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Effect of Molecular Structure on the Thermodynamics of Nitromethane + Butanol Isomers Near the Upper Critical Point

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Densities, isentropic compressibilities, and isobaric molar heat capacities were determined over the whole composition range for nitromethane + (2-butanol or isobutanol) at atmospheric pressure and at the temperatures 288.15, 293.15, 298.15, and 308.15 K. These results allowed us to obtain isobaric thermal expansivities, isothermal compressibilities, and isochoric molar heat capacities at the temperature 298.15 K. The excess quantities for the given properties were obtained. In addition, liquid–liquid phase separation temperatures were also determined, locating upper critical solution temperatures near the experimental temperatures. The variation of the properties among isomers is discussed. Also, the effect of the nonrandomness of the mixtures expected near the critical point is discussed.

KEY WORDS: excess properties; nonrandomness; second order derivatives; upper critical point.

1. INTRODUCTION

It has been shown that strong departures from ideal behavior are found for binary nonelectrolyte mixtures near an upper liquid–liquid critical point UCP [1, 2]. As a result, excess quantities, such as excess Gibbs energies or excess enthalpies, tend to take high positive values. At a microscopic level, this behavior comes from the nonrandomness of the molecular distribution in the mixture, which ultimately is responsible for phase separation.

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This pattern is frequently found for (polar + n-alkane) mixtures, and it is accompanied by a W-shaped composition dependence of the excess isobaric heat capacities $C_{\mathrm{p}}^{\mathrm{E}}$ [2–4]. Recently [5], it has been shown that systems different from (polar + n-alkane) also show a singular composition dependence of $C_{\mathrm{p}}^{\mathrm{E}}$ near the critical temperature. Thus, $C_{\mathrm{p}}^{\mathrm{E}}$ appears to be a useful indicator of changes in liquid order during the mixing process, and, in these particular cases, it reveals the degree of nonrandomness in the mixture near the critical point.

The purpose of this work is to analyze the effect of molecular structure on the thermodynamics of mixtures near the UCP. Liquid–liquid phase separation temperatures T^* depend strongly not only on the type of interactions involved in the mixture but also on the molecular size; however, although it can be expected that T^* will not be significantly affected by molecular structure, little is known about this matter. In previous work [5], the effect of nonrandomness on the thermodynamic properties of the nitromethane + 1-butanol system near its UCP was investigated, the excess isobaric heat capacity being the more interesting quantity in this respect. Now a study of mixtures containing nitromethane and 2-butanol (a secondary alkanol with a linear alkyl chain) or isobutanol (a primary alkanol with a branched alkyl chain) is presented. This permits analysis of the variation of the thermodynamic properties with both the position of the hydroxyl and the structure of the alkyl chain.

Densities ρ, isentropic compressibilities κ_{s}, and isobaric molar heat capacities $C_{\mathrm{p,m}}$ were determined over the complete composition range at atmospheric pressure and at the temperatures 288.15, 293.15, 298.15, and 308.15 K. Using these results, isobaric thermal expansivities α_{p}, isothermal compressibilities κ_T, and isochoric molar heat capacities $C_{\mathrm{v,m}}$ at the temperature 298.15 K and the excess quantities $V_{\mathrm{m}}^{\mathrm{E}}$, $C_{\mathrm{p,m}}^{\mathrm{E}}$, $(\partial H_{\mathrm{m}}^{\mathrm{E}}/\partial p)_T$, $\alpha_{\mathrm{p}}^{\mathrm{E}}$, $\kappa_{\mathrm{s}}^{\mathrm{E}}$, κ_T^{E}, and $C_{\mathrm{v,m}}^{\mathrm{E}}$ were obtained. The procedure for obtaining this comprehensive set of thermodynamic properties was validated in previous work [6]. In addition, liquid–liquid phase separation temperatures T^* were also determined. The effect of the nonrandomness of the mixtures expected near the critical point is discussed.

2. EXPERIMENTAL

2.1. Materials

Isobutanol and 2-butanol (purity, >99.4%) were from Aldrich, and nitromethane (purity, >99%) was from Fluka. The purities of the products were checked by gas chromatography (g.c.). All were partially degassed and dried over Fluka 0.4-nm molecular sieves before use.

Mixtures were prepared by weighing using a Mettler AE-240 balance whose precision is ±0.00001 g.

2.2. Equipment

Densities were determined with a vibrating-tube densimeter (Anton-Paar DMA-60/602) using Milli-Q water and *n*-heptane as standard liquids. The precision of the measurements is estimated to be $\pm 0.00003\ \mathrm{g \cdot cm^{-3}}$. Further experimental details are given in a previous paper [7].

Isentropic compressibilities are obtained by combining density data with speeds of sound u via the Laplace equation $\kappa_s = (\rho u^2)^{-1}$. Speeds of sound were obtained using a sound analyzer (Anton-Paar DSA-48), with which u is determined by the ultrasonic pulse analysis technique. Milli-Q water was used as a speed-of-sound standard liquid using the values of Bilaniuk et al. [8]. A detailed description of the apparatus and the experimental procedure can be found elsewhere [9]. This procedure results in a precision of about $\pm 0.05\ \mathrm{TPa^{-1}}$ for κ_s.

Isobaric molar heat capacities were obtained from the density data and isobaric heat capacities per unit volume $C_p V^{-1}$ provided by a Setaram Micro DSC II differential scanning calorimeter. $C_p V^{-1}$ data were determined by the stepwise method, a detailed description of which can be found in the literature [10, 11]. *n*-Heptane and 1-butanol were used as isobaric heat capacity standards, the $C_{p,m}$ values of which were taken from the literature [12]. The precision of the $C_{p,m}$ measurements was estimated to be $\pm 0.03\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$. Liquid–liquid phase separation temperatures T^* are also determined in heat capacity experiments; the procedure involves the analysis of the thermogram obtained in a temperature scan [19]. The experiments were performed using a scanning rate of $0.02\ \mathrm{K \cdot min^{-1}}$, resulting in a precision of approximately $T^* \pm 0.02$ K.

3. RESULTS AND DISCUSSION

3.1. Data Treatment

Densities, isentropic compressibilities, and isobaric molar heat capacities are reported in Tables I, II, and III, respectively. These data were fitted as a function of composition and temperature to the following equation:

$$Y = \sum_{i=0}^{n} A_i x_1^i \tag{1}$$

Table I. Densities ρ of the Mixtures at Temperature T (Compositions in Mole Fractions)

x_1	ρ ($g \cdot cm^{-3}$)	x_1	ρ ($g \cdot cm^{-3}$)	x_1	ρ ($g \cdot cm^{-1}$)	x_1	ρ ($g \cdot cm^{-3}$)
Nitromethane (1) + 2-butanol (2) at $T = 288.15$ K							
0	0.81055	0.30444	0.87423	0.60094	0.96031	0.89793	1.08496
0.05380	0.82027	0.40550	0.90041	0.63222	0.97124	0.94862	1.11253
0.10307	0.82984	0.49417	0.92596	0.69396	0.99397	1	1.14336
0.20268	0.85060	0.55579	0.94524	0.79599	1.03608		
Nitromethane (1) + 2-butanol (2) at $T = 293.15$ K							
0	0.80658	0.30565	0.86958	0.63386	0.96591	0.94790	1.10552
0.04954	0.81547	0.40547	0.89522	0.69451	0.98819	1	1.13653
0.10252	0.82546	0.47102	0.91365	0.79859	1.03098		
0.20578	0.84668	0.54135	0.93499	0.89863	1.07885		
Nitromethane (1) + 2-butanol (2) at $T = 298.15$ K							
0	0.80240	0.30224	0.86371	0.63254	0.95950	0.94912	1.09955
0.05073	0.81122	0.40349	0.88938	0.69592	0.98258	1	1.12966
0.10232	0.82091	0.48390	0.91188	0.79521	1.02326		
0.20357	0.84134	0.55454	0.93345	0.89743	1.07173		
Nitromethane (1) + 2-butanol (2) at $T = 308.15$ K							
0	0.79392	0.30643	0.85463	0.62954	0.94674	0.94746	1.08530
0.05051	0.80241	0.40518	0.87922	0.69565	0.97060	1	1.11603
0.10314	0.81196	0.47444	0.89911	0.79669	1.01136		
0.20314	0.83174	0.55491	0.92218	0.89789	1.05895		
Nitromethane (1) + isobutanol (2) at $T = 288.15$ K							
0	0.80553	0.20377	0.84786	0.89969	1.08628		
0.05312	0.81594	0.30329	0.87168	0.94897	1.11303		
0.10361	0.82618	0.79682	1.03671	1	1.14331		
Nitromethane (1) + isobutanol (2) at $T = 293.15$ K							
0	0.80172	0.29612	0.86514	0.62182	0.96151	0.94919	1.10645
0.05160	0.81171	0.40558	0.89374	0.69348	0.98787	1	1.13649
0.09969	0.82130	0.47629	0.91410	0.79778	1.03097		
0.20315	0.84329	0.55518	0.93882	0.90041	1.08013		
Nitromethane (1) + isobutanol (2) at $T = 298.15$ K							
0	0.79788	0.30294	0.86224	0.61966	0.95512	0.94840	1.09945
0.05395	0.80809	0.40075	0.88744	0.69497	0.98263	1	1.12964
0.10399	0.81800	0.47401	0.90828	0.79745	1.02468		
0.20076	0.83839	0.55781	0.93421	0.89951	1.07328		
Nitromethane (1) + isobutanol (2) at $T = 308.15$ K							
0	0.79007	0.30429	0.85290	0.61995	0.94385	0.95108	1.08764
0.05611	0.80033	0.40633	0.87881	0.69500	0.97089	1	1.11604
0.10405	0.80936	0.47469	0.89796	0.79823	1.01275		
0.20345	0.82984	0.55406	0.92214	0.89842	1.05977		

Table II. Isentropic Compressibilities κ_s of the Mixtures at Temperature T (Compositions in Mole Fractions)

	κ_s (TPa^{-1})			
x_1	$T = 288.15$ K	$T = 293.15$ K	$T = 298.15$ K	$T = 308.15$ K
Nitromethane (1) + 2-butanol (2)				
0	794.22	821.75	850.62	912.54
0.05227	783.92	811.73	840.90	903.44
0.10595	773.80	801.61	830.80	893.15
0.19992	754.72	781.98	810.76	872.55
0.29838	732.69	758.74	786.45	845.78
0.40468	707.27	731.64	757.79	814.51
0.45904	692.56	715.95	741.25	796.55
0.51562	676.01	698.38	722.79	776.32
0.54797	665.81	687.77	711.76	764.09
0.57097	658.17	679.74	703.36	754.84
0.58771	652.29	673.73	697.06	748.03
0.59169	651.15	672.55	695.86	746.86
0.67893	619.72	640.08	662.25	710.88
0.70651	608.30	628.39	650.21	697.53
0.75042	588.93	608.94	630.32	676.57
0.79626	568.82	588.48	609.39	654.19
0.90347	518.48	537.00	556.45	597.86
0.95010	496.41	514.36	533.14	573.14
1	473.37	490.50	508.55	547.23
Nitromethane (1) + isobutanol (2)				
0	833.28	861.18	890.07	950.87
0.10290	805.11	832.83	861.57	922.08
0.20128	780.50	807.31	835.37	894.45
0.27991	761.00	786.59	813.64	871.17
0.35532		765.70	791.54	846.62
0.40967		750.07	774.65	828.32
0.47407		730.41	753.59	805.63
0.52833		712.05	734.16	784.07
0.57629		694.95	716.32	764.55
0.70139		642.10	661.86	707.17
0.81060	568.68	587.15	607.14	649.96
0.95015	496.52	514.36	533.13	572.63
1	473.37	490.50	508.55	547.23

Table III. Isobaric Molar Heat Capacities $C_{p,m}$ of the Mixtures at Temperature T (Compositions in Mole Fractions)

	$C_{p,m}$ ($J \cdot mol^{-1} \cdot K^{-1}$)			
x_1	$T = 288.15$ K	$T = 293.15$ K	$T = 298.15$ K	$T = 308.15$ K
Nitromethane (1) + 2-butanol (2)				
0	186.97	192.05	197.10	207.76
0.05491	185.74	190.25	194.57	203.54
0.10611	184.42	188.41	192.04	199.86
0.20861	181.78	184.55	186.93	192.39
0.30933	179.90	180.55	181.56	184.85
0.40948	178.23	175.50	175.21	176.35
0.50971	173.95	168.77	166.99	166.56
0.54100	171.18	165.87	163.99	163.21
0.57064	168.33	162.75	160.71	159.74
0.60523	163.77	158.74	156.75	155.62
0.67672	152.47	149.11	147.43	146.45
0.70215	147.95	145.22	143.94	143.02
0.75015	139.40	138.01	137.10	136.49
0.79969	131.00	130.43	129.97	129.64
0.89946	116.15	116.21	116.18	116.53
0.94045	111.03	111.22	111.33	111.91
0.97127	107.85	108.22	108.35	109.08
1	105.65	106.00	106.21	106.94
Nitromethane (1) + isobutanol (2)				
0	173.22	177.31	181.40	190.50
0.05546	173.54	177.22	180.92	188.95
0.10635	173.00	176.56	179.95	187.32
0.20470	172.08	174.84	177.28	183.10
0.30941	173.49	173.09	174.08	177.70
0.41117		173.20	170.91	171.70
0.51059		172.00	165.72	164.05
0.53805		170.50	163.68	161.62
0.57003		168.04	160.95	158.47
0.60720		164.13	157.12	154.57
0.62808		161.05	154.67	152.15
0.65402		156.85	151.40	149.16
0.69990		148.85	145.24	143.41
0.74775		140.23	138.17	136.97
0.79857		131.52	130.64	130.13
0.89982		116.28	116.21	116.54
0.94067	110.90	111.15	111.26	111.87
0.96528	108.33	108.59	108.84	109.49
1	105.65	106.00	106.21	106.94

where Y denotes ρ (in $\mathrm{g \cdot cm^{-3}}$), κ_s (in $\mathrm{TPa^{-1}}$), or $C_{p,m}$ (in $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$) and x_1 is the mole fraction of nitromethane. Two equations were used for the temperature dependence of the coefficients A_i:

$$A_i = \sum_{j=0}^{2} A_{ij} 10^{-j} (T - T_0)^j \tag{2}$$

$$A_i = \sum_{j=0}^{1} A_{ij} 10^{-j} (T - T_0)^j + \frac{A_{i2}}{\alpha} \left(\frac{T - T^*(x_1)}{T^*(x_1)} \right)^{-\alpha} \tag{3}$$

T_0 is a reference temperature whose value is fixed to the lowest in the experimental range, i.e., 288.15 K, $\alpha = 0.11$ is the critical exponent of the isobaric heat capacity fixed at its renormalization group theory value [13], and $T^*(x_1)$ denotes the liquid–liquid phase separation temperature at a given composition. The resulting coefficients A_{ij} together with the standard deviations σ are given in Table IV; Marquardt's algorithm [14] was used for the optimization process throughout this work. Equation (2) is commonly used when regular behavior is observed so it fits ρ and k_s. On the other hand, Eq. (3) is based on the critical behavior of the isobaric heat capacity and it is used to fit $C_{p,m}$; the ability of Eq. (3) to reproduce the experimental results is supported by the small standard deviation of the fitting (see Table IV).

The liquid–liquid phase separation temperatures of Eq. (3) are given in Table V. $T^* x_1$ curves are plotted in Fig. 1, in which the solid lines are the fitted curves, which follow:

$$T^* = T_c + k \, |y - y_c|^{1/\beta} \tag{4}$$

$$y = \frac{\gamma x_1}{1 + x_1(\gamma - 1)}, \qquad y_c = \frac{\gamma x_{1,c}}{1 + x_{1,c}(\gamma - 1)} \tag{5}$$

β is the critical exponent of the shape of the coexistence curve fixed to its renormalization group theory value 0.325. k, γ, $x_{1,c}$, and T_c are adjustable parameters, the last two being the coordinates of the critical point; their final values are given in Table V.

Isobaric thermal expansivities α_p were obtained at 298.15 K from analytic differentiation of the density fitting equation. Isothermal compressibilities and isochoric molar heat capacities were calculated using the thermodynamic relations

$$\kappa_T = \kappa_s + \frac{T V_m \alpha_p^2}{C_{p,m}} \tag{6}$$

$$C_{v,m} = C_{p,m} \frac{\kappa_s}{\kappa_T} \tag{7}$$

Table IV. Fitting Coefficients A_{ij} of Eqs. (2) and (3) and Standard Deviations σ

		i							
	j	0	1	2	3	4	5	6	7
					Nitromethane + 2-butanol				
ρ ($g \cdot cm^{-3}$)					$\sigma = (0.00006)$				
	0	0.810513	0.179667	0.065604	0.143540	−0.165663	0.109661		
	1	−0.007882	−0.009202	0.022559	−0.066876	0.084143	−0.036440		
	2	−0.000221	−0.001131	−0.006024	0.018060	−0.022424	0.009491		
$C_{p,m}$ ($J \cdot mol^{-1} \cdot K^{-1}$)					$\sigma = (0.15)$				
	0	193.31	−112.02	−2,270.41	21,721.88	−84,041.05	152,738.24	−12,9864.11	41,762.01
	1	10.37	−28.85	63.08	−335.70	1504.14	−3,183.33	3,025.11	−1,055.00
	2	−0.88	19.12	106.55	−1554.45	6497.98	−12,109.75	10,391.51	−3,351.89
κ_s (TPa^{-1})					$\sigma = (0.4)$				
	0	794.0	−177.9	−158.3	437.4	−840.7	418.7		
	1	53.6	17.5	−99.1	−31.3	238.5	−145.9		
	2	2.7	0.0	−8.1	62.8	−113.3	57.6		
V_m^E ($cm^3 \cdot mol^{-1}$)					$\sigma = (0.004)$				
	0	1.7002	0.1252	0.6129	0.2364				
	1	0.4391	−0.0104	−0.0068	−0.0533				
	2	−0.04253	−0.0119	−0.0027	−0.0382				
$C_{p,m}^E$ ($J \cdot mol^{-1} \cdot K^{-1}$)					$\sigma = (0.15)$				
	0	15,932.44	−188,345.95	870,525.98	−2,029,498.58	2,529,139.16	−1,607,286.61	409,627.31	
	1	−626.89	7,235.08	−33,200.59	76,462.49	−93,848.98	58,610.41	−14,649.76	
	2	−1,297.02	15,306.92	−70,716.90	165,141.80	−206,352.49	131,584.95	−33,670.12	

					Nitromethane + isobutanol				
ρ (g · cm^{-3})					$\sigma = (0.00006)$				
	0	0.805522	0.193784	0.037118	0.189571	−0.197270	0.114576		
	1	−0.007584	−0.004000	−0.011132	0.021803	−0.016632	0.003849		
	2	−0.000073	−0.001938	0.013447	−0.031391	0.030930	−0.010954		
$C_{p,m}$ (J · mol^{-1} · K^{-1})					$\sigma = (0.15)$				
	0	89.08	574.51	−735.77	1,244.80	−20,829.36	57,669.61	−57,316.31	19,364.43
	1	10.76	−23.28	49.04	−745.96	3,606.95	−7,004.90	6,008.74	−1,899.77
	2	7.38	−53.75	68.17	73.52	771.91	−2,924.86	3,152.18	−1,090.51
κ_s (TPa^{-1})					$\sigma = (0.4)$				
	0	833.2	−276.3	9.7	504.6	−1,301.5	703.6		
	1	54.6	16.8	−139.6	−32.5	369.0	−235.1		
	2	2.1	−5.2	34.7	−17.7	−59.5	47.4		
V_m^E (cm^3 · mol^{-1})					$\sigma = (0.004)$				
	0	0.9562	0.1933	0.2176	0.5597				
	1	0.2612	−0.0386	0.0093	0.0452				
	2	0.0159	−0.0069	0.0424	−0.0854				
$C_{p,m}^E$ (J · mol^{-1} · K^{-1})					$\sigma = (0.17)$				
	0	1,892.30	−19,153.17	83,614.50	−178,437.15	177,124.83	−64,947.58		
	1	−59.55	610.85	−3,173.45	7,407.48	−7,694.16	2,904.56		
	2	−159.11	1,546.58	−6,461.10	13,525.27	−13,307.94	4,853.15		

Table V. Liquid–Liquid Phase Transition Temperatures T^*, Fitting Coefficients of Eqs. (4) and (5), and Standard Deviations σ

x_1	T^* (K)	x_1	T^* (K)	x_1	T^* (K)
		Nitromethane (1) + 2-butanol (2)			
0.40948	284.22	0.60523	284.54	0.75015	282.65
0.50971	284.57	0.67672	284.25		
0.57064	284.61	0.70215	283.82		
$x_{1,c}$	T_c (K)	k	γ	σ	
0.55410	284.59	−214.04	0.51022	0.04	
		Nitromethane (1) + isobutanol (2)			
0.25728	284.94	0.51059	290.78	0.65402	290.52
0.30941	287.56	0.55842	290.83	0.69990	290.00
0.41117	290.12	0.60720	290.80	0.79857	286.65
0.45857	290.57	0.62808	290.70		
$x_{1,c}$	T_c (K)	k	γ	σ	
0.55309	290.80	−272.16	0.87043	0.04	

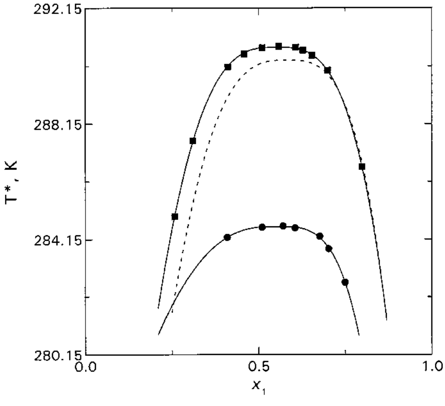

Fig. 1. Liquid–liquid phase separation temperatures T^* for (●) nitromethane (1) + 2-butanol (2) and (■) nitromethane (1) + isobutanol (2). (——) Fitted values from Eqs. (4) and (5). (- - -) Literature data [5] for nitromethane (1) + 1-butanol (2).

k_T and $C_{\mathrm{v,m}}$ were calculated at the compositions where κ_{s} was measured using the fitted ρ and $C_{\mathrm{p,m}}$ values.

Table VI shows results of this work for the properties of the pure liquids compared to literature values. As can be observed, good agreement is found with literature data, with special mention of the isobaric heat capacities and the densities of the alkanols.

The excess quantities of the above properties were calculated using the criterion of Benson and Kiyohara [16]. This criterion gives, for each thermodynamic property Y, an expression of the ideal quantity Y^{id} needed for the calculation of the excess quantity Y^{E},

$$Y^{\mathrm{E}} = Y - Y^{\mathrm{id}} \tag{8}$$

$$V_{\mathrm{m}}^{\mathrm{id}} = x_1 V_{\mathrm{m},1}^{*} + (1 - x_1)\, V_{\mathrm{m},2}^{*} \tag{9}$$

$$C_{\mathrm{p,m}}^{\mathrm{id}} = x_1 C_{\mathrm{p,m},1}^{*} + (1 - x_1)\, C_{\mathrm{p,m},2}^{*} \tag{10}$$

$$\alpha_{\mathrm{p}}^{\mathrm{id}} = \phi_1 \alpha_{\mathrm{p},1}^{*} + (1 - \phi_1)\, \alpha_{\mathrm{p},2}^{*} \tag{11}$$

$$\kappa_T^{\mathrm{id}} = \phi_1 \kappa_{T,1}^{*} + (1 - \phi_1)\, \kappa_{T,2}^{*} \tag{12}$$

$$\kappa_{\mathrm{s}}^{\mathrm{id}} = \kappa_T^{\mathrm{id}} - \frac{T V_{\mathrm{m}}^{\mathrm{id}} (\alpha_{\mathrm{p}}^{\mathrm{id}})^2}{C_{\mathrm{p,m}}^{\mathrm{id}}} \tag{13}$$

$$C_{\mathrm{v,m}}^{\mathrm{id}} = C_{\mathrm{p,m}}^{\mathrm{id}} \frac{\kappa_{\mathrm{s}}^{\mathrm{id}}}{\kappa_T^{\mathrm{id}}} \tag{14}$$

$$\phi_1 = x_1 V_{\mathrm{m},1}^{*} / V_{\mathrm{m}}^{\mathrm{id}} \tag{15}$$

where ϕ_1 is the volume fraction of component 1 and the superscript * denotes properties of the pure components. The isothermal pressure derivatives of the excess molar enthalpy $(\partial H_{\mathrm{m}}^{\mathrm{E}}/\partial p)_T$ were obtained from the excess molar volumes, using the following equation:

$$(\partial H_{\mathrm{m}}^{\mathrm{E}}/\partial p)_T = V_{\mathrm{m}}^{\mathrm{E}} - T(\partial V_{\mathrm{m}}^{\mathrm{E}}/\partial T)_{\mathrm{p}} \tag{16}$$

$C_{\mathrm{p,m}}^{\mathrm{E}}$ splits into two contributions, an energy contribution $C_{\mathrm{v,m}}^{\mathrm{E}}$ and a volume contribution $[T V_{\mathrm{m}} \alpha_{\mathrm{p}}^2 \kappa_T^{-1}]$:

$$C_{\mathrm{p,m}}^{\mathrm{E}} = C_{\mathrm{v,m}}^{\mathrm{E}} + \left[\frac{T V_{\mathrm{m}} \alpha_{\mathrm{p}}^2}{\kappa_T}\right]^{\mathrm{E}} \tag{17}$$

Results for all the excess quantities are plotted in Figs. 2–6. The solid lines in these figures correspond to the fitted values where Redlich–Kister polynomials were used:

$$Y_{\mathrm{m}}^{\mathrm{E}} = x_1(1 - x_1) \sum_{i=0}^{n} A_i (2x_1 - 1)^i \tag{18}$$

Table VI. Thermodynamic Properties of the Pure Liquids at Temperature T

Liquid	T (K)	ρ $(\mathrm{g \cdot cm^{-3}})$		$C_{\mathrm{p,m}}$ $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$		α_{p} $(10^{-3}\,\mathrm{K^{-1}})$		κ_T $(\mathrm{TPa^{-1}})$	κ_{s} $(\mathrm{TPa^{-1}})$	
		This work	Ref. 15	This work	Ref. 12	This work	Ref. 15	This work	This work	Ref. 15
Nitromethane	288.15	1.14334		105.99	105.68				473.37	
	293.15	1.13651	1.13816	106.30	105.98				490.50	
	298.15	1.12965	1.13128	106.62	106.31	1.208	1.217	729.2	508.55	
	308.15	1.11604		107.33	107.04				547.23	
2-Butanol	288.15	0.81055		186.97	186.38				794.22	
	293.15	0.80658	0.80652	192.05	191.53				821.75	
	298.15	0.80240	0.80241	197.10	196.81	1.037	1.024	1000.5	850.62	
	308.15	0.79392		207.76	207.57				912.54	
Isobutanol	288.15	0.80553		173.22	172.84				833.28	
	293.15	0.80172	0.8016	177.31	176.78				861.18	
	298.15	0.79788	0.7978	181.40	180.94	0.969	0.953	1032.5	890.07	
	308.15	0.79007		190.50	189.80				950.87	950

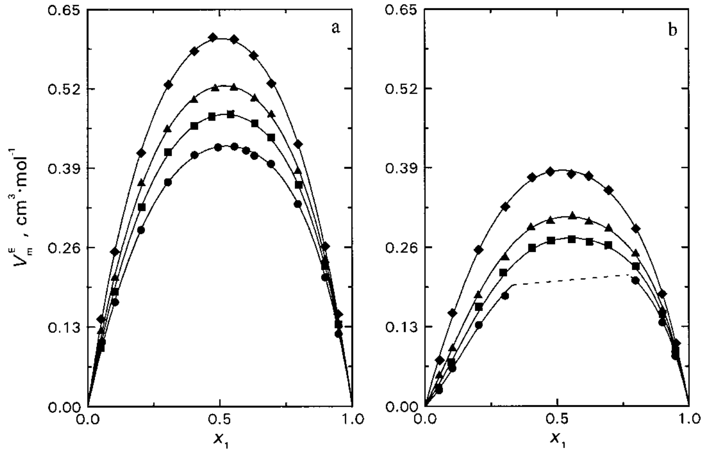

Fig. 2. Excess molar volumes V^E_m for (a) nitromethane (1) + 2-butanol (2) and (b) nitromethane (1) + isobutanol (2) at the temperatures (●) 288.15 K, (■) 293.15 K, (▲) 298.15 K, and (◆) 308.15 K. (——) Fitted values from Eqs. (18) and (2). (- - -) Data in the two-phase region.

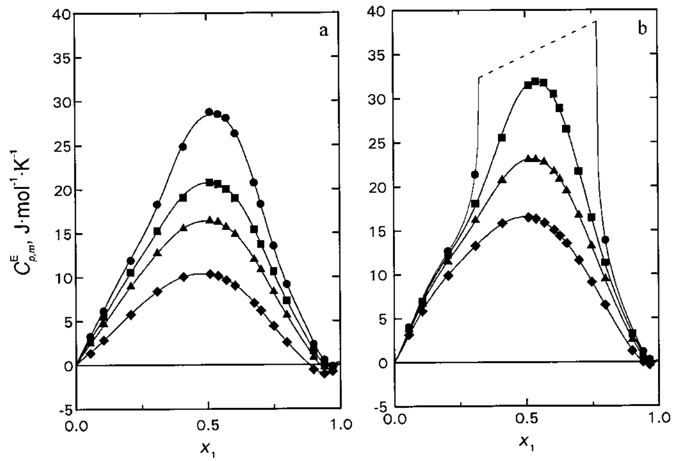

Fig. 3. Excess isobaric molar heat capacities $C^E_{p,m}$ for (a) nitromethane (1) + 2-butanol (2) and (b) nitromethane (1) + isobutanol (2) at the temperatures (●) 288.15 K, (■) 293.15 K, (▲) 298.15 K, and (◆) 308.15 K. (——) Fitted values from Eqs. (18) and (3). (- - -) Data in the two-phase region.

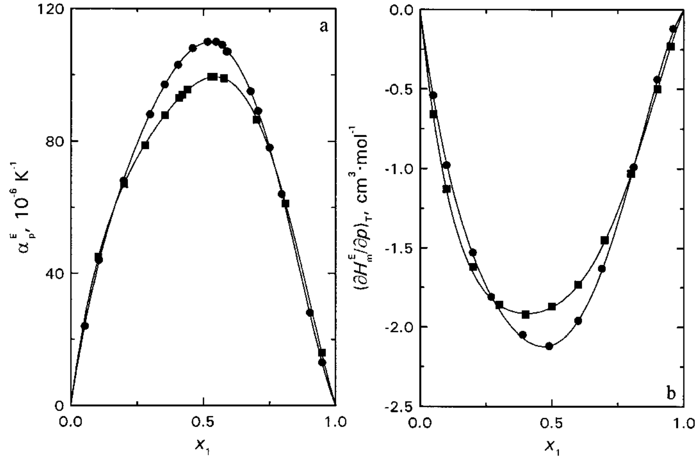

Fig. 4. (a) Excess isobaric thermal expansivities for (●) nitromethane (1) + 2-butanol (2) and (■) nitromethane (1) + isobutanol (2) at 298.15 K. (b) Isothermal partial derivatives of the excess molar enthalpy $(\partial H_{\mathrm{m}}^{\mathrm{E}}/\partial p)_T$ for (●) nitromethane (1) + 2-butanol (2) and (■) nitromethane (1) + isobutanol (2) at 298.15 K. (——) Fitted values from Eq. (18).

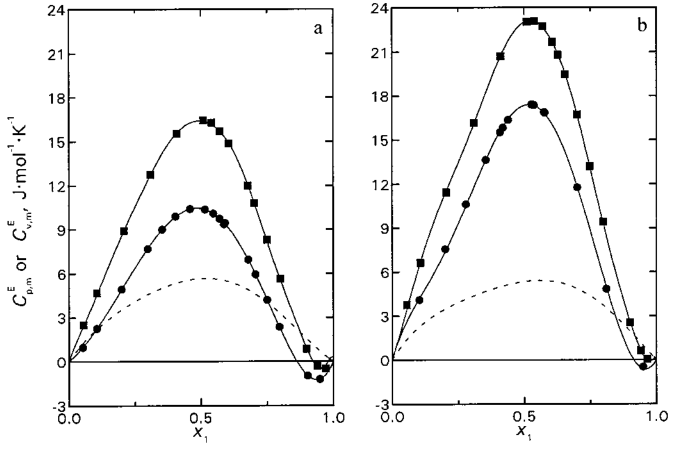

Fig. 5. Excess molar heat capacities, (●) isobaric $C_{\mathrm{p,m}}^{\mathrm{E}}$ or (■) isochoric $C_{\mathrm{v,m}}^{\mathrm{E}}$, for (a) nitromethane (1) + 2-butanol (2) and (b) nitromethane (1) + isobutanol (2) at 298.15 K. (——) Fitted values from Eqs. (18) and (2). (- - -) $C_{\mathrm{p,m}}^{\mathrm{E}} - C_{\mathrm{v,m}}^{\mathrm{E}}$.

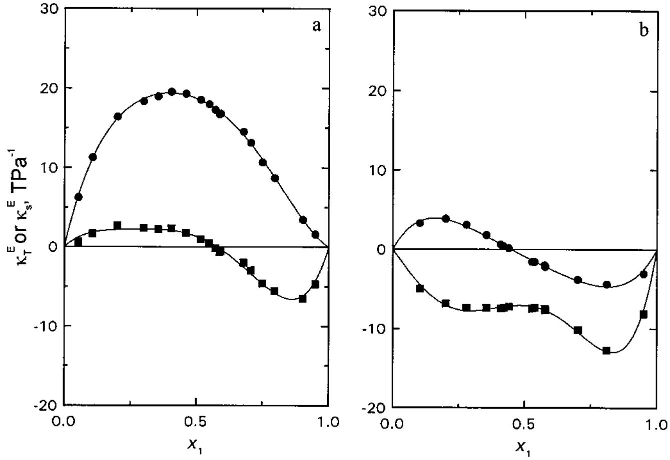

Fig. 6. Excess compressibilities, (●) isothermal κ_T^E or (■) isentropic κ_s^E, for (a) nitromethane (1) + 2-butanol (2) and (b) nitromethane (1) + isobutanol (2) at 298.15 K. (——) Fitted values from Eq. (18).

V_m^E and $C_{p,m}^E$ were fitted against x_1 and T simultaneously, taking coefficients A_i from Eqs. (2) and (3), respectively; the resulting A_{ij} together with the standard deviations are given in Table IV. On the other hand, the rest of the excess properties were fitted with A_i as temperature independent, and their final values together with the standard deviations are listed in Table VII.

Table VII. Fitting Coeficients A_i of Eq. (18) and Standard Deviations σ

	A_1	A_2	A_3	A_4	A_5	σ
			Nitromethane + 2-butanol			
α_p^E (10^6 K^{-1})	438.2	45.3	−75.1	−206.9		0.3
κ_s^E (TPa^{-1})	5.2	−24.5	−46.7	−48.3		0.4
κ_T^E (TPa^{-1})	74.9	−27.2	7.5	−35.0		0.2
$C_{v,m}^E$ (J · mol^{-1} · K^{-1})	41.7	−5.6	−53.3	−23.8	−2.8	0.03
			Nitromethane + isobutanol			
α_p^E (10^6 K^{-1})	394.3	69.3	44.4	−230.6		0.3
κ_s^E (TPa^{-1})	−28.3	−4.5	−93.3	−70.5		0.3
κ_T^E (TPa^{-1})	−3.6	−34.0	2.0	−27.7		0.3
$C_{v,m}^E$ (J · mol^{-1} · K^{-1})	69.4	12.1	−94.4	−59.0	40.1	0.1

3.2. Excess Quantities: Effect of Molecular Structure

Figure 1 shows the T^*x_1 curves of the systems in this study together with that of the nitromethane + 1-butanol system [5]. As can be seen, the transition temperatures are similar for the systems containing the primary alkanols—i.e., 1-butanol and isobutanol—whereas they are a few degrees lower for that containing 2-butanol. This indicates that T^* is more significantly affected by the position of the hydroxyl than by the structure of the alkyl chain of the alkanol. The weaker self-association of the secondary alkanols [17–19], which tends to favor mixing, can explain the results.

Figures 2–6 show the excess quantities for both systems, and they can serve for comparison. Also, the variation of the excess quantities among isomers is listed in Table VIII, where equimolar values for the systems of this study together with literature data of the nitromethane + 1-butanol system are given.

The excess molar volumes, shown in Fig. 2, are positive over the complete composition range, and they increase with temperature for both systems. The dashed line for the nitromethane + isobutanol system represents data in the two-phase region, i.e., at 288.15 K, and it is obtained from the V_m^E at the equilibrium compositions at that temperature. The rupture of the structure of the pure liquids—primarily dispersion interactions and hydrogen bonds in the alkanols—can explain the positive values. Also, the V_m^E's are significantly higher for the mixture containing 2-butanol, a fact which can be understood since hydrogen bonds in 2-butanol are more easily broken by nitromethane molecules. This can also be seen in Table VIII, where the V_m^E of the mixture containing 2-butanol is substantially higher than that of the mixtures containing primary alkanols.

Figure 3 shows the excess isobaric molar heat capacities; again, the dashed line represents data in the two-phase region. As can be observed, high positive values are found except in the nitromethane-rich region, where $C_{p,m}^E$ is small and negative. Both the composition and the temperature dependence of $C_{p,m}^E$ reflect the nonrandomness of the mixtures near the UCP, where this quantity tends to increase in a dramatic manner. Far away from the critical point, $C_{p,m}^E$ is positive, a situation which is commonly observed when hydrogen bonds are formed in the mixture. The fact that the increase in $C_{p,m}^E$ is more dramatic for the mixture containing isobutanol is ascribed to the greater proximity to its critical temperature to the working range for this system. The last conclusion can also be reached from Table VIII.

The excess isobaric thermal expansivities as well as the isothermal pressure derivatives of the excess molar enthalpy are plotted in Fig. 4.

Table VIII. Excess Quantities of Equimolar Mixtures Containing Nitromethane and a Butanol Isomer at 298.15 K

	Excess quantity						
Butanol isomer	$V_{\mathrm{m}}^{\mathrm{E}}$ $(\mathrm{cm}^3\cdot\mathrm{mol}^{-1})$	$\alpha_{\mathrm{p}}^{\mathrm{E}}$ $(10^{-6}\,\mathrm{K}^{-1})$	$\kappa_{\mathrm{s}}^{\mathrm{E}}$ (TPa^{-1})	κ_{T}^{E} (TPa^{-1})	$C_{\mathrm{p,m}}^{\mathrm{E}}$ $(\mathrm{J}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1})$	$C_{\mathrm{v,m}}^{\mathrm{E}}$ $(\mathrm{J}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1})$	$(\partial H_{\mathrm{m}}^{\mathrm{E}}/\partial p)_T$ $(\mathrm{cm}^3\cdot\mathrm{mol}^{-1})$
1-Butanol	0.342	88.3	8.5	13.3	21.00	16.2	−1.6
2-Butanol	0.524	109.5	1.3	18.7	16.39	10.4	−2.1
Isobutanol	0.308	98.6	−7.1	−0.9	23.03	17.4	−1.9

α_p^E is positive over the complete composition range, and it varies in the sequence 1-butanol < isobutanol < 2-butanol. A positive α_p^E can be due, in part, to the fact that, during the mixing process, hydrogen bonds are more easily broken at higher temperatures. Since the behavior of $(\partial H_m^E/\partial p)_T$ is dependent mainly on $(\partial V_m^E/\partial T)_p$, negative values are attained for the former property. Figure 5 compares $C_{p,m}^E$ and $C_{v,m}^E$, where it can be observed that $C_{p,m}^E$ is larger than $C_{v,m}^E$ for both mixtures. Since singular curves against composition are observed for $C_{v,m}^E$, this quantity also seems to give a measure of the nonrandomness of the mixtures. Finally, the excess compressibilities are shown in Fig. 6, where small values are encountered. The κ_T^E's are higher than the κ_s^E's for both systems; however, no systematic behavior is observed for the different isomers.

4. CONCLUSION

The thermodynamic study of this work reveals that excess heat capacities are the most sensitive quantities to the nonrandomness of the molecular distribution for nitromethane + (alkanol isomer) mixtures near the UCP. The behavior of $C_{p,m}^E$ is closely related to the proximity of phase separation, and, thus, the differences among isomers are justified since phase separation temperatures are higher for the primary alkanols. As a rule, the weaker association of 2-butanol explains the fact that excess volumetric properties, i.e., V_m^E, α_p^E, or κ_T^E, tend to attain higher values for the secondary alkanol than for the primary ones. In that sense, the proximity of phase separation, and thus nonrandomness, does not seem to be as relevant as in the case of excess heat capacities.

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REFERENCES

1. J. S. Rowlinson and F. L. Swinton, *Liquids and Liquid Mixtures*, 3rd ed. (Butterworths, Norwich, 1982).
2. M.-E. Saint-Victor and D. Patterson, *Fluid Phase Equil.* **35**:237 (1987).
3. L. M. Trejo, M. Costas, and D. Patterson, *J. Chem. Soc. Faraday Trans.* **87**:3001 (1991).
4. C. A. Tovar, E. Carballo, C. A. Cerdeiriña, M. I. Paz Andrade, and L. Romaní, *J. Chem. Soc. Faraday Trans.* **93**:3505 (1997).
5. C. A. Cerdeiriña, C. A. Tovar, D. González, E. Carballo, and L. Romaní, *Fluid Phase Equilib.*, in press.

6. C. A. Tovar, C. A. Cerdeiriña, D. González, E. Carballo, and L. Romaní, *Fluid Phase Equil.* **169**:209 (2000).
7. C. A. Cerdeiriña, C. A. Tovar, J. Troncoso, E. Carballo, and L. Romaní, *Fluid Phase Equil.* **157**:93 (1999).
8. N. Bilaniuk and G. S. K. Wong, *J. Acoust. Soc. Am.* **93**:1609 (1993).
9. J. Troncoso, E. Carballo, C. A. Cerdeiriña, D. González, and L. Romaní, *J. Chem. Eng. Data* **45**:594 (2000).
10. C. A. Tovar, E. Carballo, C. A. Cerdeiriña, J. L. Legido, and L. Romaní, *Int. J. Thermophys.* **18**:761 (1997).
11. C. A. Cerdeiriña, J. A. Míguez, E. Carballo, C. A. Tovar, E. de la Puente, and L. Romaní, *Thermochim. Acta* **347**:37 (2000).
12. M. Zabransky, V. Ruzicka, V. Mayer, and E. S. Domalski, *J. Phys. Chem. Ref. Data (Monograph No. 6), Heat Capacities of Liquids, Critical Review and Recommended Values* (1996).
13. A. Kumar, H. R. Krishnamurthy, and E. S. R. Gopal, *Phys. Rep.* **98**:57 (1983).
14. D. W. Marquardt, *J. Soc. Ind. Appl. Math.* **11**:431 (1963).
15. J. A. Riddick, W. B. Bunger, and T. Sakano, *Organic Solvents. Physical Properties and Methods of Purification, Vol. II* (Wiley, New York, 1986).
16. G. C. Benson and O. Kiyohara, *J. Chem. Thermodyn.* **11**:1061 (1979).
17. M. Cáceres-Alonso, M. Costas, L. Andreolli-Ball, and D. Patterson, *Can. J. Chem.* **66**:989 (1988).
18. M. Bures, M. Zabransky, and V. Svoboda, *Thermochim. Acta* **245**:145 (1994).
19. R. Tanaka and S. Toyama, *J. Chem. Thermodyn.* **28**:1403 (1996).