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Excess molar volumes and enthalpies of the ternary system (2-butanol + 1,3-dioxolane + *n*-hexane) at 298.15 and 313.15 K Experimental values and ERAS model calculations

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Abstract

Densities and heats of mixing for the ternary system 2-butanol + 1, 3-dioxolane + *n*-hexane have been measured at atmospheric pressure at the temperatures of 298.15 and 313.15 K. Excess molar volumes and excess molar enthalpies have been calculated from experimental data and fitted by the Redlich–Kister equation for ternary mixtures. The ERAS model has been used to calculate excess molar properties of the ternary mixture from parameters obtained from the constituent binary mixtures.

Keywords: ERAS model; Excess molar volumes; Enthalpies; Ternary mixture; 1,3-Dioxolane

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1. Introduction

Experimental data of excess thermodynamic properties of liquid mixtures provide useful information about molecular interactions and can be used to test thermodynamic models.

In our recent studies [1–5] we have reported new experimental data about excess thermodynamic properties of binary and ternary mixtures containing cyclic ethers and isomers of butanol. Continuing our studies in this paper we analyse the excess molar volumes and excess molar enthalpies of the ternary mixture 2-butanol + 1, 3-dioxolane + *n*-hexane at 298.15 and 313.15 K. The experimental data of excess molar volumes and excess molar enthalpies are used to test the applicability of the ERAS model for describing both excess properties of the ternary mixture at different temperatures from binary parameters.

As far as we know there are not references in the literature for the ternary systems studied here.

2. Experimental

The compounds used were 2-butanol (>99%), 1,3-dioxolane (>99%), and *n*-hexane (>99%) obtained from Aldrich. The purities of these compounds were checked by comparing the measured densities with those reported in the literature and also by a chromatographic method. This confirms the absence of other significant compounds. No further purification was considered necessary, but the 2-butanol was dried with activated molecular sieve type 0.3 nm from Merck.

The pure compounds properties at 298.15 K and 313.15 K, along with literature density values at 298.15 K [6,7], are given in Table 1.

Densities, ρ, of the pure compounds and their mixtures were determined with an Anton Paar DMA-58 vibrating tube densimeter whose temperature was controlled within ±0.01 K. The accuracy of density measurements was $\pm 1 \times 10^{-5}\,\mathrm{g\,cm^{-3}}$. Being the precision of the density measurements $\pm 5 \times 10^{-6}\,\mathrm{g\,cm^{-3}}$.

Mixtures were prepared by mass using a Mettler H20T balance. The uncertainty of mole fraction of the mixtures is estimated to be less than $\pm 1 \times 10^{-4}$.

Excess molar enthalpies were determined using a Thermometric 2277 thermal activity monitor with a combination

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Table 1
Physical Properties and ERAS model parameters of the pure liquids at 298.15 and 313.15 K

Property	T (K)		2-Butanol	1,3-Dioxolane	n-Hexane
ρ (g cm^{-3})	298.15	Experimental	0.80220	1.05862	0.65507
		Literature	0.80241[a]	1.05866[b]	0.65484[a]
	313.15	Experimental	0.78959	1.03997	0.64127
V_m (cm^3 mol^{-1})	298.15		92.375	69.978	131.548
	313.15		93.873	71.223	134.379
α (kK^{-1})	298.15		1.059	1.164	1.387
	313.15		1.105	1.226	1.453
u (m s^{-1})	298.15	Experimental	1211.5	1338.8	1078.5
		Literature	1212[c]	–	1076.8[d]
	313.15	Experimental	1157.1	1271.7	1008.1
κ_S (TPa^{-1})	298.15		849.1	527.0	1312.4
	313.15		945.9	594.5	1534.4
C_p (J K^{-1} mol^{-1})	298.15		196.9[e]	122.21	195.6[e]
	313.15		212.6[f]	125.01	200.1[g]
κ_T (TPa^{-1})	298.15		1006.0	758.3	1698.0
	313.15		1114.7	862.7	1978.5
s (Å^{-1})	298.15		1.484	1.230	0.967
	313.15				
K_i	298.15		72	4	–
	313.15		44	3.1	–
V^{*0} (cm^3 mol^{-1})	298.15		74.951	57.422	99.470
	313.15		75.169	57.238	99.818
P^* (J mol^{-1})	298.15		421	544	426
	313.15		423	557	417

[a] Ref. [6].
[b] Ref. [7].
[c] Ref. [19].
[d] Ref. [20].
[e] Ref. [21].
[f] Ref. [22].
[g] Ref. [23].

measuring cylinder (LKB 2277-204) running under constant flow conditions, total flow rate $= 5 \times 10^{-3}$ mL s^{-1}. During the experiments the temperature is kept constant within $\pm 2 \times 10^{-4}$ K. Two Shimadzu LC-10ADVP HPLC pumps were used to drive the liquids. One of the pumps delivered pure 2-butanol while the other pump delivered a liquid mixture of 1,3-dioxolane and n-hexane of known composition. Each pump was calibrated with pure 2-butanol or the binary mixture, respectively, before calorimetric measurements were registered. The uncertainty in the mole fractions of the ternary mixture, calculated from the uncertainty in the flow delivered by the pumps, is ±0.001. The accuracy in the determination of the excess molar enthalpies could be expected to be ±1%. More details about procedure and calibration can be found in a previous paper [8].

3. Results and discussion

The experimental densities of the ternary system 2-butanol + 1,3-dioxolane + n-hexane at 298.15 and 313.15 K are shown in Table 2 along with calculated excess molar volumes. The excess molar enthalpies at 298.15 and 313.15 K are presented in Table 3. H^E was determined according to the following relation:

$$H^E = \frac{\dot{Q} + (\dot{n}_1 + \dot{n}_3) H_{23}^E}{\dot{n}_1 + \dot{n}_2 + \dot{n}_3} \quad (1)$$

where $\dot{Q}$ is the measured heat effect upon mixing, $\dot{n}_i$ the molar flux of the components ($i = 1, 2, 3$) and H_{23}^E is the molar excess enthalpy of the binary mixture 1, 3-dioxolane+ n-hexane delivered by one of the pumps.

Both excess molar properties of the ternary system were fitted to the following equation for ternary mixtures [9]:

$$Y^E = Y_{\text{bin}}^E + x_1 x_2 (1 - x_1 - x_2) [C_1 + C_2 x_1 + C_3 x_2] \quad (2)$$

where Y^E is the excess property (V^E or H^E) of the ternary mixture, x_i the mole fraction of component i in the mixture, C_i are adjustable parameters obtained by the least squares method and Y_{bin}^E the contribution to the excess property of the constituent binary mixtures, which is given by

$$Y_{\text{bin}}^E = Y_{12}^E + Y_{13}^E + Y_{23}^E \quad (3)$$

each Y_{ij}^E is obtained by means of a Redlich–Kister polynomial equation

$$Y_{ij}^E = x_i x_j \sum_{p=0}^{n} A_{p,ij} (x_i - x_j)^p \quad (4)$$

Table 2
Densities, ρ, and excess molar volumes, V^E, of the ternary mixture 2-butanol (1) + 1, 3-dioxolane (2) + n-hexane (3) at 298.15 and 313.15 K

$T = 298.15$ K				$T = 313.15$ K			
x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})
0.8925	0.0609	0.80292	0.154	0.8986	0.0518	0.78751	0.168
0.8542	0.0951	0.80820	0.212	0.8426	0.1077	0.79716	0.280
0.1013	0.8474	0.98863	0.156	0.1009	0.8487	0.97187	0.156
0.0555	0.8926	1.00288	0.078	0.0573	0.8936	0.98617	0.093
0.8446	0.0549	0.79068	0.171	0.8455	0.0535	0.77720	0.180
0.8073	0.0895	0.79612	0.229	0.8011	0.0965	0.78394	0.283
0.7082	0.1892	0.81417	0.375	0.6970	0.1995	0.80166	0.457
0.6083	0.2958	0.83659	0.446	0.6106	0.2889	0.81930	0.529
0.5126	0.3865	0.85438	0.476	0.5065	0.3936	0.84068	0.572
0.4139	0.4900	0.87873	0.471	0.4071	0.4973	0.86460	0.551
0.2224	0.6752	0.92286	0.355	0.3030	0.6045	0.89120	0.459
0.1923	0.7161	0.93729	0.297	0.2009	0.7078	0.91823	0.342
0.0969	0.8075	0.96197	0.178	0.0971	0.8054	0.94327	0.201
0.0503	0.8523	0.97522	0.069	0.0581	0.8443	0.95481	0.113
0.7113	0.0952	0.7789	0.311	0.7122	0.0968	0.76596	0.351
0.6045	0.2078	0.79948	0.443	0.6025	0.2094	0.78527	0.514
0.5030	0.2916	0.81095	0.536	0.5004	0.2952	0.79718	0.585
0.4002	0.4020	0.83434	0.546	0.3956	0.4063	0.81976	0.611
0.3050	0.5092	0.86001	0.510	0.3042	0.5043	0.84168	0.568
0.2057	0.5952	0.87635	0.441	0.2016	0.6021	0.86229	0.480
0.1052	0.6977	0.90200	0.304	0.1075	0.6969	0.88506	0.360
0.6099	0.1014	0.76194	0.414	0.6104	0.0940	0.74575	0.445
0.5053	0.2001	0.77715	0.488	0.5060	0.1976	0.76157	0.601
0.4069	0.3003	0.79464	0.573	0.4057	0.3011	0.77975	0.641
0.3814	0.3388	0.80444	0.558	0.3055	0.3873	0.79215	0.675
0.2180	0.4883	0.83029	0.561	0.2073	0.4970	0.81560	0.625
0.1043	0.5981	0.85305	0.425	0.1066	0.6135	0.84395	0.472
0.5096	0.1048	0.74572	0.477	0.5141	0.0969	0.72975	0.553
0.4029	0.1970	0.75720	0.601	0.4014	0.1963	0.74212	0.675
0.3003	0.2991	0.77370	0.649	0.3153	0.2761	0.75344	0.725
0.1952	0.3992	0.79044	0.608	0.1897	0.4066	0.77638	0.695
0.0938	0.5031	0.81034	0.539	0.1035	0.4979	0.79418	0.607
0.4001	0.1046	0.72812	0.547	0.3996	0.1048	0.71380	0.627
0.3036	0.2058	0.74357	0.632	0.3098	0.2108	0.73129	0.726
0.2054	0.2956	0.75610	0.662	0.2115	0.2843	0.73830	0.749
0.0993	0.3878	0.76898	0.623	0.1004	0.3893	0.75412	0.692
0.3018	0.1100	0.71526	0.573	0.3081	0.0951	0.69775	0.637
0.2021	0.2027	0.72709	0.641	0.2031	0.1963	0.71060	0.726
0.1060	0.2927	0.73948	0.641	0.1083	0.2930	0.72487	0.701
0.1995	0.1109	0.70170	0.559	0.2026	0.0957	0.68360	0.663
0.1056	0.2121	0.71610	0.623	0.1086	0.2033	0.69917	0.720
0.1065	0.1061	0.68903	0.493	0.0889	0.1042	0.67180	0.603
0.0915	0.0491	0.67424	0.349	0.1017	0.0575	0.66255	0.535
0.0505	0.1071	0.68301	0.402	0.0573	0.1046	0.66835	0.555
0.0592	0.0378	0.66832	0.285	0.0596	0.0499	0.65650	0.434

where x_i is the mole fraction of component i in the ternary mixture and $A_{p,ij}$ are adjustable parameters obtained by the least squares method. Table 4 shows the parameters of the constituent binary mixtures, obtained either from experimental measurements carried out in our laboratory or taken from previous papers [4,5,10]. The standard deviations of the fits, σ, are also tabulated.

In Table 4 the parameters obtained for the excess molar enthalpies of the binary mixture 2-butanol + n-hexane are included. These were fitted with the fractional equation proposed by Treszczanowicz and Benson [11]:

$$H_{13}^E = x_1 x_3 \sum_{p=0}^{m} A_p x_1^{p/2} \tag{5}$$

where H_{13}^E is the excess molar enthalpy of the binary mixture, x_1 and x_3 are the mole fractions of 2-butanol and n-hexane, respectively, and A_p are adjustable parameters obtained by the least squares method.

Parameters, C_i, of the Cibulka equation for ternary mixtures (2) are given in Table 5 along with the standard deviations, σ.

Table 3
Excess molar enthalpies, H^E, of the ternary mixture 2-butanol (1) + 1, 3-dioxolane (2) + n-hexane (3) at 298.15 and 313.15 K

$T = 298.15$ K			$T = 313.15$ K		
x_1	x_2	H^E (J mol^{-1})	x_1	x_2	H^E (J mol^{-1})
0.045	0.812	1073.4	0.045	0.812	980.3
0.089	0.775	1327.2	0.089	0.774	1244.0
0.180	0.698	1718.2	0.180	0.697	1667.7
0.273	0.618	1965.0	0.273	0.618	1946.2
0.369	0.537	2088.6	0.369	0.536	2093.4
0.467	0.453	2103.5	0.467	0.453	2129.7
0.568	0.367	2000.2	0.568	0.367	2036.4
0.672	0.279	1774.8	0.673	0.278	1810.8
0.780	0.188	1392.5	0.780	0.187	1414.0
0.890	0.094	815.9	0.890	0.094	815.3
0.946	0.046	436.5	0.946	0.046	432.9
0.050	0.665	1608.5	0.050	0.666	1443.9
0.099	0.631	1773.7	0.099	0.632	1643.7
0.198	0.562	1963.4	0.197	0.563	1900.7
0.296	0.493	2016.9	0.296	0.493	2017.3
0.396	0.423	1980.9	0.396	0.424	2013.8
0.495	0.353	1874.1	0.495	0.354	1931.6
0.595	0.283	1690.2	0.595	0.284	1755.2
0.696	0.213	1428.3	0.696	0.213	1496.6
0.797	0.142	1067.9	0.797	0.143	1116.8
0.898	0.071	594.4	0.111	0.445	1918.9
0.949	0.036	308.6	0.219	0.391	1981.6
0.056	0.472	1877.0	0.325	0.338	1920.6
0.111	0.445	1961.2	0.428	0.286	1789.8
0.219	0.391	1962.4	0.529	0.236	1615.2
0.325	0.338	1874.3	0.628	0.186	1390.9
0.428	0.286	1731.8	0.725	0.138	1121.9
0.529	0.236	1555.1	0.959	0.020	207.9
0.628	0.186	1336.1	0.063	0.281	1610.6
0.725	0.138	1075.5	0.123	0.263	1728.1
0.820	0.090	765.3	0.239	0.228	1734.8
0.913	0.043	403.1	0.350	0.195	1636.6
0.959	0.020	202.7	0.456	0.163	1485.6
0.063	0.291	1614.2	0.557	0.133	1307.3
0.123	0.273	1703.7	0.654	0.104	1092.3
0.238	0.237	1687.1	0.746	0.076	849.3
0.349	0.202	1577.2	0.920	0.024	284.1
0.454	0.170	1431.0	0.072	0.139	1167.4
0.555	0.138	1258.4	0.140	0.129	1342.5
0.652	0.108	1055.3	0.267	0.110	1415.0
0.745	0.079	826.0	0.385	0.092	1392.6
0.834	0.052	567.4	0.494	0.076	1280.6
0.919	0.025	287.9	0.596	0.061	1130.5
0.072	0.133	1077.4	0.691	0.046	940.9
0.140	0.123	1188.9	0.779	0.033	720.3
0.268	0.105	1225.3	0.862	0.021	474.2
0.386	0.088	1178.1	0.940	0.009	231.9

Isolines at constant values of excess molar volumes and enthalpies of the ternary mixture at 298.15 and 313.15 K are plotted in Figs. 1 and 2, respectively. The mixtures exhibit relatively large positive excess molar volumes and enthalpies throughout the entire composition range. Both excess molar properties increase slightly with increasing temperature. We have observed a similar behaviour in the ternary system 2-butanol + 1, 3-dioxolane + cyclohexane [1], but excess molar volumes are bigger for the system containing cyclohexane instead of n-hexane, while excess molar enthalpies are very similar for both systems.

The observed behaviour of the excess molar properties has been interpreted in terms of molecular interactions. In particular the mixtures show positive excess molar volumes and enthalpies, which result from the breaking up of alcohol agglomerates and ether–ether interactions that dominate over the negative contributions from heteromolecular interaction.

Table 4
Coefficients of Redlich–Kister equation (Eq. (4)) or Treszczanowicz and Benson equation (Eq. (5)), A_p, for the excess molar volumes, V^E, and excess molar enthalpies, H^E, of the constituent binary mixtures of the ternary system 2-butanol (1) + 1, 3-dioxolane (2) + n-hexane (3) at 298.15 and 313.15 K

Property	T (K)	A_0	A_1	A_2	A_3	A_4	σ (Y^E)
2-Butanol (1) + 1,3-dioxolane (2)							
V^E (cm^3 mol^{-1})[a]	298.15	1.731	0.352	0.251	0.072	–	0.001
	313.15	1.891	0.769	0.641	−0.089	–	0.001
H^E (J mol^{-1})[b]	298.15	9340	147	20	−1065	–	16
	313.15	9582	−45	509	725	–	17
2-Butanol (1) + n-hexane (3)							
V^E (cm^3 mol^{-1})[c]	298.15	1.704	−1.138	−0.398	−0.639	1.313	0.003
	313.15	1.984	−1.244	−0.517	−1.320	1.768	0.005
H^E (J mol^{-1})[d]	298.15	20052	−78452	144796	−119975	35882	5
	313.15	23125	−81816	133716	−96035	23595	6
1,3-Dioxolane (2) + n-hexane (3)							
V^E (cm^3 mol^{-1})[e]	298.15	1.960	−2.053	−1.133	−0.154	–	0.002
	313.15	2.073	−1.408	−0.023	−2.457	–	0.004
H^E (J mol^{-1})[e]	298.15	6762	485	−21962	503	–	10
	313.15	6313	−859	−2588	2841	–	10

[a] Ref. [4].
[b] Ref. [5].
[c] Ref. [10].
[d] Unpublished results correlated with the Treszczanowicz and Benson equation.
[e] Unpublished results correlated with the Redlich–Kister equation.

Table 5
Coefficients of the Cibulka equation (Eq. (2)) for the excess molar volumes, V^E, and excess molar enthalpies, H^E, of the ternary system 2-butanol (1) + 1, 3-dioxolane (2) + n-hexane (3) at 298.15 and 313.15 K

Property	T (K)	C_1	C_2	C_3	σ (Y^E)
V^E (cm^3 mol^{-1})	298.15	−1.931	0.083	7.191	0.012
	313.15	−0.102	−2.198	5.051	0.013
H^E (J mol^{-1})	298.15	1545	−26822	−7811	21
	313.15	2940	−29391	−10975	39

Although both H^E and V^E are related to molecular interactions, V^E is a better indicator of structural and packing effects. This might indicate that the breaking of the self-interactions in the ternary mixture 2-butanol + 1, 3-dioxolane + n-hexane is partially balanced by structural effects which contribute negatively to V^E. These effects are related with differences in shape and size between the components and they are more relevant in the mixture containing n-hexane than in the ternary system with cyclohexane.

We also can compare our results with previously reported excess thermodynamic data for the ternary system 1-butanol + 1, 3-dioxolane + n-hexane [3]. We observe that the composition dependence of the excess molar functions is very similar in both systems, but the H^E and V^E values are slightly larger in the ternary system containing 2-butanol.

4. ERAS model calculations

The ERAS theory combines the real associated solution model [12–15] with Flory's equation of state [16]. The version of the ERAS model used here [17,18] allows a description of excess molar properties of mixtures containing two associating components provided one of these shows a weak self-association. In the present work n-hexane was assumed to be an inert component, 2-butanol presents strong association while 1,3-dioxolane is a weak associated compound. Cross association between alcohol and ether was also considered.

The ERAS parameters of the pure compounds along with their physical properties are collected in Table 1. Molar volumes, V_m, and thermal expansion coefficients, α, were derived from the densities determined in the laboratory. Isothermal compressibilities, κ_T, at a given temperature T, were calculated from molar volumes, thermal expansion coefficients, isentropic compressibilities, κ_S, and molar heat capacities, $C_{p,m}$, by using the thermodynamic equation

$$\kappa_T = \kappa_S + \frac{TV_m\alpha^2}{C_{p,m}} \qquad (6)$$

Values of κ_S were evaluated from experimental densities, ρ, and ultrasonic velocities, u (trough the relation $\kappa_S=(\rho u^2)^{-1}$). An Anton Paar DSA-48 density and sound analyser was used to determine ρ and u. $C_{p,m}$ values for 1,3-dioxolane were determined with a programmable differential scanning microcalorimeter Setaram DSC II, while

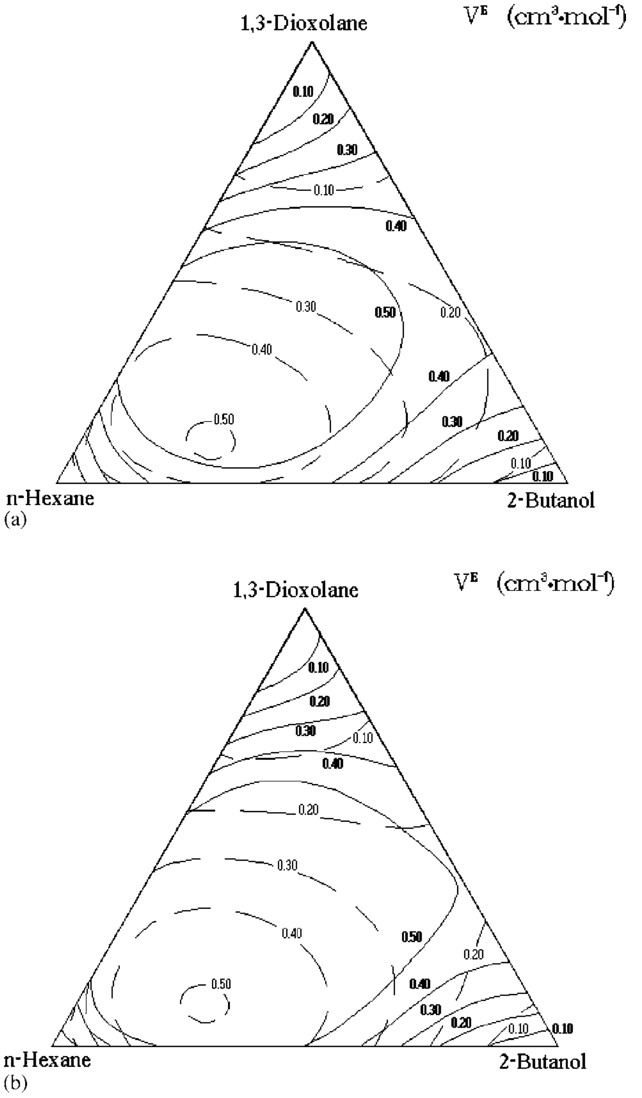

Fig. 1. Isolines of constant excess molar volumes, V^E, for the ternary system 2-butanol (1) + 1, 3-dioxolane (2) + n-hexane (3): experimental correlation (continuous lines) and ERAS model predictions (dashed lines). (a) At 298.15 K; (b) at 313.15 K.

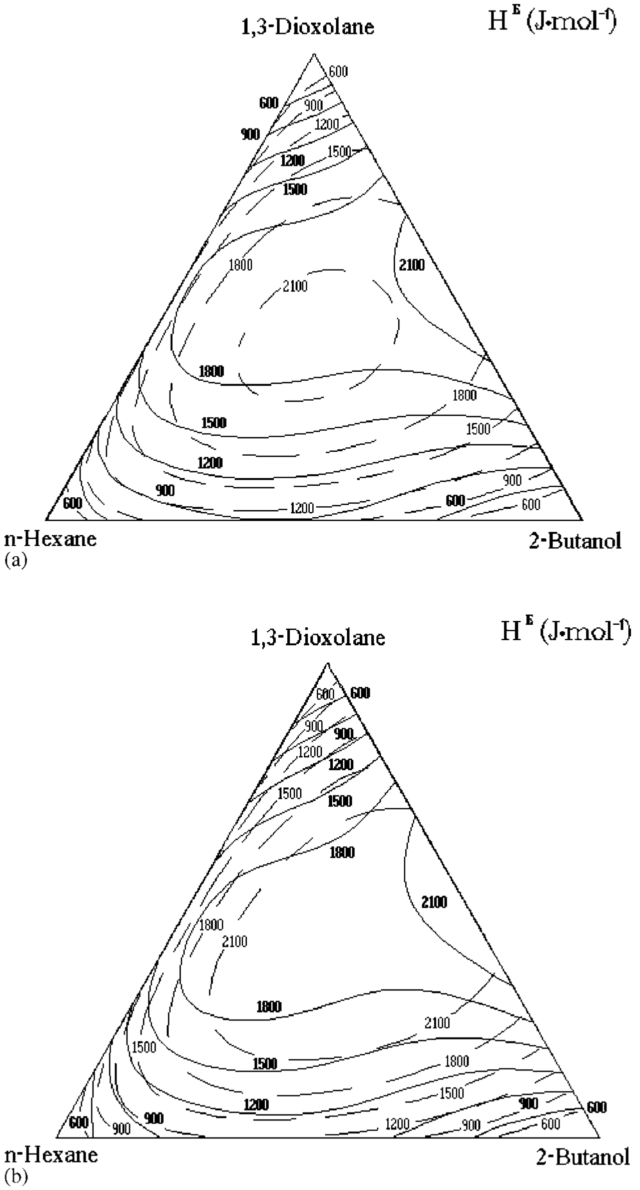

Fig. 2. Isolines of constant excess molar enthalpies, H^E, for the ternary system 2-butanol (1) + 1, 3-dioxolane (2) + n-hexane (3): experimental correlation (continuous lines) and ERAS model predictions (dashed lines). (a) At 298.15 K; (b) at 313.15 K.

molar heat capacities of 2-butanol and n-hexane were taken from literature data [21–23]. Finally, the surface to volume ratios, s, were estimated using Bondi's method [24].

The association parameters for 2-butanol and 1,3-dioxolane were obtained from the literature [25,1]. In the ERAS model the parameters Δv_i^* and Δh_i^*, are considered non-temperature dependent and the parameter K_i can be obtained at a given temperature using the van't Hoff equation from the corresponding K_i and Δh_i^* values at 298.15 K.

The adjustable parameters of the ERAS model are: the energetic interaction parameter (X_{ij}), for the three binary mixtures, and the cross-association parameters for the 2-butanol + 1, 3-dioxolane mixture (K_{AB}, Δv_{AB}^*, Δh_{AB}^*). For the mixture 2-butanol + 1, 3-dioxolane at 313.15 K, it can be pointed out that the only adjustable parameter is X_{AB} since Δv_{AB}^* and Δh_{AB}^* are non-temperature dependent and K_{AB} is calculated using the vant' Hoff equation from Δh_{AB}^* and K_{AB} values at 298.15 K.

Evaluation, at each temperature, of the parameters was based on minimisation, using the simulated annealing method [26,27], of an objective function, F, defined in terms of experimental and calculated V^E and H^E values of the binary mixtures.

$$F = \sum_{i=1}^{i=N} \left[\left(\frac{V_{i,\mathrm{ERAS}}^E - V_{i,\mathrm{exp}}^E}{V_{i,\mathrm{exp}}^E} \right)^2 + \left(\frac{H_{i,\mathrm{ERAS}}^E - H_{i,\mathrm{exp}}^E}{H_{i,\mathrm{exp}}^E} \right)^2 \right] \quad (7)$$

Table 6
ERAS model parameters for the constituent binary mixtures of the ternary system 2-butanol (1) + 1, 3-dioxolane (2) + n-hexane (3) at 298.15 and 313.15 K

Mixture	T (K)	X_{ij} (J cm^{-3})	K_{AB}	Δv^*_{AB} (cm^3 mol^{-1})	Δh^*_{AB} (J mol^{-1})
2-Butanol (1) + 1,3-dioxolane (2)	298.15	7.2	3	−15	−3150
	313.15	12	2.8	−15	−3150
2-Butanol (1) + n-hexane (3)	298.15	21.7	–	–	–
	313.15	24.1	–	–	–
1,3-Dioxolane (2) + n-hexane (3)	298.15	22.4	–	–	–
	313.15	19.9	–	–	–

Table 7
ERAS model predictions: relative root mean square deviations, RMSD (%), for V^E and H^E of the ternary system 2-butanol (1) + 1, 3-dioxolane (2) + n-hexane (3) at 298.15 and 313.15 K

Property	T (K)	RMSD (%)
V^E (cm^3 mol^{-1})	298.15	50.3
	313.15	55.6
H^E (J mol^{-1})	298.15	22.8
	313.15	26.6

where N is the number of experimental data. The parameter values are given in Table 6.

From these parameters, ERAS model calculations for the ternary system have been made. These calculations are graphically represented in Figs. 1 and 2. We also have obtained the corresponding relative root mean square deviations (RMSD) between experimental and calculated excess molar properties defined as

$$\text{RMSD}\,(\%) = \left[\frac{1}{N}\sum_{i=1}^{i=N}\left(\frac{Y^E_{i,\text{ERAS}} - Y^E_{i,\exp}}{Y^E_{i,\exp}}\right)^2\right]^{1/2} \times 100 \tag{8}$$

where $Y^E_{\exp}$ and Y^E_{ERAS} are, respectively, the experimental and calculated excess molar properties of the ternary mixture (H^E or V^E) and N is the number of experimental points. RMSD values are given in Table 7.

In Figs. 1 and 2 we can see that the ERAS model predictions are closer to experimental H^E than V^E. In general the ERAS model correctly describes the variation with composition of the excess molar volumes and enthalpies at high mole fractions of n-hexane. This might be related with structural effects we discuss above which are more relevant at small mole fractions of n-hexane.

ERAS model predictions could be considered moderately satisfactory since the model only uses parameters obtained from the constituent binary mixtures.

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