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Densities and speeds of sound in the ternary mixture (2-butanol + *n*-hexane + 1-chlorobutane) at 298.15 and 313.15 K

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Abstract

The densities and speeds of sound of the ternary mixture (2-butanol + *n*-hexane + 1-chlorobutane) have been measured at $T = 298.15$ and 313.15 K for the binary mixture (2-butanol + 1-chlorobutane) at $T = 313.15$ K. The excess molar volumes, and excess isentropic compressibilities were calculated and fitted to Cibulka's equation. The Flory's theory and the extended real associated solution (ERAS) model have been applied at $T = 298.15$ K to predict the excess molar volume of the ternary mixture. The isentropic compressibilities have been compared with calculated values from the collision factor theory (CFT) and free length theory (FLT). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Density; Speed of sound; Excess molar volume; Isentropic compressibility; Excess isentropic compressibility; Flory's theory; ERAS model; CFT; FLT; 2-Butanol; *n*-Hexane; 1-Chlorobutane

1. Introduction

This paper is a continuation of our work related to the study of thermodynamic and transport properties of binary and ternary mixtures [1–7] containing butanols, *n*-hexane, 1-chlorobutane and 1-butylamine. In this work, we report the excess molar volume and excess isentropic compressibility for the ternary mixture (2-butanol + *n*-hexane + 1-chlorobutane) at $T = 298.15$ and 313.15 K, and also the excess isentropic compressibility for the binary mixture (2-butanol + 1-chlorobutane) at $T = 313.15$ K. The excess molar volumes together with excess enthalpies found in literature at $T = 298.15$ K [1,8–11] for the three binary mixtures involved in the ternary mixture, have been used in applying the Flory's theory [12,13] and extended real associated solution (ERAS) model [14] to predict the excess molar volumes of ternary mixture. The Jacobson's free length theory (FLT) [15,16] and Schaaffs's collision factor theory (CFT) [17–19] have been used in this work to compare their predictions of isentropic compressibilities with the present experimental values at $T = 298.15$ and 313.15 K.

2. Experimental

2-Butanol (purities > 99.0%), *n*-hexane (purities > 99.5%) and 1-chlorobutane (purities > 99.0%) were obtained from Aldrich. The purity of the chemicals was checked not only by comparing the measured densities with those reported in the literature but also by GC–LC using a semi-capillary methyl silicone column (o.d. = 530 μm) and a flame-ionization detector. No further purification was considered

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Table 1

Experimental densities, ρ and speeds of sound, u, of pure substances and comparison with literature data

Component	ρ (g cm^{-3})				u (m s^{-1})			κ_S (TPa^{-1})		α^g (mK^{-1})		C_p (J mol^{-1} K^{-1})	
	298.15 K		313.15 K		298.15 K		313.15 K	298.15 K	313.15 K	298.15 K	313.15 K	298.15 K	313.15 K
	Experimental	Literature	Experimental	Literature	Experimental	Literature	Experimental						
2-Butanol	0.80239	0.80241^a, 0.8026^b	0.78939	0.7897^b	1212.1		1156.6	848.3	947.0	1.059	1.105	196.9^h	212.6^i
n-Hexane	0.65493	0.65484^a, 0.65489^c	0.64106	0.64110^c	1077.7	1076.42^e, 1076.37	1010.1	1314.5	1528.8	1.387	1.453	195.6^h	200.1^j
1-Chlorobutane	0.88085	0.88095^a, 0.8804^d	0.86388	0.8639^d	1117.4	1117.11^f	1056.6	909.3	1037.2	1.222	1.303	158.9^k	162.0^l

[a] Data taken from [20].

[b] Data taken from [21].

[c] Data taken from [22].

[d] Data taken from [23].

[e] Data taken from [24].

[f] Data taken from [25].

[g] Calculated from density data of TRC tables (Thermodynamics Research Center, Texas A&M University, College Station, TX).

[h] Data taken from [26].

[i] Data taken from [27].

[j] Data taken from [28].

[k] Data taken from [29].

[l] Data taken from [30].

necessary. 2-Butanol was dried with activated molecular sieve type 0.3 nm from Merck.

Densities, ρ, of the pure components and ternary mixture, were determined with an Anton Paar Model DMA-58 vibrating tube densimeter whose temperature was controlled to within ±0.01 K. The calibration of the densimeter was carried out with deionized double distilled water and dry air. The accuracy for the density measurements was $\pm 1 \times 10^{-5}$ g cm^{-3}, and the corresponding precision $\pm 0.5 \times 10^{-5}$ g cm^{-3}. $T = 298.15$ and 313.15 K compared with those found in the literature.

Speeds of sound, u, of the pure liquids and the mixtures, were measured by means of a vibrating tube densimeter and a sound analyser, Anton Paar Model DSA-48. The measuring principles are based on mechanical oscillations and time internal averaging, respectively. The samples were automatically thermostated with an accuracy of ±0.01 K. The calibration of the apparatus was carried out with deionized double-distilled water and dry air. The established accuracies of the density and speed of sound measurements are $\pm 1 \times 10^{-4}$ g cm^{-3} and ± 1 m s^{-1}, respectively, and the corresponding precisions are $\pm 3 \times 10^{-5}$ g cm^{-3} and ± 0.1 m s^{-1}, respectively. The experimental values of speed of sound for the pure components at $T = 298.15$ and 313.15 K are shown in Table 1, compared with literature data.

The compositions (mole fractions) of the binary and ternary mixtures were determined gravimetrically using a Mettler H20T balance. The precision of the mass was ±0.1 mg, and the uncertainty of the mole fraction is estimated to be greater than $\pm 1 \times 10^{-4}$.

3. Results and discussion

The experimental densities and speeds of sound of the binary mixture (2-butanol + 1-chlorobutane) at $T = 313.15$ K are given in Table 2. In previous papers, the V^{E} and $\kappa_{\mathrm{S}}^{\mathrm{E}}$ of the binary mixtures (2-butanol + n-hexane [4,5], 2-butanol + 1-chlorobutane [8,31], and n-hexane + 1-chlorobutane [1,3]) have been reported at $T = 298.15$ and 313.15 K. The experimental densities and speeds of sound for the ternary mixture (2-butanol + n-hexane + 1-chlorobutane) at $T = 298.15$ and 313.15 K are shown in Tables 3 and 4, respectively.

Table 2
Experimental densities, ρ, speeds of sound, u, along with calculated isentropic compressibilities, κ_{S}, and excess isentropic compressibilities, $\kappa_{\mathrm{S}}^{\mathrm{E}}$, for the binary mixture (2-butanol + 1-chlorobutane) at $T = 313.15$ K

x_1	ρ (g cm^{-3})	u (m s^{-1})	κ_{S} (TPa^{-1})	$\kappa_{\mathrm{S}}^{\mathrm{E}}$ (TPa^{-1})
0.1003	0.8548	1055.6	1049.9	13.0
0.1930	0.8475	1056.9	1056.3	21.6
0.2957	0.8398	1061.7	1056.4	26.2
0.3902	0.8328	1068.3	1052.1	28.0
0.4882	0.8257	1077.1	1043.9	27.7
0.5903	0.8185	1088.2	1031.7	25.7
0.6864	0.8117	1100.7	1016.9	22.1
0.7707	0.8057	1113.2	1001.6	18.0
0.8982	0.7967	1135.4	973.7	9.4
0.9487	0.7932	1145.2	961.3	5.4

The excess molar volume was calculated using the following expression:

$$V^{\mathrm{E}}\,(\mathrm{cm^3\,mol^{-1}}) = \sum_{i=1}^{n} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i}\right) \quad (1)$$

where M_i, x_i and ρ_i are the molecular weights, mole fractions and densities of components, respectively, ρ the density of mixture, and n is the number of components in the mixture. The error propagation from experimental error on densities is less than $\pm 1 \times 10^{-3}$ cm^3 mol^{-1}.

Assuming that the absorption of the acoustic wave is negligible, the isentropic compressibility κ_{S} can be calculated from Laplace's equation

$$\kappa_{\mathrm{S}} = \frac{1}{\rho u^2} \quad (2)$$

The excess isentropic compressibility $\kappa_{\mathrm{S}}^{\mathrm{E}}$ is defined as

$$\kappa_{\mathrm{S}}^{\mathrm{E}} = \kappa_{\mathrm{S}} - \kappa_{\mathrm{S}}^{\mathrm{id}} \quad (3)$$

where the isentropic compressibility for the ideal mixture, $\kappa_{\mathrm{S}}^{\mathrm{id}}$, was obtained according to Benson and Kiyohara [32] and Acree [33]

$$\kappa_{\mathrm{S}}^{\mathrm{id}} = \sum_{i=1}^{n} \phi_i \left\{ \kappa_{\mathrm{S},i} + \frac{T V_i (\alpha_i)^2}{C_{p,i}} \right\} - T\left(\sum_{i=1}^{n} x_i V_i\right) \frac{\left(\sum_{i=1}^{n} \phi_i \alpha_i\right)^2}{\sum_{i=1}^{n} x_i C_{p,i}} \quad (4)$$

where ϕ_i is the volume fraction of component i in the mixture referred to the unmixed state ($\phi_i =$

Table 3

Experimental densities, ρ, speeds of sound u, along with calculated excess molar volumes V^E, isentropic compressibilities, κ_S, and excess isentropic compressibilities, κ_S^E, for the ternary mixture (2-butanol (1) + n-hexane (2) + 1-chlorobutane (3)) at $T = 298.15$ K

x_1	x_2	ρ (g cm^{-3})	V^E (cm^{-3} mol^{-1})	u (m s^{-1})	κ_S (TPa^{-1})	κ_S^E (TPa^{-1})
0.0556	0.0511	0.86110	0.193	1112.1	939.0	3.5
0.0526	0.1022	0.84732	0.204	1107.2	962.7	1.7
0.0552	0.8449	0.67839	0.221	1075.4	1274.6	7.5
0.0550	0.8956	0.66887	0.204	1075.2	1293.4	9.1
0.1038	0.0516	0.85689	0.272	1111.5	944.5	9.0
0.1056	0.1007	0.84325	0.288	1106.6	968.4	8.0
0.1027	0.1996	0.81728	0.313	1099.0	1013.0	4.5
0.1022	0.3020	0.79154	0.336	1092.3	1058.8	3.0
0.1085	0.4037	0.76665	0.363	1086.5	1105.0	4.5
0.0985	0.5061	0.74408	0.372	1081.8	1148.4	5.5
0.0992	0.6050	0.72266	0.355	1078.3	1190.2	8.2
0.1009	0.7034	0.70200	0.367	1076.0	1230.4	11.1
0.1021	0.7969	0.68351	0.321	1074.7	1266.7	13.6
0.0962	0.8539	0.67310	0.293	1074.3	1287.3	14.6
0.1981	0.0996	0.83606	0.378	1108.0	974.2	15.1
0.1970	0.2014	0.80906	0.412	1099.9	1021.6	11.9
0.2025	0.3002	0.78370	0.435	1093.5	1067.1	10.8
0.1932	0.4072	0.75879	0.447	1087.3	1114.7	10.7
0.1980	0.5079	0.73546	0.457	1082.9	1159.4	12.7
0.1984	0.6044	0.71450	0.449	1079.8	1200.4	14.7
0.1939	0.7039	0.69428	0.426	1077.6	1240.3	16.6
0.2984	0.0972	0.82870	0.441	1112.1	975.7	19.7
0.2963	0.2048	0.80024	0.462	1103.5	1026.1	15.4
0.2890	0.3121	0.77378	0.481	1095.9	1076.0	13.8
0.2932	0.4082	0.75058	0.472	1090.8	1119.7	13.9
0.2907	0.5092	0.72772	0.479	1086.2	1164.7	15.4
0.2897	0.6086	0.70621	0.473	1083.1	1207.1	17.0
0.3954	0.1021	0.81991	0.442	1118.1	975.6	20.0
0.3966	0.2025	0.79299	0.464	1109.8	1023.9	16.0
0.3960	0.3036	0.76745	0.474	1102.6	1071.9	14.3
0.3930	0.4041	0.74353	0.477	1096.6	1118.5	14.1
0.3888	0.5120	0.71924	0.472	1091.7	1166.7	14.8
0.4948	0.1020	0.81226	0.424	1126.6	970.1	18.6
0.4943	0.2012	0.78573	0.436	1117.8	1018.6	14.3
0.4926	0.3035	0.75990	0.440	1110.2	1067.7	11.8
0.4887	0.4098	0.73473	0.423	1103.9	1116.9	10.5
0.5951	0.1017	0.80474	0.363	1137.2	960.9	14.9
0.5927	0.2024	0.77821	0.324	1128.0	1010.2	9.1
0.5955	0.3019	0.75237	0.355	1121.0	1057.6	5.4
0.6920	0.1018	0.79730	0.289	1149.4	949.4	9.4
0.6933	0.2031	0.76997	0.273	1140.4	998.6	2.1
0.7960	0.1019	0.78935	0.177	1164.6	934.0	1.6
0.8464	0.0523	0.79940	0.135	1177.9	901.6	3.6
0.8435	0.1030	0.78541	0.118	1172.0	926.9	−2.2
0.8950	0.0522	0.79562	0.085	1186.2	893.3	−0.1

$x_iV_i/\sum x_iV_i$), x_i the corresponding mole fraction, n the number of components, T the temperature, and κ_S V_i, α_i, and $C_{p,i}$ are the isentropic compressibility, molar volume, cubic expansion coefficient, and the molar heat capacity of pure components, respectively. These properties are shown in Table 1.

The excess isentropic compressibility of the binary mixture (2-butanol + 1-chlorobutane) at $T = 313.15$ K

Table 4
Experimental densities, ρ, speeds of sound, u, along with calculated excess molar volumes, V^{E}, isentropic compressibilities, κ_{S}, and excess isentropic compressibilities, $\kappa_{\mathrm{S}}^{\mathrm{E}}$, for the ternary mixture (2-butanol $(1) + n$-hexane $(2) +$ 1-chlorobutane (3)) at $T = 313.15$ K

x_1	x_2	ρ (g cm^{-3})	V^{E} (cm^{-3} mol^{-1})	u (m s^{-1})	κ_{S} (TPa^{-1})	$\kappa_{\mathrm{S}}^{\mathrm{E}}$ (TPa^{-1})
0.0542	0.0499	0.84486	0.209	1051.2	1071.1	2.6
0.0518	0.0977	0.83204	0.223	1046.7	1097.1	−0.4
0.0564	0.8461	0.66354	0.305	1008.6	1481.6	9.6
0.0552	0.8956	0.65470	0.242	1008.0	1503.3	10.9
0.0996	0.0518	0.84047	0.312	1050.7	1077.7	8.2
0.1002	0.0999	0.82731	0.334	1046.1	1104.6	5.5
0.0994	0.1933	0.80294	0.356	1038.2	1155.5	1.4
0.1023	0.2887	0.77884	0.390	1031.1	1207.7	−0.1
0.0997	0.3927	0.75434	0.406	1024.5	1263.1	−0.3
0.0991	0.4938	0.73154	0.417	1019.1	1316.3	1.7
0.1020	0.5948	0.70954	0.428	1014.7	1368.9	5.3
0.1052	0.6936	0.68894	0.435	1011.3	1419.3	10.0
0.1050	0.7918	0.66983	0.392	1008.9	1466.8	14.1
0.0972	0.8531	0.65900	0.340	1007.9	1493.8	15.7
0.1930	0.1000	0.81988	0.460	1047.6	1111.3	13.1
0.1945	0.1959	0.79456	0.492	1039.5	1164.7	8.7
0.1956	0.2940	0.76999	0.514	1031.8	1219.9	7.7
0.1984	0.3999	0.74464	0.534	1025.1	1278.0	8.3
0.1989	0.4986	0.72232	0.546	1019.7	1331.5	10.7
0.2001	0.5964	0.70123	0.541	1015.5	1382.9	14.0
0.1987	0.6991	0.68037	0.513	1012.4	1433.9	17.0
0.2946	0.1015	0.81173	0.527	1051.8	1113.6	17.3
0.2925	0.1969	0.78673	0.557	1043.1	1168.3	13.1
0.2940	0.3030	0.76016	0.572	1034.9	1228.2	11.1
0.2964	0.3959	0.73790	0.590	1028.9	1280.1	11.5
0.2990	0.4994	0.71443	0.570	1023.2	1337.0	13.8
0.3021	0.5984	0.69296	0.552	1019.6	1388.1	15.1
0.3934	0.0984	0.80520	0.547	1058.4	1108.7	19.0
0.3933	0.1940	0.77996	0.560	1049.6	1163.7	13.5
0.3936	0.2982	0.75381	0.571	1041.1	1223.9	11.3
0.3968	0.4017	0.72903	0.563	1034.2	1282.5	11.3
0.3975	0.5017	0.70650	0.538	1029.0	1336.8	11.7
0.4985	0.1024	0.79639	0.528	1066.8	1103.3	17.8
0.4958	0.2005	0.77071	0.528	1057.4	1160.5	11.3
0.4972	0.2993	0.74588	0.519	1049.4	1217.4	7.7
0.4961	0.4035	0.72136	0.480	1042.2	1276.2	6.0
0.5918	0.1027	0.78964	0.462	1076.9	1092.0	14.0
0.5968	0.2014	0.76320	0.443	1067.8	1149.2	6.0
0.5975	0.3026	0.73786	0.410	1059.4	1207.5	0.9
0.6956	0.1023	0.78243	0.351	1090.3	1075.2	7.6
0.6953	0.2026	0.75599	0.305	1080.2	1133.6	−2.3
0.7945	0.1034	0.77514	0.220	1105.2	1056.2	−0.7
0.8449	0.0524	0.78560	0.183	1119.3	1016.0	3.3
0.8455	0.1030	0.77173	0.131	1113.8	1044.6	−5.6
0.8948	0.0528	0.78199	0.104	1128.4	1004.3	−1.5

were fitted with a Redlich–Kister type equation [34]

$$X^{\mathrm{E}} = x_i x_j \sum_{p=0}^{p} A_p (x_i - x_j)^p \tag{5}$$

where X^{E} is $\kappa_{\mathrm{S}}^{\mathrm{E}}$ (TPa^{-1}), and A_p is adjustable parameter obtained by the least-squares method. In Table 5, these parameters are listed along with the corresponding to all the binary mixtures involved in the ternary mixture.

Table 5
Values of the parameters A_p of Redlich–Kister equation (Eq. (5)) and C_i of Cibulka's equation (Eq. (8)) and the corresponding standard deviations, σ, for the binary and ternary mixtures at $T = 313.15$ K

T (K)		A_0	A_1	A_2	A_3	A_4	σ
2-Butanol (1) + n-hexane (2)							
298.15	V^E (cm^3 mol^{-1})[a]	1.704	−1.138	−0.398	−0.639	1.313	0.003
	κ_S^E (TPa^{-1})[b]	36.1	−122.6	−51.8	−47.0	104.4	0.4
313.15	V^E (cm^3 mol^{-1})[a]	1.984	−1.244	−0.517	−1.320	1.768	0.005
	κ_S^E (TPa^{-1})[b]	18.3	−147.2	−45.1	−82.1	86.7	0.4
2-Butanol (1) + 1-chlorobutane (2)							
298.15	V^E (cm^3 mol^{-1})[c]	1.639	−0.550	0.374	−0.630		0.004
	κ_S^E (TPa^{-1})[d]	103.6	−39.8	13.0	−21.1		0.3
313.15	V^E (cm^3 mol^{-1})[c]	2.105	−0.500	0.620	−0.890		0.005
	κ_S^E (TPa^{-1})[e]	110.3	−28.2	24.2			0.2
n-Hexane (1) + 1-chlorobutane (2)							
298.15	V^E (cm^3 mol^{-1})[f]	0.505	0.255	−0.108	−0.202		0.003
	κ_S^E (TPa^{-1})[g]	−47.9	37.7	−0.1	11.8		0.1
313.15	V^E (cm^3 mol^{-1})[f]	0.509	0.226	−0.220	−0.297		0.002
	κ_S^E (TPa^{-1})[g]	−60.4	38.1	8.4	12.0		0.1
				C_1	C_2	C_3	
2-Butanol (1) + n-hexane (2) + 1-chlorobutane (3)							
298.15	V^E (cm^3 mol^{-1})[e]			4.491	−6.519	−1.539	0.014
	κ_S^E (TPa^{-1})[e]			149.2	−141.9	119.4	0.8
313.15	V^E (cm^3 mol^{-1})[e]			5.175	−8.526	−0.341	0.015
	κ_S^E (TPa^{-1})[e]			38.6	−91.8	325.0	0.5

[a] Data taken from [4].
[b] Data taken from [5].
[c] Data taken from [31].
[d] Data taken from [32].
[e] Data taken from this work.
[f] Data taken from [1].
[g] Data taken from [3].

The standard deviation was defined by

$$\sigma = \left[\frac{\sum (X^E - X^E_{\mathrm{calc}})^2}{m - p}\right]^{1/2} \tag{6}$$

where m is the number of experimental points and p the number of adjustable parameters. The excess isentropic compressibilities for the binary mixture (2-butanol + 1-chlorobutane) are plotted in Fig. 1. According to these results, the κ_S^E are positive over the whole composition range. When the temperature rises, the curves do not change when the molar fraction of butanol is small but is slightly more positive for κ_S^E when the amount of alcohol increases.

Densities, ρ, speeds of sound, u, and isentropic compressibilities, κ_S, of the ternary mixtures were fitted to a polynomial of the form

$$Q = \sum_{i=1}^{3}\sum_{j=1}^{m} B_{ij} x_i^j \tag{7}$$

where Q is ρ (g cm^{-3}) or u (m s^{-1}) or κ_S (TPa^{-1}), and x_i is the mole fraction of component i. The adjustable coefficients B_{ij} and the standard deviations of the fittings, σ, calculated by means of the method of least-squares, are listed in Table 6.

The excess molar volumes and excess isentropic compressibilities for the ternary mixture have been fitted to Cibulka's equation [35]

$$X^E = X^E_{\mathrm{bin}} + x_1 x_2 (1 - x_1 - x_2)(C_1 + C_2 x_1 + C_3 x_2) \tag{8}$$

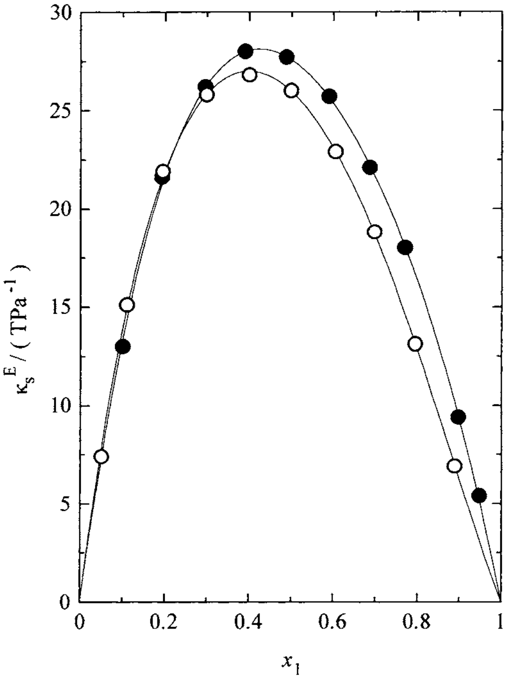


Fig. 1. Excess isentropic compressibilities, κ_S^E, of the binary mixture (2-butanol (1) + 1-chlorobutane (2)): (○) at $T = 298.15$ K, [31]; (●) experimental values at $T = 313.15$ K and (—) Redlich–Kister equation.

where X^E is V^E (cm^3 mol^{-1}) or κ_S^E (TPa^{-1}).

$$X_{\text{bin}}^E = X_{12}^E + X_{13}^E + X_{23}^E \tag{9}$$

where X_{ij}^E are the contribution of binary mixtures i, j to the excess property given by Eq. (5). The C_i are adjustable parameters also obtained by a least-squares method. Table 5 presents the values of these parameters and the corresponding standard deviations, σ, defined by Eq. (6).

The isolines of V^E (cm^3 mol^{-1}) obtained from the Cibulka's equation for the ternary mixture (2-butanol + n-hexane + 1-chlorobutane) at $T = 298.15$ and 313.15 K are plotted in Fig. 2. These V^E are positive in all the triangular diagram. A rise of temperature makes the V^E takes values more positive. If we compare this results with those obtained for the ternary mixture (1-butanol + n-hexane + 1-chlorobutane) [2], we can observe that the sigmoidal shape has disappeared.

The isolines of κ_S^E (TPa^{-1}) for the ternary mixture (2-butanol + n-hexane + 1-chlorobutane) at $T = 298.15$ and 313.15 K are plotted in Fig. 3. According to the results of present work, the κ_S^E values are negative in the regions rich in 2-butanol, but become slightly positive when the amount of alcohol decreases. When the temperature rises, the κ_S^E become more positive, in the regions where they are positive and more negative where they are negative. If we compare with the ternary mixture (1-butanol + n-hexane + 1-chlorobutane) [3], we can observe that the κ_S^E are more positive in the regions where they are positive, and less negative (where they are negative) when the butanol is secondary.

The maximum and saddle point coordinates for V^E and κ_S^E of the studied binary curves and ternary surfaces are listed in Table 7.

4. Theoretical analysis

We have used the Flory's theory [12,13] and the extension of this theory to multicomponent systems by Brostow and Sochansky [36] to predict excess molar volumes of binary and ternary mixtures from the properties of pure components and from excess molar enthalpies of binary mixtures. The needed parameters of the pure substances are gathered in Table 8. We have used excess molar enthalpies at equimolar fraction (H^E, $x_1 = 0.5$) of binary mixtures at 298.15 K to determine binary interaction parameters X_{ij} and then we have used those parameters to predict V^E of binary and ternary mixtures at the same temperature. These interaction parameters and standard deviations of predictions are shown in Table 9.

The ERAS model has been also applied to predict the excess molar volume of the ternary mixture (2-butanol + n-hexane + 1-chlorobutane) at $T = 298.15$ K from the adjustable parameters of the binary mixtures involved. According to this model, the thermodynamic excess properties of ternary mixtures containing a self-associated compound A (2-butanol) + an inert compound B (n-hexane) + a compound C acting as a polar molecule with no self-association (1-chlorobutane) can be expressed as the sum of a physical (the same of Flory's theory) and a chemical contribution. Table 8 shows the parameters of the pure components needed in the application of the model. X_{ij}, K_{ij}, ΔH_{ij}^* and Δv_{ij}^* reported in Table 9 are fitting parameters and the following procedure has been carried out for their determination.

Table 6
Parameters B_{ij}, of Eq. (7) and standard deviations, σ, of the density, speed of sound, and isentropic compressibility for the ternary mixture (2-butanol (1) + n-hexane (2) + 1-chlorobutane (3)), where i denotes a component of the mixture

T (K)	i	B_{i1}	B_{i2}	B_{i3}	B_{i4}	σ
ρ (g cm^{-3})						
298.15	1	0.7956	0.0077	0.0060	−0.0069	0.0001
	2	0.5900	0.0846	−0.0269	0.0074	
	3	0.8804	0.0073	−0.0162	0.0092	
313.15	1	0.7785	0.0179	−0.0030	−0.0039	0.0001
	2	0.5765	0.0869	−0.0308	0.0085	
	3	0.8592	0.0212	−0.0327	0.0162	
u (m s^{-1})						
298.15	1	1089.6	142.6	−30.7	10.6	0.3
	2	1002.6	120.2	−80.7	35.6	
	3	1124.6	−14.9	18.0	−10.2	
313.15	1	1027.7	156.1	−54.6	27.4	0.2
	2	934.4	119.5	−76.1	32.0	
	3	1064.1	−3.7	0.8	−4.7	
κ_S (TPa^{-1})						
298.15	1	1097.1	−348.7	87.8	12.1	0.5
	2	1409.9	−109.7	85.3	−70.8	
	3	881.0	20.6	−3.9	11.4	
313.15	1	1261.5	−462.8	157.4	−9.3	0.6
	2	1633.9	−125.7	109.0	−87.8	
	3	1017.0	−43.8	84.9	−21.2	

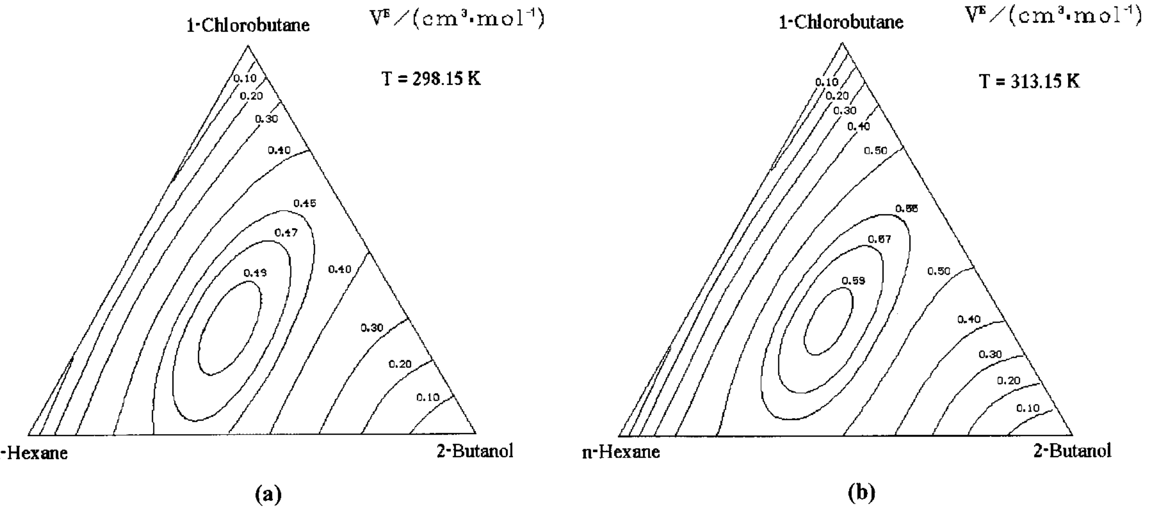


Fig. 2. Isolines of excess molar volumes V^E for the ternary mixture (2-butanol (1) + n-hexane (2) + 1-chlorobutane (3)): (a) at T = 298.15 K and (b) at T = 313.15 K.

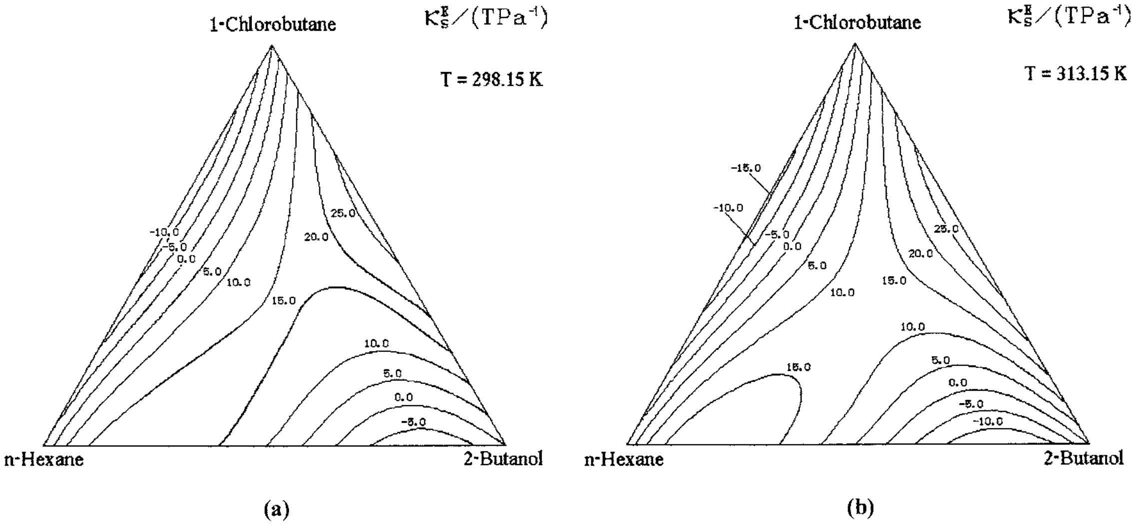


Fig. 3. Isolines of excess isentropic compressibilities, κ_S^E for the ternary mixture (2-butanol (1) + n-hexane (2) + 1-chlorobutane (3)): (a) at $T = 298.15$ K and (b) at $T = 313.15$ K.

X_{ij}, K_{ij}, ΔH_{ij}^* are obtained from correlation of bibliographic excess enthalpy binary data, and Δv_{ij}^* is adjusted separately from experimental excess volume binary data. Once all binary parameters are known, we have predicted the excess molar volume for the ternary mixture.

Fig. 4 shows the results of prediction for the isolines of V^E according to Flory's theory and ERAS model.

Table 7
Maximum and saddle points of the excess volumes, V^E, and excess isentropic compressibilities, κ_S^E, for the binary and ternary mixtures studied in the present work

T (K)	Maximum		T (K)	Maximum			Saddle point		
	x_1	κ_S^E (TPa^{-1})		x_1	x_2	V^E (cm^3 mol^{-1})	x_1	x_2	κ_S^E (TPa^{-1})
2-Butanol (1) + 1-chlorobutane (2)			2-Butanol (1) + n-hexane (2) + 1-chlorobutane (3)						
298.15[a]	0.398	27.0	298.15	0.131	0.410	0.498			
313.15	0.425	28.1	313.15	0.318	0.390	0.596			
			298.15				0.343	0.344	15.5
			313.15				0.346	0.319	11.9

[a] Data taken from [31].

Table 8
Parameters of the pure substances used in application of the Flory's theory and the ERAS model at $T = 298.15$ K

Component	V_i (cm^3 mol^{-1})	$\kappa_{S,i}$ (TPa^{-1})	V_i^* (cm^3 mol^{-1})	P_i^* (J cm^{-3})	K_{ij}	σ_i[b] (nm^{-1})	ΔH_i^* (kJ mol^{-1})	Δv_i^* (cm^3 mol^{-1})
2-Butanol	92.38	1005.3	75.04	417.2	55[a]	14.842	−25.1	−5.6
n-Hexane	131.59	1700.6	99.54	425.0	0	14.122	–	–
1-chlorobutane	105.10	1203.8	81.37	504.9	0	14.237	–	–

[a] Data taken from [37].

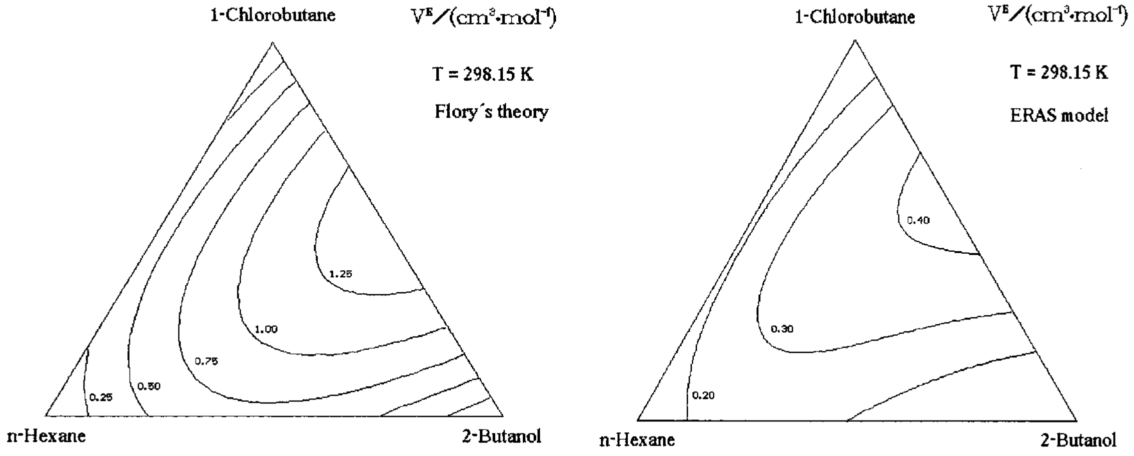
[b] Calculated according to [38].

Table 9
Adjustable parameters of the binary mixtures (van der Waals interaction parameters X_{ij}, association constants of component i with component j, K_{ij}, cross association volume of components i and j, Δv^*_{ij}, association enthalpy of component i with j, ΔH^*_{ij}) and standard deviations at $T = 298.15$ K of the predictions of the Flory's theory and the ERAS model for binary and ternary mixtures

Mixture	X_{ij} (J cm^{-3})		K_{ij} (ERAS)	Δv^*_{ij} (cm^3 mol^{-1}) (ERAS)	ΔH^*_{ij} (kJ mol^{-1}) (ERAS)	σV^E (cm^3 mol^{-1})		σH^E (kJ mol^{-1})		Reference	
	Flory	ERAS				Flory	ERAS	Flory	ERAS	V^E	H^E
2-Butanol (1) + *n*-hexane (2)	39.3	9.3[a], 4.32[b]				0.191	0.163	0.2073	0.0662	[4]	[9]
2-Butanol (1) + 1-chlorobutane (2)	73.9	16.9	6.1	−4.5	−10.9	0.808	0.017	0.1306	0.1113	[8]	[10]
n-Hexane (1) + 1-chlorobutane (2)	20.9	12.8				0.196	0.038	0.0276	0.1452	[1]	[11]
2-Butanol (1) + *n*-hexane (2) + 1-chlorobutane (3)						0.522	0.101			This work	–

[a] Data taken from [4].

[b] Data taken from [9].



(a) (b)

Fig. 4. Isolines for the predictions of V^E for the ternary mixture (2-butanol (1) + n-hexane (2) + 1-chlorobutane (3)) at $T = 298.15$ K: (a) according to Flory's theory and (b) ERAS model.

According to these figures and the corresponding standard deviations obtained, we can say that ERAS model, with an additional term for a chemical contribution, reproduces better the experimental results in the mixtures with an associated component.

Finally, in the present work, we have applied the FLT and CFT to predict the isentropic compressibility of the binary and ternary mixtures. Table 10 presents the relative root mean square deviation ($\mathrm{RMSD_r}$) between the experimental and calculated isentropic compressibilities for the two models (FLT and CFT) defined by the following equation:

$$\mathrm{RMSD_r} = \left[\frac{1}{m}\sum\left(\frac{\kappa_S^{\mathrm{cal}} - \kappa_S^{\mathrm{exp}}}{\kappa_S^{\mathrm{exp}}}\right)^2\right]^{1/2} \quad (10)$$

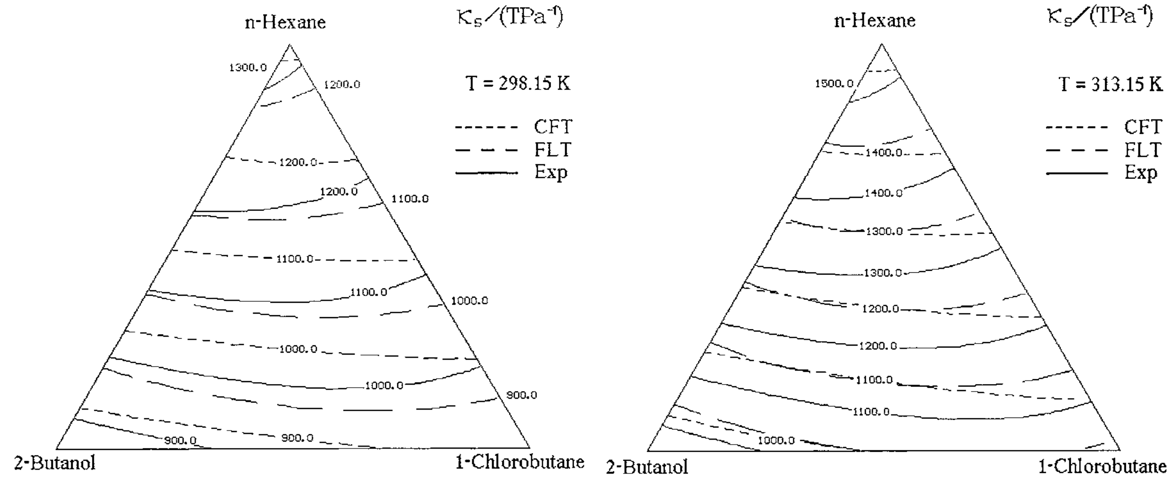
where m is the number of experimental points, κ_S^{cal} and κ_S^{exp}, are the calculated and experimental values for isentropic compressibility of the mixture.

In Fig. 5, we present the isolines of isentropic compressibility predicted by both models (CFT and FLT) and we compare them with the experimental correlation for the ternary mixture.

It can be observed that the CFT results in a smaller $\mathrm{RMSD_r}$ at both temperatures and the isentropic compressibilities predicted by this model are closer to the experimental values. The FLT model performs less but its simplicity makes it attractive. This model neglects the possible aggregates that could be formed between the molecules of the mixture or in the pure liquid, thus we obtain the same L (free length) independently of

Table 10
Relative root mean square deviations ($\mathrm{RMSD_r}$) of the predicted isentropic compressibilities by means of the FLT and CFT theories

Mixture	$\mathrm{RMSD_r} \times 100$			
	$T = 298.15$ K		$T = 313.15$ K	
	FLT	CFT	FLT	CFT
2-Butanol (1) + n-hexane (2)	7.5	3.3	4.1	3.6
2-Butanol (1) + 1-chlorobutane (2)	7.1	2.5	3.7	2.6
n-Hexane (1) + 1-chlorobutane (2)	6.8	0.9	4.2	1.0
2-Butanol (1) + n-hexane (2) + 1-chlorobutane (3)	7.4	3.3	4.0	3.5



(a) (b)

Fig. 5. Isolines of isentropic compressibilities, κ_S, for the ternary mixture (2-butanol $(1) + n$-hexane $(2) + $ 1-chlorobutane (3)): (—) experimental; (— — —) FLT; (- - -) CFT; (a) at $T = 298.15$ K and (b) at $T = 313.15$ K.

the molecular species that exist. However, this particularity is important in the alkanols where the formation of aggregates by hydrogen bonding is firmly established. Comparing with the results obtained in the ternary mixture (1-butanol $(1) + n$-hexane $(2) + $ 1-chlorobutane (3)) [3], we can see that $\mathrm{RMSD_r}$ in FLT for the ternary mixtures containing secondary butanol is better than those obtained for the mixture with 1-butanol, whereas $\mathrm{RMSD_r}$ in CFT are similar for the two mixtures.

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