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Volumetric and Acoustic Properties of the Ternary Mixture 1-Butanol + 1-Chlorobutane + Tetrahydrofuran at 283.15, 298.15, and 313.15 K

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Experimental densities (ρ) and speeds of sound (u) were obtained for the ternary system (1-butanol + 1-chlorobutane + tetrahydrofuran) at three temperatures: 283.15, 298.15, and 313.15 K. Excess molar volumes (V^{E}) and isentropic compressibility deviations ($\Delta\kappa_S$) have been calculated from experimental data. A discussion of the thermodynamic behavior of the ternary system with temperature variation is presented.

KEY WORDS: 1-butanol; 1-chlorobutane; density; excess molar volumes; isentropic compressibilities; speeds of sound; ternary mixture; tetrahydrofuran.

1. INTRODUCTION

The study of thermodynamic properties of binary and ternary mixtures contributes to an understanding of the behavior of different liquids and functional groups. This information is very useful in the design of industrial processes and in the development of theories for the liquid state and predictive methods.

Our research group have been studying many different properties of ternary mixtures [1–4]. For the present paper we have chosen three liquids of similar size and different functional groups: an alcohol (1-butanol), an halogenated compound (1-chlorobutane), and a cyclic ether (tetrahydrofuran), which we have already analyzed in other binary [5, 6] and ternary

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[1–4] mixtures. Here, we have measured densities, ρ, and speeds of sound, u, at three temperatures, 283.15, 298.15, and 313.15 K, to observe more appropriately the effect of temperature.

2. EXPERIMENTS

The liquids used were 1-butanol (better then 99.8 mol%), 1-chlorobutane (better than 99 mol%), and tetrahydrofuran (better than 99.5 mol%) obtained from Aldrich. The purity of the chemicals was checked using chromatographic methods, the main impurity in the compounds is water (0.012 mol% in 1-chlorobutane, 0.00019 mol% in 1-butanol and 0.008 mol% in tetrahydrofuran), and tetrahydrofuran also contains 0.002 mol% of peroxide. Considering the quality of the chemicals, they were used without additional purification, although the 1-butanol was dried over activated molecular sieve (0.3 nm) from Merck. The pure compounds properties, along with literature values of density [7, 8], are shown in Table I.

Densities to calculate excess molar volumes were obtained with an Anton Paar DMA-58 vibrating tube densimeter, automatically controlled to within ± 0.01 K. This instrument gives a precision of the density measurements of $\pm 5 \times 10^{-6}\ \mathrm{g \cdot cm^{-3}}$. The estimated uncertainty in the density measurements is $\pm 1 \times 10^{-5}\ \mathrm{g \cdot cm^{-3}}$.

Isentropic compressibilities have been calculated from densities and speeds of sound. The speeds of sound were determined with an Anton Paar DSA-48 density and sound analyzer automatically thermostated, which gives a precision of $\pm 0.1\ \mathrm{m \cdot s^{-1}}$. The uncertainty in the speed-of-sound measurements is $\pm 1\ \mathrm{m \cdot s^{-1}}$.

Table I. Densities, ρ, Speeds of Sound, u, and Isentropic Compressibilities, κ_S, of the Pure Compounds and Comparisons with Literature Data

	T (K)	ρ (kg·m^{-3})		u (m·s^{-1})	κ_S (TPa^{-1})
Compound		Exp.	Lit.	Exp.	Exp.
1-Butanol	283.15	817.13	817.0 [7]	1290.3	735.1
	298.15	805.76	805.75 [8]	1240.2	806.9
	313.15	794.22	794.6 [7]	1189.9	889.3
1-Chlorobutane	283.15	897.26	896.2 [7]	1179.4	801.2
	298.15	880.69	880.95 [8]	1118.1	908.3
	313.15	863.87	863.9 [7]	1056.6	1036.9
Tetrahydrofuran	283.15	898.38	895.3 [7]	1350.4	610.4
	298.15	881.96	881.97 [8]	1277.8	694.4
	313.15	865.38	870.5 [7]	1206.0	794.5

The calibrations of both apparatus at each temperature were carried out with deionized doubly distilled water and dry air.

3. RESULTS AND DISCUSSION

Densities, ρ, speeds of sound, u, isentropic compressibilities, κ_S, excess molar volumes, V^E, and isentropic compressibility deviations, $\Delta\kappa_S$, at 283.15, 298.15, and 313.15 K for the ternary mixture 1-butanol+1-chlorobutane+tetrahydrofuran are given in Table II.

The expressions which relate κ_S and $\Delta\kappa_S$ with r and u are

$$\kappa_S = \frac{1}{\rho u^2} \tag{1}$$

$$\Delta\kappa_S = \kappa_S - \sum_i x_i \kappa_{S,i} \tag{2}$$

where x_i and $\kappa_{S,i}$ are, respectively, the mole fraction and the isentropic compressibility of component i.

The values of both excess properties of the ternary mixture have been fitted to the Cibulka equation [9]:

$$Y^E = Y^E_{\text{bin}} + (C_1 + C_2 x_1 + C_3 x_2) \tag{3}$$

where Y^E is the excess molar volume or the isentropic compressibility deviation, x_i is the mole fraction of component i in the ternary mixture, C_i's are adjustable parameters obtained by the least-squares method, and Y^E_{bin} is the binary contribution, which is given by

$$Y^E_{\text{bin}} = \sum_{i \neq j} Y^E_{ij} = Y^E_{12} + Y^E_{13} + Y^E_{23} \tag{4}$$

where Y^E_{ij} is a Redlich–Kister polynomial equation,

$$Y^E_{ij} = x_i x_j \sum_{p=0}^{n} A_p (x_i - x_j)^p \tag{5}$$

where x_i and x_j are the mole fractions in the binary mixture and A_p's are binary adjustable parameters obtained by least squares.

The Redlich–Kister parameters for all the constituent binary mixtures have been taken from literature values [5, 6], and they are presented in Table III along with standard deviations in the properties correlation. Parameters of the Cibulka equation are reported in Table IV along with the corresponding standard deviations.

Table II. Densities, ρ, Speeds of Sound, u, Isentropic Compressibilities, κ_S, Excess Molar Volumes, V^E, and Isentropic Compressibility Deviations, $\Delta\kappa_S$, of the Ternary Mixture 1-Butanol(1) + 1-Chlorobutane(2) + Tetrahydrofuran(3)

x_1	x_2	ρ (g·cm^{-3})	u (m·s^{-1})	κ_S (TPa^{-1})	V^E (cm^3·mol^{-1})	$\Delta\kappa_S$ (TPa-1)
			283.15 K			
0.0461	0.0542	0.89418	1333.6	628.8	−0.002	2.3
0.0460	0.0948	0.89424	1324.5	637.5	−0.008	3.3
0.1074	0.0549	0.88870	1328.4	637.7	0.002	3.4
0.0917	0.0959	0.89023	1321.0	643.7	−0.008	3.6
0.0954	0.1949	0.89015	1299.9	664.9	−0.023	5.4
0.0988	0.3012	0.89006	1278.8	687.0	−0.033	6.8
0.1027	0.4965	0.88995	1243.2	727.1	−0.037	9.1
0.1036	0.6011	0.88988	1226.0	747.6	−0.028	9.6
0.1076	0.7124	0.88950	1207.7	770.8	−0.009	11.1
0.0924	0.8059	0.89050	1194.2	787.4	0.013	11.7
0.0912	0.846	0.89048	1187.9	795.8	0.028	12.6
0.1998	0.0963	0.88094	1312.5	659.0	−0.010	5.3
0.1898	0.1975	0.88224	1292.6	678.4	−0.024	6.6
0.1954	0.3051	0.88228	1271.7	700.8	−0.043	7.8
0.2004	0.4017	0.88219	1253.7	721.2	−0.047	9.2
0.2043	0.5039	0.88211	1235.3	742.9	−0.040	10.8
0.1910	0.6074	0.88317	1218.7	762.4	−0.017	12.3
0.1960	0.7024	0.88274	1201.4	784.9	0.015	16.0
0.2956	0.0993	0.87305	1305.8	671.8	−0.024	5.6
0.3046	0.2011	0.87303	1284.9	693.8	−0.041	7.0
0.2944	0.5090	0.87520	1228.5	757.1	−0.030	12.9
0.3007	0.5993	0.87482	1211.6	778.7	0.003	16.5
0.3950	0.0995	0.86495	1300.2	683.9	−0.029	5.2
0.3901	0.2040	0.86625	1279.7	705.0	−0.045	7.0
0.4010	0.2976	0.86616	1260.9	726.1	−0.057	8.9
0.3921	0.4114	0.86745	1239.9	749.8	−0.042	12.0
0.4023	0.4994	0.86700	1222.8	771.4	−0.015	15.5
0.4975	0.0998	0.85684	1294.1	696.9	−0.039	5.5
0.4935	0.2064	0.85828	1274.1	717.7	−0.054	6.4
0.4879	0.3005	0.85947	1255.9	737.7	−0.048	9.1
0.4993	0.4025	0.85927	1235.5	762.4	−0.027	12.9
0.6009	0.1025	0.84884	1289.6	708.4	−0.044	3.5
0.5995	0.2097	0.85019	1268.0	731.6	−0.049	6.4
0.5944	0.3075	0.85154	1248.6	753.3	−0.042	10.1
0.6888	0.1041	0.84225	1284.8	719.3	−0.054	3.2
0.6902	0.1949	0.84336	1266.2	739.6	−0.060	5.9
0.8004	0.1042	0.83379	1279.2	732.9	−0.039	2.9
0.8264	0.0606	0.83111	1287.3	726.0	−0.029	1.0
0.8965	0.0452	0.82563	1286.5	731.8	−0.020	1.0

Table II. *(Continued)*

x_1	x_2	ρ $(\mathrm{g \cdot cm^{-3}})$	u $(\mathrm{m \cdot s^{-1}})$	κ_S $(\mathrm{TPa^{-1}})$	V^E $(\mathrm{cm^3 \cdot mol^{-1}})$	$\Delta\kappa_S$ $(\mathrm{TPa^{-1}})$
			298.15 K			
0.0470	0.0536	0.87805	1263.9	713.0	−0.012	1.8
0.0474	0.0944	0.87810	1255.4	722.6	−0.022	2.6
0.1090	0.0560	0.87285	1259.8	721.8	−0.005	3.2
0.0933	0.0941	0.87427	1253.1	728.4	−0.016	3.4
0.0946	0.1940	0.87444	1233.4	751.7	−0.038	5.1
0.0979	0.3013	0.87436	1213.1	777.1	−0.050	7.3
0.1010	0.3956	0.87420	1196.9	798.5	−0.053	8.1
0.1021	0.4958	0.87413	1180.6	820.8	−0.049	8.9
0.1044	0.5995	0.87391	1164.4	844.0	−0.037	9.7
0.1094	0.7104	0.87337	1146.7	870.8	−0.008	12.2
0.0927	0.8039	0.87425	1133.8	889.8	0.029	13.0
0.0922	0.8473	0.87414	1127.8	899.4	0.048	13.4
0.2008	0.0970	0.86563	1246.9	743.0	−0.017	5.3
0.1919	0.1953	0.86678	1228.4	764.6	−0.036	6.8
0.1962	0.3044	0.86679	1208.7	789.6	−0.043	8.0
0.2014	0.4022	0.86663	1191.0	813.5	−0.042	10.4
0.2100	0.5010	0.86616	1174.0	837.7	−0.033	12.5
0.1928	0.6084	0.86741	1157.2	860.9	−0.009	14.7
0.2000	0.6990	0.86669	1141.9	884.9	0.039	18.5
0.2985	0.0981	0.85799	1242.7	754.8	−0.021	5.8
0.3058	0.2012	0.85810	1222.1	780.3	−0.038	8.4
0.3008	0.3083	0.85901	1203.2	804.2	−0.044	10.0
0.3078	0.4064	0.85889	1185.5	828.4	−0.040	12.5
0.2948	0.5089	0.86002	1168.1	852.2	−0.016	15.8
0.3001	0.5985	0.85964	1152.1	876.4	0.025	20.2
0.3969	0.0980	0.85050	1239.2	765.6	−0.027	5.6
0.3897	0.2036	0.85183	1219.1	790.0	−0.038	8.2
0.3999	0.2967	0.85175	1201.6	813.2	−0.047	10.3
0.3944	0.4121	0.85269	1180.4	841.7	−0.031	14.8
0.4035	0.4974	0.85221	1164.2	865.8	0.007	19.6
0.4975	0.1015	0.84302	1234.7	778.1	−0.032	6.0
0.4937	0.2068	0.84429	1214.9	802.5	−0.043	8.4
0.4920	0.2995	0.84516	1197.2	825.5	−0.044	11.7
0.5007	0.4006	0.84507	1177.6	853.3	−0.015	16.9
0.6022	0.1012	0.83540	1232.2	788.4	−0.037	4.6
0.6024	0.2080	0.83652	1210.9	815.3	−0.041	8.7
0.5972	0.3041	0.83768	1191.8	840.5	−0.026	13.8
0.6919	0.1026	0.82896	1229.2	798.5	−0.034	4.3
0.6886	0.1951	0.83033	1210.9	821.4	−0.039	7.8
0.8003	0.1044	0.82136	1225.3	810.9	−0.031	4.1
0.8556	0.1054	0.81756	1222.8	818.0	−0.029	4.8
0.8985	0.045	0.81362	1234.3	806.7	−0.021	1.7

Table II. *(Continued)*

x_1	x_2	ρ ($g \cdot cm^{-3}$)	u ($m \cdot s^{-1}$)	κ_S (TPa^{-1})	V^E ($cm^3 \cdot mol^{-1}$)	$\Delta\kappa_S$ (TPa^{-1})
313.15 K						
0.0555	0.8414	0.86029	1071.2	1013.1	0.028	9.4
0.0576	0.9009	0.85986	1063.2	1028.9	0.062	10.5
0.0928	0.0951	0.85818	1185.1	829.7	−0.010	3.3
0.0962	0.1955	0.85813	1166.3	856.7	−0.030	5.7
0.0962	0.3012	0.85821	1147.9	884.3	−0.037	7.7
0.1008	0.3948	0.85791	1133.1	907.8	−0.039	8.1
0.1028	0.4975	0.85777	1117.4	933.8	−0.036	9.0
0.1052	0.6019	0.85747	1101.5	961.1	−0.018	10.8
0.1092	0.7105	0.85695	1085.9	989.6	0.017	12.6
0.0908	0.8074	0.85790	1073.2	1012.1	0.047	13.3
0.2012	0.0959	0.85006	1181.3	843.0	−0.011	6.2
0.1906	0.1982	0.85120	1163.0	868.6	−0.026	8.0
0.1953	0.3064	0.85118	1145.0	896.2	−0.038	8.9
0.2016	0.4014	0.85087	1129.0	922.1	−0.031	11.2
0.2070	0.5030	0.85054	1112.8	949.4	−0.013	13.4
0.1937	0.6089	0.85137	1096.6	976.8	0.015	16.3
0.1973	0.7007	0.85085	1081.9	1004.2	0.069	21.1
0.2978	0.0981	0.84301	1178.8	853.7	−0.013	7.2
0.2979	0.3094	0.84400	1141.6	909.2	−0.030	11.4
0.3054	0.4068	0.84369	1124.8	936.9	−0.012	14.8
0.2949	0.5081	0.84457	1108.2	964.1	0.008	18.5
0.3005	0.5984	0.84400	1092.8	992.2	0.069	24.2
0.3947	0.0997	0.83614	1176.4	864.1	−0.019	8.1
0.3892	0.2030	0.83726	1157.6	891.4	−0.035	10.8
0.3981	0.2976	0.83708	1140.5	918.4	−0.025	14.1
0.3934	0.4129	0.83781	1121.1	949.7	−0.003	17.9
0.4014	0.4986	0.83726	1105.5	977.3	0.052	23.9
0.5062	0.1025	0.82846	1174.3	875.4	−0.030	8.0
0.4924	0.2073	0.83026	1154.8	903.2	−0.037	11.7
0.4898	0.2995	0.83100	1138.2	929.0	−0.027	15.4
0.5051	0.3982	0.83013	1119.6	961.0	0.037	22.1
0.6012	0.1017	0.82196	1173.9	882.8	−0.030	6.7
0.6017	0.2102	0.82292	1152.5	914.9	−0.029	12.4
0.5965	0.3055	0.82372	1134.7	942.8	0.015	17.7
0.6911	0.1035	0.81587	1172.2	892.1	−0.020	7.0
0.6904	0.1950	0.81682	1153.4	920.2	−0.011	13.0
0.8419	0.0448	0.80519	1182.7	887.8	−0.015	2.7
0.8574	0.1030	0.80495	1170.1	907.3	−0.011	6.6
0.8982	0.0445	0.80155	1181.5	893.8	−0.016	3.4

Table III. Parameters of the Redlich-Kister Eq. (5), A_p, for the Constituent Binary Mixtures and Standard Deviations, $\sigma\ (Y^E)$

Property	T (K)	A_0	A_1	A_2	A_3	$\sigma\ (Y^E)$
		1 – Butanol(1) + 1 – Chlorobutane (2)				
V^E	283.15	0.079	−0.583	0.097	−0.162	0.002
	298.15	0.299	−0.681	0.246	−0.186	0.001
	313.15	0.565	−0.590	0.363	−0.619	0.002
$\Delta\kappa_S$	283.15	77.7	−57.6	39.2	−48.3	0.1
	298.15	103.7	−68.7	36.9	−29.3	0.2
	313.15	128.6	−75.9	19.7	−14.4	0.5
		1 – Butanol(1) + Tetrahydrofuran(2)				
V^E	283.15	−0.060	−0.131	0.048	0.017	0.001
	298.15	0.004	−0.151	0.032	0.033	0.001
	313.15	0.043	−0.131	−0.006	0.043	0.001
$\Delta\kappa_S$	283.15	11.6	−18.5	−10.7	1.6	0.1
	298.15	12.5	−17.6	−13.3	2.3	0.1
	313.15	15.2	−17.4	−8.0	3.9	0.1
		1 – Chlorobutane(1) + Tetrahydrofuran(2)				
V^E	283.15	−0.221	0.010	0.016	−0.060	0.001
	298.15	−0.235	0.000	0.025	−0.023	0.001
	313.15	−0.281	0.006	−0.064	−0.045	0.001
$\Delta\kappa_S$	283.15	26.2	−1.4	0.7	−2.4	0.1
	298.15	24.3	−2.8	−4.2	9.8	0.1
	313.15	22.6	−0.6	−8.0	7.6	0.1

Table IV. Parameters of the Cibulka Eq. (3), C_i, for the Ternary Mixture 1-Butanol(1) + 1-Chlorobutane(2) + Tetrahydrofuran(3) and Standard Deviations, $\sigma\ (Y^E)$

Property	T (K)	C_1	C_2	C_3	$\sigma\ (Y^E)$
V^E	283.15	0.582	−1.308	−2.606	0.004
	298.15	−0.133	−1.161	−3.274	0.006
	313.15	0.616	−3.882	−3.651	0.006
$\Delta\kappa_S$	283.15	−15.1	−31.9	−240.1	0.3
	298.15	5.9	−82.0	−345.6	0.4
	313.15	7.6	10.4	−466.3	0.4

Isolines at constant values of excess molar volumes for the ternary mixture have been graphically represented in Figs. 1 to 3, while isentropic compressibility deviations are plotted in Figs. 4 to 6.

Absolute V^E values for the ternary mixture at the three temperatures are small. Values are slightly negative in most of the composition regions and become positive for small mole fractions of tetrahydrofuran. The largest values correspond to the binary mixture 1-butanol + 1-chlorobutane and the smallest values to the binary mixture 1-chorobutane + tetrahydrofuran. We also observe that the V^E values become more positive with an increase in temperature.

Isentropic compressibility deviations show positive values at the three temperatures and, as observed for the excess molar volumes, $\Delta\kappa_S$ values are larger for small mole fractions of tetrahydrofuran. It is also observed that $\Delta\kappa_S$ values increase with an increase in temperature.

The sign and magnitude of deviations of the volume and isentropic compressibility of the real mixture from ideal mixtures depend on the strength of the interaction between the molecules, on the structural effects, and on the differences in shape and size, with $\Delta\kappa_S$ more closely related with packing phenomena [10]. To explain the thermodynamic behavior of our mixture, there exist many different effects to consider. For the pure components, 1-butanol is self-associated with hydrogen bonds, while 1-chlorobutane and tetrahydrofuran show dipole-dipole interactions. When the

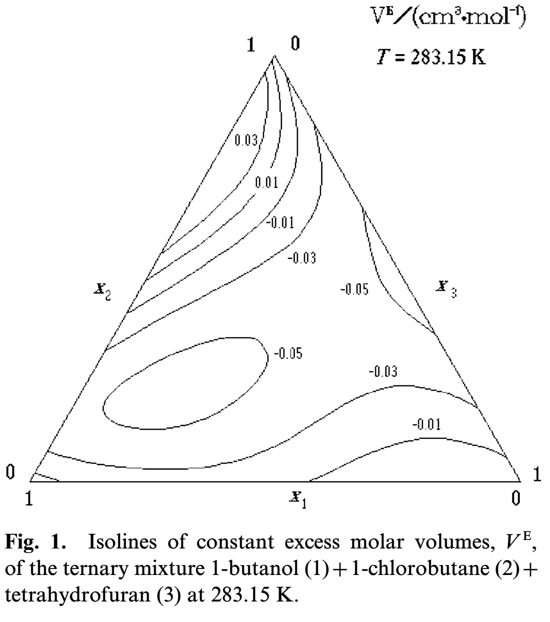

Fig. 1. Isolines of constant excess molar volumes, V^E, of the ternary mixture 1-butanol (1) + 1-chlorobutane (2) + tetrahydrofuran (3) at 283.15 K.

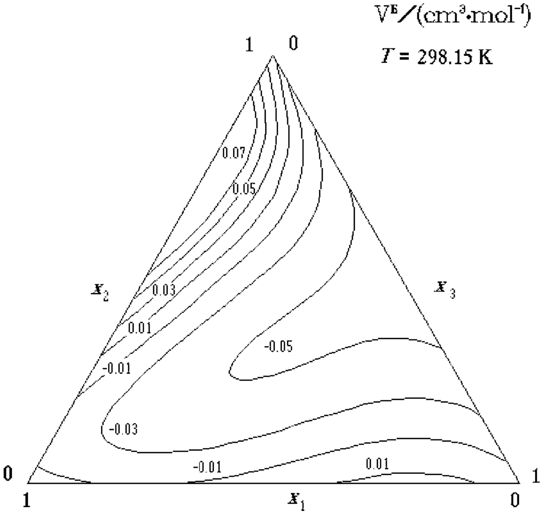

Fig. 2. Isolines of constant excess molar volumes, V^E, of the ternary mixture 1-butanol (1) + 1-chlorobutane (2) + tetrahydrofuran (3) at 298.15 K.

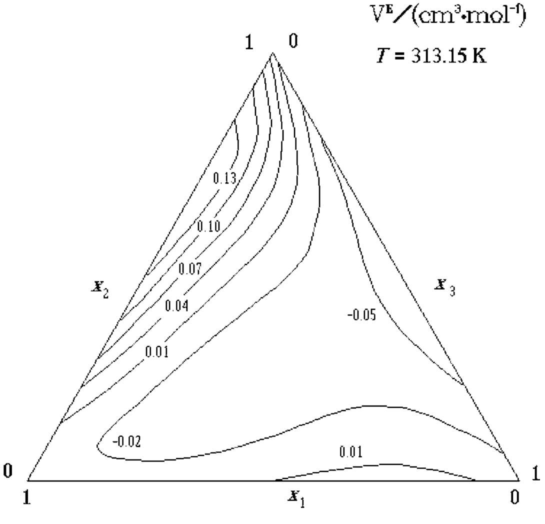

Fig. 3. Isolines of constant excess molar volumes, V^E, of the ternary mixture 1-butanol (1) + 1-chlorobutane (2) + tetrahydrofuran (3) at 313.15 K.

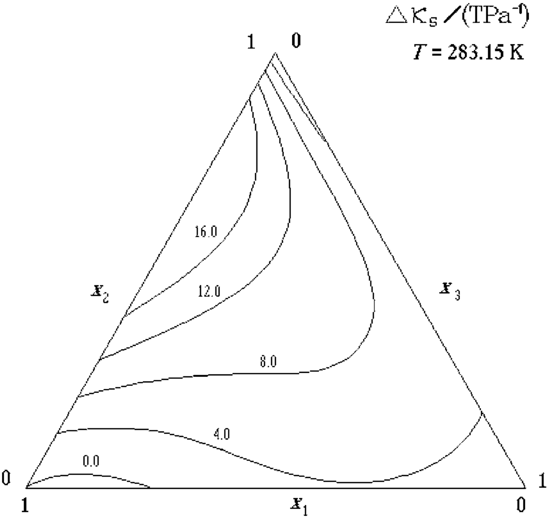

Fig. 4. Isolines of constant isentropic compressibility deviations, $\Delta\kappa_S$, of the ternary mixture 1-butanol (1) + 1-chlorobutane (2) + tetrahydrofuran (3) at 283.15 K.

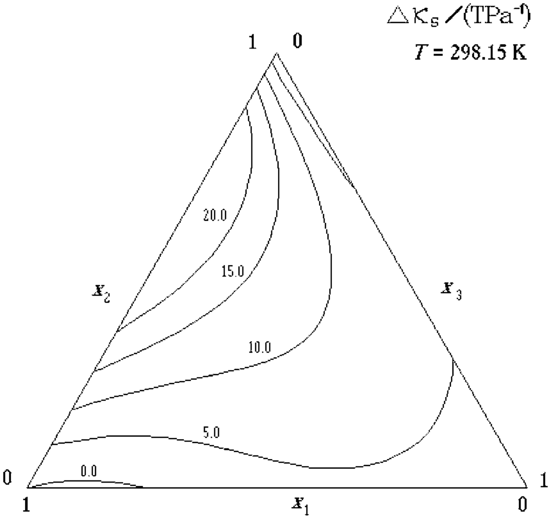

Fig. 5. Isolines of constant isentropic compressibility deviations, $\Delta\kappa_S$, of the ternary mixture 1-butanol (1) + 1-chlorobutane (2) + tetrahydrofuran (3) at 298.15 K.

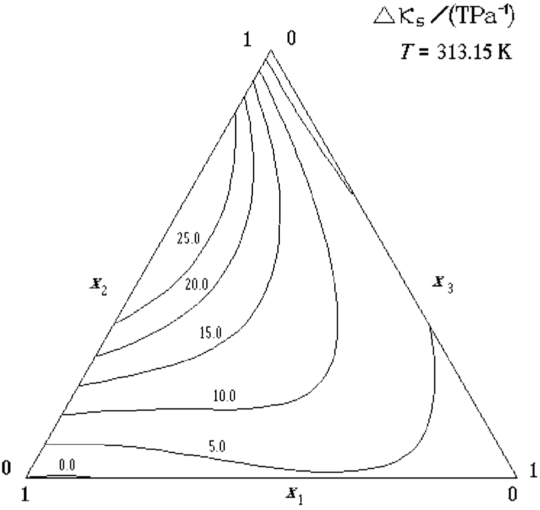

Fig. 6. Isolines of constant isentropic compressibility deviations, $\Delta\kappa_S$, of the ternary mixture 1-butanol (1) + 1-chlorobutane (2) + tetrahydrofuran (3) at 313.15.

mixing process occurs, like interactions weaken but specific interactions between the different components become more significant. The breaking or weakness of self-association and dipole-dipole interactions lead to negative V^E and $\Delta\kappa_S$ values, while specific interactions between the different functional groups, O-OH, Cl-OH, and O-Cl result in positive values.

Small absolute values of V^E indicate that all the effects are quite balanced; however, the positive values of $\Delta\kappa_S$ seems to indicate that the packing of molecules in the mixture is less compact than in the pure compounds.

Concerning the increase of the excess functions with temperature, it can be explained by the increase of thermal energy, which contributes to weaken the like interactions.

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