustic; eine einfuehurng in die zusammenhaenge zwischen ultrachall and molecuelstruktur in fluessigkeiten und gasen*, Springer Verlag, Bonn (1963).

Schaffs, W., "Problem of a theoretical calculation of velocity of sound for binary-liquid mixtures," *Acustica*, **33**(4), 272 (1975).

Tejraj, M. A., Mirtyunjaya, I. A., Aralaguppi, B. G and Rajashekhar, S. K., "Densities, shear viscosities, refractive-indexes, and speeds of sound of bis(2-methoxyethyl) ether with hexane, heptane, octane, and 2,2,4-trimethylpentane in the temperature interval 298.15-k-318.15-k," *J. Chem. Eng. Data*, **39**, 522 (1994).

TRC Thermodynamic Tables (Thermodynamic Research Center, Texas A&M University: College Station, TX, 1994).