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Isothermal Vapor−Liquid Equilibrium of (1-Butanol + 1,8-Cineole) at 10 Temperatures between (278.15 and 323.15) K

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ABSTRACT: Vapor pressures of (1-butanol + 1,8-cineol) at 10 temperatures between (278.15 and 323.15) K were measured by a static method. The reduction of the vapor pressures for obtaining activity coefficients and excess molar Gibbs energies was carried out by fitting the vapor pressure data to the Wilson equation according with Barker's method. Four equations of state (EOS) were used to correlate the vapor−liquid equilibrium (VLE) and for describing the volumetric behavior of the mixture. Two of them are modifications of the temperature-dependent function $\alpha(T_r)$ in the attractive term of Peng−Robinson equation as proposed by Mathias (PRM) and by Stryjek−Vera (PRSV). In both cases a volume translation (VT) according to Peneloux was considered. The other two models applied are based on the theory of perturbations: statistical associating fluid theory (SAFT) and perturbed-chain statistical associating fluid theory (PC-SAFT). The best description of the phase equilibrium was achieved by the Stryjek−Vera modification, whereas SAFT and PC-SAFT provided the best volumetric results.

INTRODUCTION

1,3,3-Trimethyl-2-oxabicyclo[2.2.2]octane (1,8-cineole or eucalyptol) is a very common terpenoid in essential oils. Essential oils are natural products obtained from aromatic plants with many applications in cosmetic, pharmaceutical, and food industries.

On the other hand, in the supercritical fluid extraction, alkanols of short chain are commonly employed as modifiers. These modifiers are added to the carbon dioxide to increase the polarity of the solvent, thus improving its performance in separating the most polar components. 1,8-Cineole is not a very polar compound, but the presence of the modifier could affect its extraction. In this sense information about the thermophysical behavior of mixtures (1-alkanol + 1,8-cineole), and models or equations of state to describe them in wide conditions, could be of interest for those extraction processes, even if the temperature and pressure conditions are rather different.

In previous papers[1−3] we reported the values of some thermophysical properties for the systems (1-alkanol ranging from ethanol to 1-pentanol + 1,8-cineole). Then we report here vapor pressures at 10 temperatures between (278.15 and 323.15) K of (1-butanol + 1,8-cineole). As far as we know, there are no data available in the open literature on vapor pressures of this binary system. From the vapor−liquid equilibrium (VLE), the activity coefficients and the excess molar Gibbs energies were determined.

Four equations of state (EOS) have been tested to describe the VLE of the system. Two of them cubic in the molar volume (Peng−Robinson−Mathias,[4] PRM, and Peng−Robinson−Stryjek−Vera,[5] PRSV) were used with volume translation (VT) according to Peneloux,[6] and the other two were based on perturbation models, statistical associating fluid theory (SAFT)[7] and perturbed-chain statistical association fluid theory (PC-SAFT).[8] The interaction parameters, k_{ij}, were adjusted to VLE experimental data, showing a lineal dependence with temperature.

Table 1. Molar Volumes $V°$ and Vapor Pressures $P°$ of Pure Compounds; Experimental and Literature Values

	1-butanol			1,8-cineole			
	$V° \cdot 10^6$ / $m^3 \cdot mol^{-1}$	$P°$/Pa		$V° \cdot 10^6$ / $m^3 \cdot mol^{-1}$		$P°$/Pa	
T/K	lit.[a,b]	exp.[a]	lit.[c]	exp.[a]	lit.	exp.[a]	lit.[i]
278.15	90.3	200	189	164.6	-	71	-
283.15	90.7	306	286	165.3	-	93	-
288.15	91.1	452	427	166.1	-	130	133
293.15	91.5	664	625	166.9	167.5[d]; 167.6[e,f,g]	178	-
298.15	92.0	939	901	167.7	-	253	-
303.15	92.4	1316	1280	168.5	-	346	-
308.15	92.8	1831	1793	169.2	-	477	-
313.15	93.3	2526	2477	170.0	170.0 [e,h]	627	-
318.15	93.7	3435	3380	170.9	-	828	-
323.15	94.2	4545	4556	171.7	-	1101	-

[a] Used in the Barker analysis. [b] Ref 16. [c] Ref 17. [d] Ref 3. [e] Ref 2. [f] Ref 18. [g] Ref 19. [h] Ref 20. [i] Ref 21.

EXPERIMENTAL SECTION

Materials. 1-Butanol and 1,8-cineole were supplied by Aldrich (mole fraction purity > 0.998 and > 0.990, respectively). All of the chemicals were of low water content, stored over molecular sieve (4 Å), and used without further purification. The mass fraction purity was checked by gas chromatography and found to be 0.9999 for 1-butanol and 0.9970 for 1,8-cineole.

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Table 2. Values of the Vapor Pressure P, Deviations $\Delta P = P - P_{calc}$, Activity Coefficients γ_1 and γ_2, and Excess Molar Gibbs Energies G^E_m

	P	ΔP			G^E_m		P	ΔP			G^E_m
x_2	Pa	Pa	γ_1	γ_2	$J \cdot mol^{-1}$	x_2	Pa	Pa	γ_1	γ_2	$J \cdot mol^{-1}$
					1-Butanol (1) + 1,8-Cineole (2)						
					T/K = 278.15						
0.0771	196	0	1.0035	1.8330	115	0.5995	147	−5	1.2877	1.1571	436
0.1369	195	4	1.0112	1.7196	194	0.6508	146	−1	1.3571	1.1212	419
0.1976	190	3	1.0239	1.6160	263	0.6810	142	−1	1.4041	1.1023	404
0.2736	182	1	1.0475	1.5011	335	0.7741	128	−2	1.5855	1.0534	334
0.3487	181	6	1.0804	1.4020	389	0.8852	111	3	1.9051	1.0147	201
0.4857	162	−2	1.1711	1.2531	441	0.9346	95	1	2.1012	1.0050	123
					T/K = 283.15						
0.0771	310	13	1.0036	1.8383	118	0.5995	219	−3	1.2896	1.1549	443
0.1369	292	3	1.0114	1.7223	198	0.6508	215	2	1.3587	1.1194	425
0.1976	296	15	1.0244	1.6169	269	0.6810	202	−5	1.4054	1.1005	409
0.2736	271	0	1.0483	1.5003	342	0.7741	182	−3	1.5848	1.0523	338
0.3487	255	−6	1.0816	1.4002	397	0.8852	153	3	1.8978	1.0143	203
0.4857	240	−2	1.1803	1.2506	456	0.9346	133	4	2.0890	1.0046	124
					T/K = 288.15						
0.0771	442	5	1.0037	1.8485	122	0.5995	352	29	1.2930	1.1507	448
0.1369	429	3	1.0119	1.7273	204	0.6508	308	−1	1.3615	1.1157	429
0.1976	424	11	1.0253	1.6181	276	0.6810	285	−15	1.4075	1.0972	413
0.2736	388	−10	1.0499	1.4984	350	0.7741	261	−6	1.5828	1.0502	339
0.3487	378	−4	1.0839	1.3964	405	0.8852	222	8	1.8830	1.0136	203
0.4857	343	−9	1.1764	1.2459	456	0.9346	181	−2	2.0626	1.0046	124
					T/K = 293.15						
0.0771	640	0	1.0037	1.8410	123	0.5995	478	12	1.2910	1.1490	452
0.1369	635	13	1.0119	1.7208	206	0.6508	441	−3	1.3587	1.1143	432
0.1976	595	−8	1.0252	1.6123	279	0.6810	428	−2	1.4042	1.0960	416
0.2736	566	−13	1.0497	1.4936	353	0.7741	383	2	1.5771	1.0495	342
0.3487	554	−1	1.0835	1.3924	409	0.8852	305	3	1.8721	1.0134	204
0.4857	510	1	1.1754	1.2432	460	0.9346	249	−7	2.0481	1.0045	124
					T/K = 298.15						
0.0771	909	3	1.0038	1.8394	125	0.5995	668	9	1.2907	1.1455	455
0.1369	901	22	1.0121	1.7174	209	0.6508	636	8	1.3575	1.1114	435
0.1976	843	−10	1.0256	1.6079	283	0.6811	597	−11	1.4022	1.0935	418
0.2736	807	−12	1.0503	1.4885	358	0.7742	532	−7	1.5711	1.0480	343
0.3487	789	4	1.0843	1.3872	414	0.8852	434	8	1.8561	1.0129	204
0.4857	718	−2	1.1761	1.2387	464	0.9346	359	−3	2.0243	1.0043	124
					T/K = 303.15						
0.0771	1278	10	1.0037	1.8242	125	0.5996	908	−7	1.2864	1.1432	456
0.1369	1254	24	1.0119	1.7049	210	0.6509	882	11	1.3520	1.1097	436
0.1976	1185	−7	1.0252	1.5976	284	0.6811	840	−3	1.3960	1.0920	419
0.2736	1143	0	1.0496	1.4804	359	0.7742	742	−2	1.5616	1.0472	344
0.3487	1089	−6	1.0831	1.3810	415	0.8852	604	16	1.8401	1.0127	205
0.4858	997	−5	1.1736	1.2350	466	0.9346	480	−17	2.0041	1.0042	124
					T/K = 308.15						
0.0771	1774	11	1.0037	1.8142	126	0.5996	1257	−10	1.2836	1.1409	459
0.1369	1730	20	1.0119	1.6961	211	0.6509	1212	7	1.3482	1.1078	438
0.1976	1654	−2	1.0251	1.5899	286	0.6811	1164	−2	1.3915	1.0904	421
0.2736	1596	8	1.0493	1.4739	362	0.7742	1034	5	1.5540	1.0463	345

Table 2. Continued

x_2	P / Pa	ΔP / Pa	γ_1	γ_2	G_m^E / $J\cdot mol^{-1}$	x_2	P / Pa	ΔP / Pa	γ_1	γ_2	G_m^E / $J\cdot mol^{-1}$
0.3487	1518	−2	1.0826	1.3756	417	0.8853	814	4	1.8259	1.0125	205
0.4858	1377	−12	1.1722	1.2314	468	0.9347	680	−5	1.9852	1.0041	125
					T/K = 313.15						
0.0771	2435	8	1.0037	1.8057	128	0.5996	1724	1	1.2812	1.1390	461
0.1369	2377	26	1.0118	1.6886	213	0.6509	1643	6	1.3450	1.1063	441
0.1976	2277	4	1.0250	1.5834	288	0.6812	1580	−2	1.3877	1.0891	423
0.2737	2169	−8	1.0491	1.4686	364	0.7743	1369	−20	1.5477	1.0456	347
0.3488	2076	−4	1.0821	1.3712	420	0.8853	1102	15	1.8142	1.0123	206
0.4858	1894	−1	1.1710	1.2284	472	0.9347	915	2	1.9698	1.0041	125
					T/K = 318.15						
0.0771	3304	7	1.0037	1.7958	128	0.5997	2330	9	1.2784	1.1357	462
0.1370	3168	−22	1.0118	1.6792	215	0.6510	2215	14	1.3411	1.1036	441
0.1977	3088	6	1.0250	1.5747	290	0.6812	2124	−2	1.3828	1.0868	423
0.2737	2935	−13	1.0490	1.4608	366	0.7743	1858	−3	1.5387	1.0443	346
0.3488	2809	−4	1.0819	1.3645	422	0.8853	1440	−8	1.7961	1.0119	205
0.4859	2557	0	1.1699	1.2236	473	0.9347	1213	1	1.9453	1.0039	125
					T/K = 323.15						
0.0771	4392	31	1.0036	1.7843	129	0.5997	3060	−7	1.2750	1.1358	466
0.1370	4253	34	1.0116	1.6708	216	0.6511	2917	7	1.3373	1.1038	445
0.1977	4082	5	1.0245	1.5688	291	0.6813	2833	23	1.3789	1.0870	428
0.2737	3891	−7	1.0481	1.4572	368	0.7744	2453	−8	1.5345	1.0445	350
0.3488	3708	−12	1.0804	1.3624	425	0.8854	1924	6	1.7923	1.0120	208
0.4860	3358	−22	1.1674	1.2231	477	0.9348	1596	−12	1.9424	1.0040	126

Apparatus and Procedures. The vapor pressure measurements were performed by a static method. The apparatus is similar to that of Marsh,[9] except for some experimental details which have been described previously.[10,11] To prevent condensation effects on the mercury meniscus, the temperature of the manometer and the connecting tube containing the vapor phase was maintained at 325.0 K by circulating water thermostatted to within ± 0.1 K. The cell volume was about 12 cm^3, and 8 cm^3 to 10 cm^3 of sample was used in each experiment. Each liquid was degassed by magnetic stirring under its own vapor pressure before mixing. They were added successively, by gravity, into the cell immersed in liquid nitrogen. The masses of both components were determined by weighing, and the expanded uncertainty in the mole fraction is 0.0003 (coverage factor $k = 2$). Manometric levels were read with a cathetometer to within ± 0.01 mm, and pressure reproducibility was 10 Pa. The temperature of the liquid was measured by means of a digital thermometer AΣΛ with a Pt sensor, with an uncertainty of ± 0.01 K.

Densities to calculate molar volumes were obtained by means of a vibrating tube densimeter Anton Paar DMA 5000. The expanded uncertainty ($k = 2$) of this property is ± 0.04 $kg\cdot m^{-3}$. A comparison between experimental and literature data of densities of 1,8-cineole at atmospheric pressure is reported in Table 1. It can be observed that there is a good agreement between both sets of values.

RESULTS AND DISCUSSION

The molar volumes of the pure components used in the Barker analysis together with the experimental vapor pressures, which are compared with values calculated from equations found in the literature, are presented in Table 1. Experimental vapor pressure data of 1-butanol and 1,8-cineole at 10 temperatures between (278.15 and 323.15) K were fitted to the Antoine equations

$$\text{1-butanol}: \ln(P/\text{Pa}) = 22.34191 - \frac{3421.246}{T/\text{K} - 77.34400} \quad (1)$$

$$\text{1,8-cineole}: \ln(P/\text{Pa}) = 38.40231 - \frac{17305.69}{T/\text{K} + 228.2116} \quad (2)$$

Vapor pressures obtained from eqs 1 and 2 show a standard deviation of 12 Pa and a maximum deviation of 25 Pa at 318.15 K for 1-butanol and a standard deviation of 8 Pa and a maximum deviation of 14 Pa at 308.15 K for 1,8-cineole.

The second virial coefficient, at T = 325.0 K, of 1-butanol ($B_{11} = -3918\cdot 10^{-6}\ m^3\cdot mol^{-1}$) and 1,8-cineole ($B_{22} = -5490\cdot 10^{-6}\ m^3\cdot mol^{-1}$) were calculated from the Tsonopoulos[12] correlation. The mixed virial coefficient was calculated according to a cubic combination rule

$$B_{12} = \frac{1}{8}({B_{11}}^{1/3} + {B_{22}}^{1/3})^3 \quad (3)$$

Table 2 shows our vapor pressure measurements along with the activity coefficients and γ_1, γ_2, and the excess molar Gibbs free energy G_m^E values fitted by Barker's method[13] to the Wilson[14] correlation. The activity coefficients are given by

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \quad (4)$$

Table 3. Parameters and Standard Deviations s(Pa) of eqs 4, 5, and 11

	1-butanol (1) + 1,8-cineole (2)		
T/K	Λ_{12}	Λ_{21}	s/Pa
278.15	0.5395	0.4146	9
283.15	0.5482	0.4120	10
288.15	0.5525	0.4106	11
293.15	0.5474	0.4173	9
298.15	0.5490	0.4227	16
303.15	0.5620	0.4172	15
308.15	0.5759	0.4094	16
313.15	0.5873	0.4043	15
318.15	0.6063	0.3920	16
323.15	0.6160	0.3909	25

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \qquad (5)$$

with:

$$\Lambda_{ij} = \frac{V_j^0}{V_i^0}\exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \qquad (6)$$

where the subscripts 1 and 2 stand for 1-butanol and 1,8-cineole, respectively, V° is the molar volume, and λ's are the interaction constants between the molecules designated in the subscripts. The vapor pressure is then given by

$$P_{\text{calc}} = x_1\gamma_1P_1^\circ R_1 + x_2\gamma_2P_2^\circ R_2 \qquad (7)$$

where the nonideality of the vapor phase is accounted for with the corrections

$$R_1 = \exp\{[(V_1^\circ - B_{11})(P - P_1^\circ) - P\delta_{12}{y_2}^2]/RT\} \qquad (8)$$

$$R_2 = \exp\{[(V_2^\circ - B_{22})(P - P_2^\circ) - P\delta_{12}{y_1}^2]/RT\} \qquad (9)$$

where y_1 and y_2 are the vapor phase mole fractions of 1-butanol and 1,8-cineole, respectively, and δ_{12}

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \qquad (10)$$

For a given composition, the sample temperature is changed, and a slight variation of the true liquid mole fraction may be detected in Table 2, according to the variable composition of the vapor phase. In Table 3, the Wilson parameters Λ_{12} and Λ_{21} are collected, together with the standard deviations defined by

$$s(\text{Pa}) = \{\sum_{i=1}^{N}(\Delta P)_i^2/(N - m)\}^{1/2} \qquad (11)$$

ΔP's are the residual pressures according to Barker's method, N is the number of experimental points, and m is the number of parameters in the corresponding analytical equation. Vapor pressure−liquid composition curves are shown in Figure 1. Figure 2 shows the analytic results for G_m^E.

We tested the consistency of the enthalpies and free energies by means of the Gibbs−Helmholtz equation. We have fitted G_m^E/T data with a second-degree polynomial in $1/T$, and according to the Gibbs−Helmholtz equation the derivative gives H_m^E. The H_m^E values, calculated at T = 298.15 K, are shown as curves in Figure 3 together with the H_m^E experimental data found in the literature. The agreement is reasonable considering that the quantitative evaluation of H_m^E from vapor pressures involves considerable

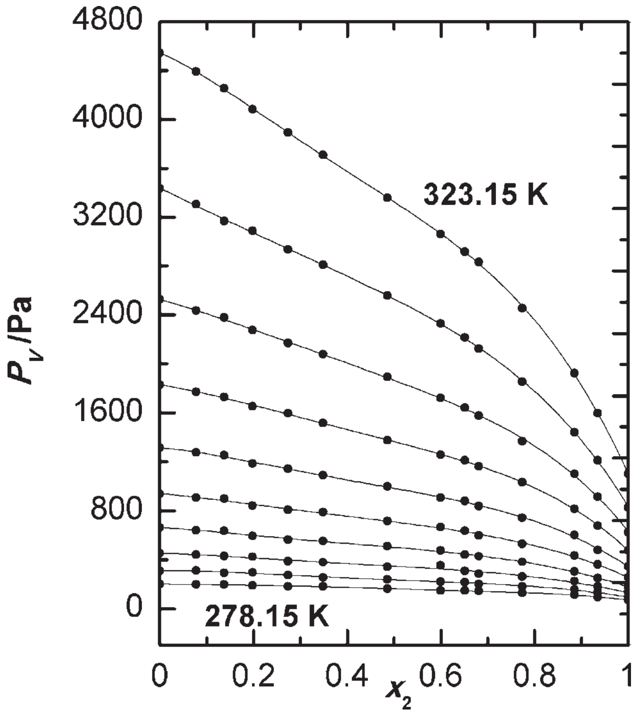

Figure 1. Vapor pressures plotted against liquid-phase composition of 1,8-cineole, at working temperatures between (278.15 and 323.15) K; ●, experimental data; —, eq 7, for 1-butanol (1) + 1,8-cineole (2).

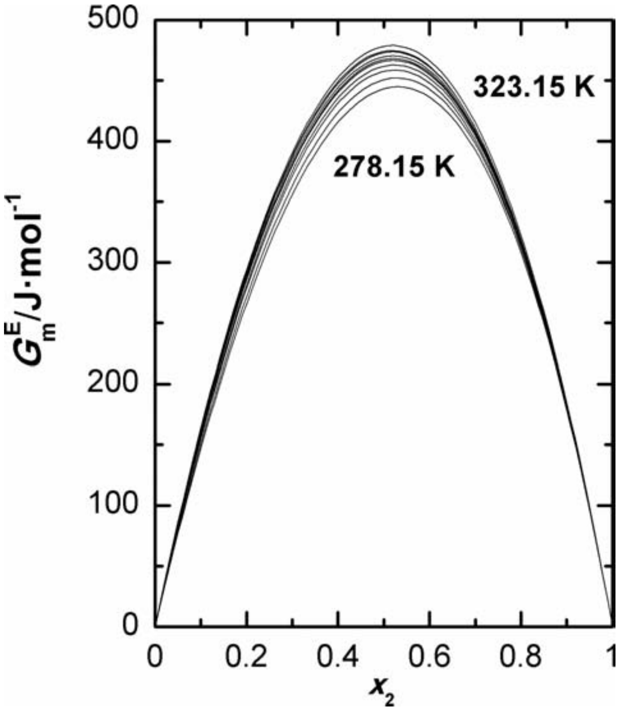

Figure 2. Excess molar Gibbs energies G_m^E at temperatures between (278.15 and 323.15) K, for 1-butanol (1) + 1,8-cineole (2), plotted as a function of mole fraction of 1,8-cineole.

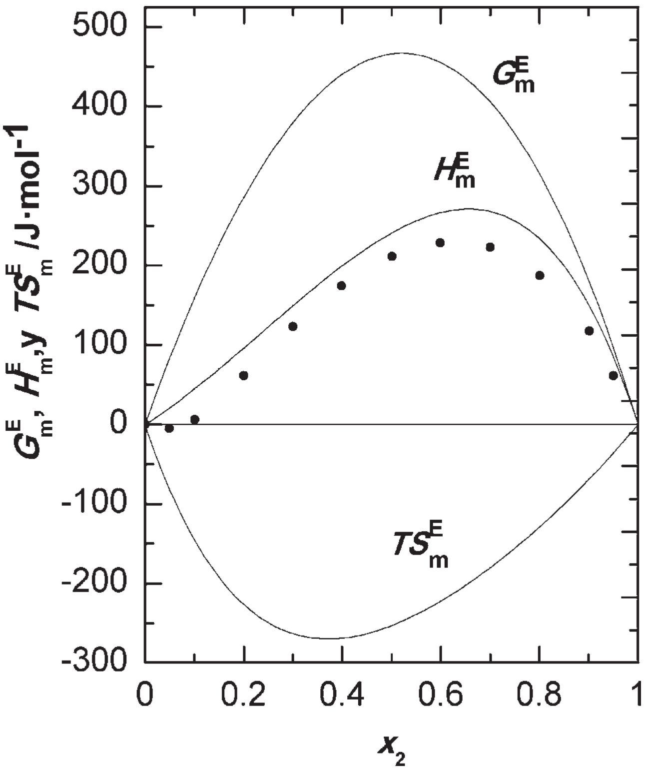

Figure 3. Thermal excess molar functions, at 298.15 K for 1-butanol (1) + 1,8-cineole (2): ●, experimental H_m^E (ref 2); —, Gibbs−Helmholtz H_m^E, G_m^E, and TS_m^E.

Table 4. Pure Component Properties and Parameters Used for the Application of the Studied Equations of State

		M_w	T_b	T_c	P_c	
		g·mol^{-1}	K	K	MPa	ω
1,8-cineole[a]		154.25	449.6	661.12	3.019	0.338
1-butanol[b]		74.122	390.88	563.05	4.423	0.590
PRM-VT		P_1		c/b		range T/K
1,8-cineole[c]		−0.003518		−0.086491		278−450
1-butanol[c]		−0.317609		0.009533		278−450
PRSV-VT		k_{ap}		c/b		range T/K
1,8-cineole[c]		0.007355		−0.086427		278−450
1-butanol[c]		0.277918		0.008677		278−450
		v^{oo}	$u^o \cdot k^{-1}$		$\varepsilon \cdot k^{-1}$	
SAFT	m	L·mol^{-1}	K	κ	K	range T/K
1,8-cineole[c]	4.842	0.0178	263.43	-	-	278−450
1-butanol[d]	3.971	0.0120	225.96	0.01639	2605	313−493
		σ_i	$\epsilon_{ij} \cdot k^{-1}$		$\epsilon^{A_iB_i} \cdot k^{-1}$	
PC-SAFT	m_i	Å	K	$k^{A_iB_i}$	K	range T/K
1,8-cineole[c]	3.213	4.1566	301.92	-	-	278−450
1-butanol[e]	2.751	3.6139	259.59	0.006692	2544.6	184−563

[a] Ref 1. [b] Database from PE ref 22. [c] This work. [d] Ref 7. [e] Ref 8.

Table 5. Values of the Coefficients *a* and *b* in eq 12 and Regression Coefficient, *R*

model	a	b	R^2
PRM	0.0923	$-2.6356 \cdot 10^{-4}$	0.998
PRSV	−0.0184	$9.238 \cdot 10^{-5}$	0.980
SAFT	−0.0445	$1.5491 \cdot 10^{-4}$	0.993
PC-SAFT	−0.0516	$1.2805 \cdot 10^{-4}$	0.985

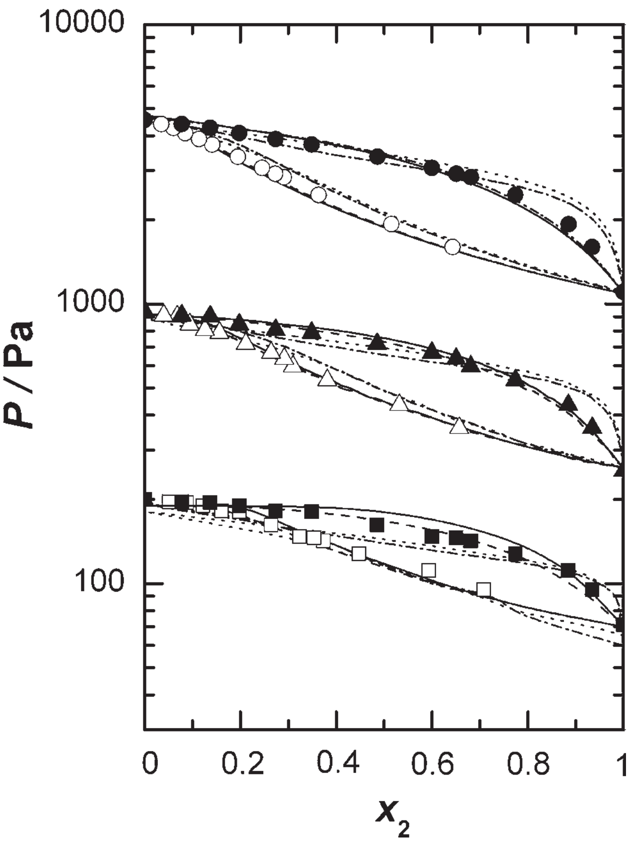

Figure 4. Isothermal vapor liquid equilibrium of the 1-butanol (1) + 1,8-cineole (2) system. Full symbols experimental data: ■, T = 278.25 K; ▲, T = 298.15 K; ●, T = 323.15 K. Open symbols were obtained from the Wilson equation. Lines, EOS correlations: —, PRM-VT; − − −, PRSV-VT; · · · ·, SAFT; −·−·−, PC-SAFT.

uncertainty.[15] In the same figure and at the same temperature, TS_m^E curves, obtained from $TS_m^E = H_m^E - G_m^E$, are also plotted.

Equations of State (EOS). Four EOS were tested to describe the phase equilibrium and the volumetric behavior of the 1-butanol (1) + 1,8-cineole (2) mixture. Two of them are modifications of the temperature-dependent function $\alpha(T_r)$ in the attractive term of Peng−Robinson equation as proposed by Mathias (PRM)[4] and by Stryjek−Vera (PRSV).[5] To improve the volumetric results, VT according to Peneloux[6] was considered in both modifications. The other two models applied are based on the theory of perturbations: SAFT[7] and PC-SAFT.[8]

The properties of the pure compounds used in this work are gathered in Table 4. The cubic EOS parameters for 1,8-cineole and 1-butanol were calculated from the correlation of vapor pressure and saturation properties. The SAFT and PC-SAFT parameters for 1-butanol were taken from literature,[7,8] and those corresponding to 1,8-cineole were reevaluated to increase their range of application.

To determine the $P\rho T$ behavior of the mixtures, the van der Waals one-fluid mixing rules were used, and classical quadratic combining rules for the cross-terms were selected in all cases. The so-called interaction parameters, k_{ij}, were optimized for each

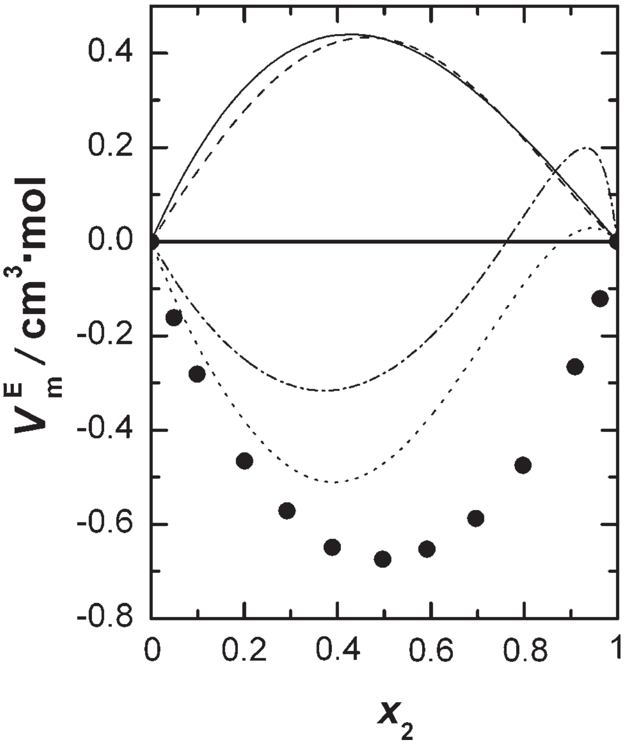

Figure 5. Volumetric behavior of the 1-butanol (1) + 1,8-cineole (2) system at 298.15 K. ●, ref 2; —, PRM-VT; − − −, PRSV-VT; · · · ·, SAFT; −·−·−, PC-SAFT.

model showing a lineal dependence with temperature in the experimental range considered.

The fitted parameters for the equation

$$k_{ij} = a + b \cdot T/\mathrm{K} \qquad (12)$$

appear in Table 5 together with the regression coefficients.

Figure 4 shows the experimental VLE at three temperatures together with the obtained results using the selected EOS. The best results for the correlations of the experimental data of the mixture under study were achieved with PRSV-VT and PRM-VT. The absolute average percentage deviation values (ADD) for these models were (14.22 and 16.70) %, respectively. The ADD obtained for SAFT and PC-SAFT were, respectively, (21.50 and 21.25) %.

The ability of the four EOS to reproduce the volumetric behavior of the system was also tested at 298.15 K. As Figure 5 shows, PRSV-VT and PRM-VT, despite the VT used, give worse results for the excess molar volume compared with the experimental data reported by Alfaro et al.[2] Although SAFT results for VLE are not as accurate as those of the cubic equations, SAFT is able to approach to the correct volumetric behavior of the real system. PC-SAFT gives the correct sign of the excess molar volume of the binary mixture at least.

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