Vapor Pressures at Several Temperatures and Excess Functions at 298.15 K of Butanone with Di-*n*-propyl Ether or Diisopropyl Ether

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Vapor pressures of butanone + di-*n*-propyl ether (*n*-propyl ether) or + diisopropyl ether (isopropyl ether) were measured at seven temperatures between 288.15 K and 323.15 K by a static method. Excess molar enthalpies and volumes were also measured at $T = 298.15$ K. Reduction of the vapor pressures to obtain activity coefficients and excess molar Gibbs free energies was carried out by fitting the vapor pressure data to the Redlich−Kister correlation according to Barker's method. Azeotropic mixtures with a minimum boiling temperature were observed over the whole temperature range. The apparent excess enthalpy and volume due to the specific interaction between unlike molecules were calculated.

Introduction

In recent publications (Garriga et al., 1996a−d, 1997a−c, 1998a−c), we present excess thermodynamic properties for mixtures (an alkanol + butanone or *n*-propyl ether). As an extension of these studies we report here vapor pressures at seven temperatures between 288.15 K and 323.15 K of butanone + *n*-propyl ether or isopropyl ether, as well as excess enthalpies and volumes at $T = 298.15$ K. Binary mixtures (ketone + ether) have received little experimental attention, and previous measurements of these properties for these mixtures were not found in the literature.

Experimental Section

Butanone (mole fraction > 0.995) and isopropyl ether (mole fraction > 0.990) were Fluka products, and *n*-propyl ether (mole fraction > 0.990) was from Aldrich. The chemicals were stored over molecular sieve (3 Å) and were used for the experiments without further purification.

The vapor pressure measurements were performed by a static method. The apparatus is similar to that of Marsh (1968), except for experimental details which are described elsewhere (Pardo et al.,1987; Gracia et al., 1992). To prevent condensation effects on the mercury meniscus, the temperature of the manometer was maintained at 325.0 K by circulating water thermostated to within ±0.1 K. Most of the vapor phase was also maintained at 325.0 K. The cell containing the liquid mixture was built of a Young valve (POR/LN/6 type) with a glass plunger consisting of a combination of toric joints of polytetrafluoroethylene (PTFE) and viton. An inner Teflon-covered iron piece was used for magnetic stirring. The cell volume was about 12 cm^3, and 8−10 cm^3 were used in each experiment. The liquids were first degassed under their own vapor pressure. They were added successively, by gravity, into the cell immersed in liquid nitrogen. The masses of both components were determined by weighing. Uncertainties in the mole fractions are estimated to be less than 0.0003. Manometric readings were performed with a cathetometer to within ±0.01 mm, and pressure reproducibility was estimated to be better than 15 Pa. The temperature of the liquid was controlled to within ±10 mK.

Excess enthalpies were measured with a calorimeter which is an original design working at constant pressure and in the absence of vapor phase (Gutiérrez Losa and Gracia, 1971). A densimeter (Anton Paar DMA 60/DMA 602) was used for density measurements on the pure liquids and mixtures. The precision of the excess enthalpy determinations is estimated to be about 1% of the maximum value of H^E, and the accuracy for V^E is 0.002 $cm^3 \cdot mol^{-1}$.

Results

Table 1 shows the molar volumes of the pure compounds used in the Barker analysis together with the experimental vapor pressures which are compared with values calculated from equations found in the literature. Experimental vapor pressures of isopropyl ether at 10 temperatures between 278.15 K and 323.15 K (Table 1) were fitted to an Antoine equation

isopropyl ether:

$$\ln(P/\text{kPa}) = 13.504452 - \frac{2502.117}{(T/\text{K}) - 60.180} \qquad (1)$$

Vapor pressures obtained from eq 1 show a standard deviation of 9 Pa and a maximum deviation of +19 Pa at $T = 298.15$ K. For butanone and *n*-propyl ether the experimental vapor pressures were fitted previously (Garriga et al., 1996b, 1997a).

The second virial coefficient, at $T = 325.0$ K, of *n*-propyl ether ($B_{BB} = -2000$ $cm^3 \cdot mol^{-1}$) was calculated from the Tsonopoulos (1974) correlation with critical constants and the acentric factor taken from Reid et al. (1987) and the dipole moment from McClelland (1963), and those of butanone ($B_{AA} = -1840$ $cm^3 \cdot mol^{-1}$) and isopropyl ether ($B_{BB} = -1630$ $cm^3 \cdot mol^{-1}$) were obtained from Dymond and Smith (1980). The mixed virial coefficient was calculated according to a cubic combination rule

$$B_{AB} = {}^1/_8(B_{AA}{}^{1/3} + B_{BB}{}^{1/3})^3 \qquad (2)$$

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Table 1. Molar Volumes V° and Vapor Pressures P° of the Pure Compounds Used in Barker Analysis

	butanone			*n*-propyl ether			isopropyl ether		
	V° [a]/	P°/kPa		V° [b]/	P°/kPa		V° [b]/	P°/kPa	
T/K	($cm^3 \cdot mol^{-1}$)	*b*	*c*	($cm^3 \cdot mol^{-1}$)	*b*	*d*	($cm^3 \cdot mol^{-1}$)	*b*	*d*
278.15		4.277	4.278		2.878	2.879		7.573	7.612
283.15		5.644	5.638		3.826	3.822		9.803	9.831
288.15	88.99	7.334	7.342	135.86	5.006	5.012	140.15	12.531	12.559
293.15	89.56	9.435	9.459	136.77	6.493	6.498	141.12	15.851	15.880
298.15	90.14	12.071	12.060	137.68	8.331	8.334	142.25	19.905	19.887
303.15	90.72	15.281	15.231	138.58	10.596	10.580	143.29	24.695	24.682
308.15	91.32	19.110	19.060	139.53	13.346	13.306	144.36	30.379	30.374
313.15	91.93	23.683	23.649	140.51	16.639	16.585	145.49	37.086	37.081
318.15		29.132	29.106		20.558	20.499		44.933	44.929
323.15	93.19	35.540	35.548	142.28	25.145	25.136	147.77	54.041	54.051

[a] TRC (1991). [b] This work. [c] Ambrose et al. (1975). [d] Ambrose et al. (1976).

Table 2 presents our vapor pressure measurements together with the activity coefficients γ_A and γ_B, and the excess molar Gibbs free energy G^E values fitted by Barker's method (Barker, 1953) with a Redlich−Kister polynomial. The activity coefficients are given by

$$\ln \gamma_A = x_B^2[A_0 + \sum_{j=1}^{m}\{A_j(x_B - x_A)^j - 2jA_j x_A(x_B - x_A)^{j-1}\}] \quad (3)$$

$$\ln \gamma_B = x_A^2[A_0 + \sum_{j=1}^{m}\{A_j(x_B - x_A)^j + 2jA_j x_B(x_B - x_A)^{j-1}\}] \quad (4)$$

where the subscripts A and B stand for butanone and ether, respectively. The vapor pressure is then given by

$$P_{calc} = x_A\gamma_A P_A^\circ R_A + x_B\gamma_B P_B^\circ R_B \quad (5)$$

where the corrections for nonideality of the vapor-phase are given by

$$R_A = \exp\{[(V_A^\circ - B_{AA})(P - P_A^\circ) - P\delta_{AB}y_B^2]/RT\} \quad (6)$$

$$R_B = \exp\{[(V_B^\circ - B_{BB})(P - P_B^\circ) - P\delta_{AB}y_A^2]/RT\} \quad (7)$$

where y_A and y_B are the vapor-phase mole fractions of ketone and ether, respectively, and δ_{AB} is given by

$$\delta_{AB} = 2B_{AB} - B_{AA} - B_{BB} \quad (8)$$

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 due to an enrichment of the vapor phase in the most volatile component. In Figure 1, vapor pressure−liquid composition curves are plotted. In Table 3, the Redlich−Kister parameters are given, together with the standard deviations defined by

$$\sigma(P) = [\sum_{j=1}^{N}(\Delta P)_j^2/(N - m)]^{1/2} \quad (9)$$

are shown; 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.

Experimental excess molar enthalpies and volumes, at 298.15 K, are given in Table 4. A polinomial has been fitted to the results

$$Q^E = x_A x_B \sum_{j=0}^{m} A_j(x_B - x_A)^j \quad (10)$$

where Q^E denotes H^E or V^E and x_A and x_B the mole fractions of butanone and ether, respectively. Table 5 presents the A_j coefficients along with the standard deviations.

In the absence of independent values of the activity coefficients we cannot use the Gibbs−Duhem relation to test the thermodynamic consistency of the vapor pressure measurements. We can, however, test the consistency of the enthalpies and free energies by means of the Gibbs−Helmholtz equation. By fitting the Redlich−Kister coefficients which appear in Table 3 to a linear function of the temperature, the H^E-calculated values according to the Gibbs−Helmholtz equation are shown as curves in Figure 2, together with the H^E-experimental data, at $T = 298.15$ K. The Gibbs−Helmholtz curves are favorably compared with the experimental behavior as the quantitative evaluation of excess enthalpies from pressures involves considerable uncertatinty (Rowlinson and Swinton, 1982). In the same figure and at the same temperature, TS^E (calculated from $TS^E = H^E - G^E$) and G^E-curves are also plotted. V^E-experimental values and analytical equations are shown in Figure 3.

Azeotropic mixtures with a minimum boiling temperature were observed over the whole range of temperature. Azeotropic mole fractions z were graphically calculated, assuming ideal behavior of the vapor, from the well-known equation, $\gamma_B/\gamma_A = P_A^\circ/P_B^\circ$. Azeotropic compositions show a linear relation with the temperature according to the equation

$$z = a + b(T/K) \quad (11)$$

For butanone + *n*-propyl ether $a = 0.5508$ and $b = 0.674 \times 10^{-3}$ K^{-1}, and for butanone + isopropyl ether $a = -0.1910$ and $b = 1.116 \times 10^{-3}$ K^{-1}.

Along the azeotropic line, assuming both ideal behavior of the vapor phase and negligible volume of the liquid phase, the Clapeyron−Clausius equation

$$d \ln P_z/dT = \Delta_{vap}H_z/RT^2 \quad (12)$$

is satisfied. If we accept that the enthalpy of azeotropic vaporization is constant, the azeotropic pressure is related with the temperature in a way similar to that shown by a

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

x_A	P/kPa	ΔP/Pa	γ_A	γ_B	G^E/(J·mol^{-1})	x_A	P/kPa	ΔP/Pa	γ_A	γ_B	G^E/(J·mol^{-1})
Butanone(A) + *n*-Propyl Ether (B)											
288.15 K											
0.0951	5.941	17	1.9395	1.0089	170	0.6490	7.674	21	1.0941	1.3901	417
0.2316	6.694	−26	1.5769	1.0501	343	0.7277	7.685	−2	1.0559	1.5034	361
0.2912	6.954	−1	1.4640	1.0781	394	0.7862	7.661	−20	1.0344	1.6031	305
0.4274	7.341	4	1.2738	1.1653	458	0.8670	7.615	−4	1.0134	1.7680	209
0.4707	7.433	9	1.2283	1.2003	463	0.9288	7.519	0	1.0039	1.9211	120
0.5809	7.591	2	1.1366	1.3080	448						
293.15 K											
0.0950	7.667	27	1.9068	1.0086	168	0.6489	9.847	12	1.0908	1.3790	412
0.2314	8.597	−49	1.5591	1.0487	340	0.7277	9.882	3	1.0538	1.4880	357
0.2909	8.951	8	1.4501	1.0758	390	0.7862	9.837	−35	1.0330	1.5833	302
0.4271	9.431	1	1.2656	1.1607	453	0.8670	9.791	−5	1.0128	1.7398	206
0.4705	9.557	14	1.2213	1.1949	459	0.9288	9.678	5	1.0037	1.8836	118
0.5808	9.775	21	1.1321	1.2996	443						
298.15 K											
0.0948	9.797	19	1.8920	1.0089	170	0.6488	12.506	−43	1.0905	1.3672	412
0.2311	10.986	−47	1.5428	1.0493	340	0.7277	12.616	8	1.0544	1.4726	357
0.2906	11.420	14	1.4361	1.0762	390	0.7863	12.610	6	1.0337	1.5661	302
0.4268	12.051	27	1.2581	1.1585	452	0.8671	12.506	−7	1.0133	1.7228	208
0.4704	12.192	23	1.2155	1.1913	457	0.9288	12.374	14	1.0039	1.8706	119
0.5807	12.438	−5	1.1302	1.2912	442						
303.15 K											
0.0947	12.420	46	1.8560	1.0085	167	0.6489	15.911	−7	1.0925	1.3537	413
0.2308	13.895	−54	1.5274	1.0470	335	0.7277	16.021	20	1.0563	1.4585	359
0.2902	14.388	−38	1.4265	1.0725	385	0.7862	15.999	−2	1.0353	1.5528	306
0.4269	15.281	54	1.2560	1.1512	449	0.8670	15.887	−6	1.0141	1.7139	211
0.4704	15.460	44	1.2151	1.1827	455	0.9288	15.675	−24	1.0042	1.8691	122
0.5806	15.737	−37	1.1320	1.2791	442						
308.15 K											
0.0944	15.500	22	1.8213	1.0073	162	0.6488	19.904	13	1.0877	1.3527	412
0.2309	17.448	−14	1.5228	1.0428	331	0.7277	19.989	6	1.0519	1.4567	357
0.2905	18.041	−24	1.4252	1.0674	382	0.7863	19.972	−3	1.0317	1.5473	302
0.4264	19.052	−6	1.2554	1.1457	448	0.8671	19.810	−20	1.0122	1.6946	206
0.4702	19.302	13	1.2131	1.1780	455	0.9288	19.577	−16	1.0035	1.8282	118
0.5807	19.744	19	1.1276	1.2772	441						
313.15 K											
0.0946	19.366	46	1.8260	1.0093	170	0.6487	24.651	34	1.0914	1.3299	408
0.2307	21.582	−48	1.4930	1.0488	336	0.7276	24.795	38	1.0572	1.4268	358
0.2901	22.313	−21	1.3964	1.0738	384	0.7862	24.739	−25	1.0367	1.5169	306
0.4261	23.529	−6	1.2399	1.1469	443	0.8672	24.610	0	1.0151	1.6777	213
0.4699	23.857	30	1.2027	1.1756	449	0.9289	24.255	−62	1.0046	1.8397	124
0.5805	24.382	−8	1.1275	1.2625	436						
323.15 K											
0.0939	28.915	−3	1.7721	1.0083	164	0.6485	36.862	45	1.0896	1.3141	408
0.2298	32.340	19	1.4726	1.0444	329	0.7275	37.064	37	1.0559	1.4085	357
0.2889	33.355	−15	1.3835	1.0674	377	0.7863	36.986	−52	1.0357	1.4962	305
0.4249	35.162	−17	1.2351	1.1364	439	0.8675	36.813	4	1.0146	1.6516	212
0.4693	35.634	8	1.1987	1.1643	445	0.9290	36.374	−4	1.0044	1.8059	124
0.5801	36.446	−28	1.1252	1.2484	434						
Butanone(A) + Isopropyl Ether (B)											
288.15 K											
0.0511	12.680	24	1.9570	1.0024	88	0.5784	11.496	−9	1.1290	1.2700	410
0.1115	12.686	−29	1.7757	1.0110	177	0.6569	11.071	16	1.0848	1.3545	378
0.1956	12.704	20	1.5796	1.0326	276	0.7601	10.295	−7	1.0418	1.4948	306
0.2903	12.536	1	1.4155	1.0695	356	0.8226	9.739	9	1.0232	1.6008	245
0.3467	12.400	0	1.3386	1.0978	388	0.9292	8.454	−8	1.0038	1.8328	111
0.4637	12.008	−12	1.2152	1.1724	421						
293.15 K											
0.0511	15.977	−18	1.9030	1.0020	85	0.5788	14.609	−8	1.1232	1.2678	408
0.1115	16.048	−21	1.7467	1.0097	172	0.6576	14.015	−39	1.0789	1.3530	374
0.1957	16.068	28	1.5684	1.0296	272	0.7607	13.100	−6	1.0373	1.4891	300
0.2902	15.828	−39	1.4117	1.0649	353	0.8230	12.402	18	1.0201	1.5869	239
0.3469	15.711	4	1.3354	1.0929	386	0.9294	10.800	0	1.0031	1.7867	107
0.4633	15.315	63	1.2114	1.1678	420						
298.15 K											
0.0511	20.116	5	1.9016	1.0022	87	0.5785	18.425	−7	1.1182	1.2640	405
0.1115	20.230	9	1.7383	1.0102	175	0.6568	17.764	31	1.0761	1.3449	371
0.1956	20.226	28	1.5560	1.0306	275	0.7604	16.532	−16	1.0360	1.4747	297
0.2904	19.970	−20	1.3986	1.0664	355	0.8234	15.655	9	1.0193	1.5686	236
0.3467	19.774	−20	1.3238	1.0942	387	0.9295	13.706	−7	1.0031	1.7584	106
0.4642	19.217	−4	1.2021	1.1684	419						
303.15 K											
0.0511	25.015	31	1.8907	1.0024	88	0.5789	22.985	−6	1.1197	1.2525	404
0.1115	25.155	13	1.7196	1.0108	176	0.6577	22.168	24	1.0790	1.3299	372
0.1956	25.181	47	1.5360	1.0316	275	0.7607	20.733	−10	1.0392	1.4577	301
0.2904	24.851	−38	1.3835	1.0667	353	0.8230	19.712	23	1.0219	1.5542	242
0.3469	24.595	−56	1.3124	1.0933	385	0.9294	17.340	−27	1.0036	1.7667	110
0.4646	23.970	19	1.1984	1.1631	416						
308.15 K											
0.0511	30.783	28	1.8801	1.0023	88	0.5793	28.451	2	1.1134	1.2549	404
0.1114	30.983	7	1.7143	1.0105	177	0.6590	27.380	−14	1.0730	1.3326	370
0.1957	31.000	3	1.5327	1.0311	277	0.7613	25.657	−17	1.0354	1.4544	297
0.2905	30.685	−43	1.3798	1.0664	356	0.8235	24.401	27	1.0194	1.5436	237
0.3471	30.440	−12	1.3078	1.0935	388	0.9296	21.548	−12	1.0031	1.7304	106
0.4656	29.656	46	1.1918	1.1651	418						
313.15 K											
0.0511	37.557	−7	1.8640	1.0023	89	0.5798	34.830	−23	1.1125	1.2494	404
0.1114	37.866	14	1.6997	1.0105	178	0.6595	33.588	−1	1.0729	1.3252	370
0.1957	37.945	46	1.5211	1.0309	277	0.7620	31.528	4	1.0356	1.4457	298
0.2907	37.565	−24	1.3714	1.0657	357	0.8237	30.023	40	1.0197	1.5340	238
0.3474	37.213	−46	1.3014	1.0922	388	0.9297	26.572	−42	1.0032	1.7233	107
0.4674	36.269	33	1.1876	1.1629	419						
323.15 K											
0.0510	54.737	65	1.7812	1.0019	84	0.5813	51.082	−57	1.1149	1.2350	407
0.1113	55.037	−41	1.6481	1.0088	170	0.6631	49.383	24	1.0738	1.3137	374
0.1957	55.102	−84	1.4968	1.0265	269	0.7635	46.503	−41	1.0365	1.4348	303
0.2911	54.875	55	1.3634	1.0577	349	0.8244	44.415	6	1.0203	1.5247	243
0.3482	54.393	5	1.2984	1.0823	383	0.9304	39.649	25	1.0033	1.7204	110
0.4697	53.070	66	1.1887	1.1504	418						

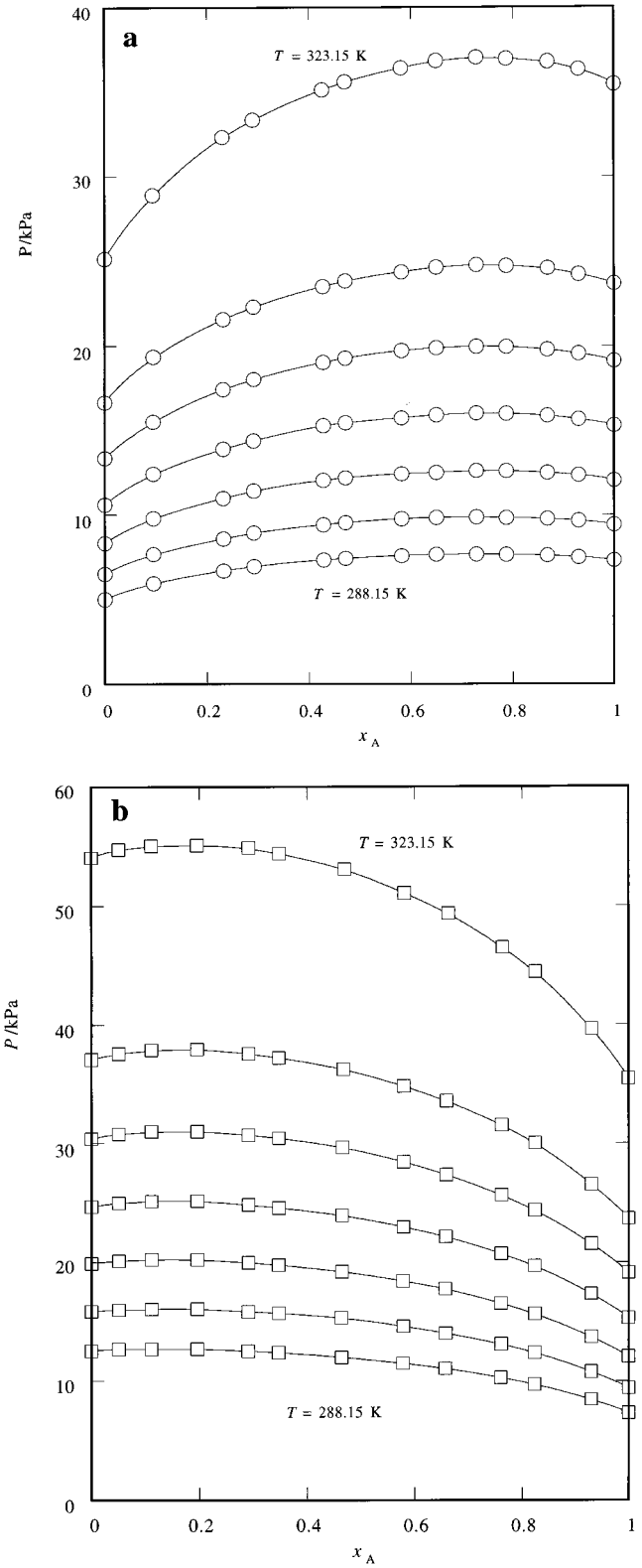

Figure 1. Vapor pressures at seven temperatures: (a) {x_A butanone + x_B *n*-propyl ether}; (b) {x_A butanone + x_B isopropyl ether}, plotted against the liquid-phase composition of butanone.

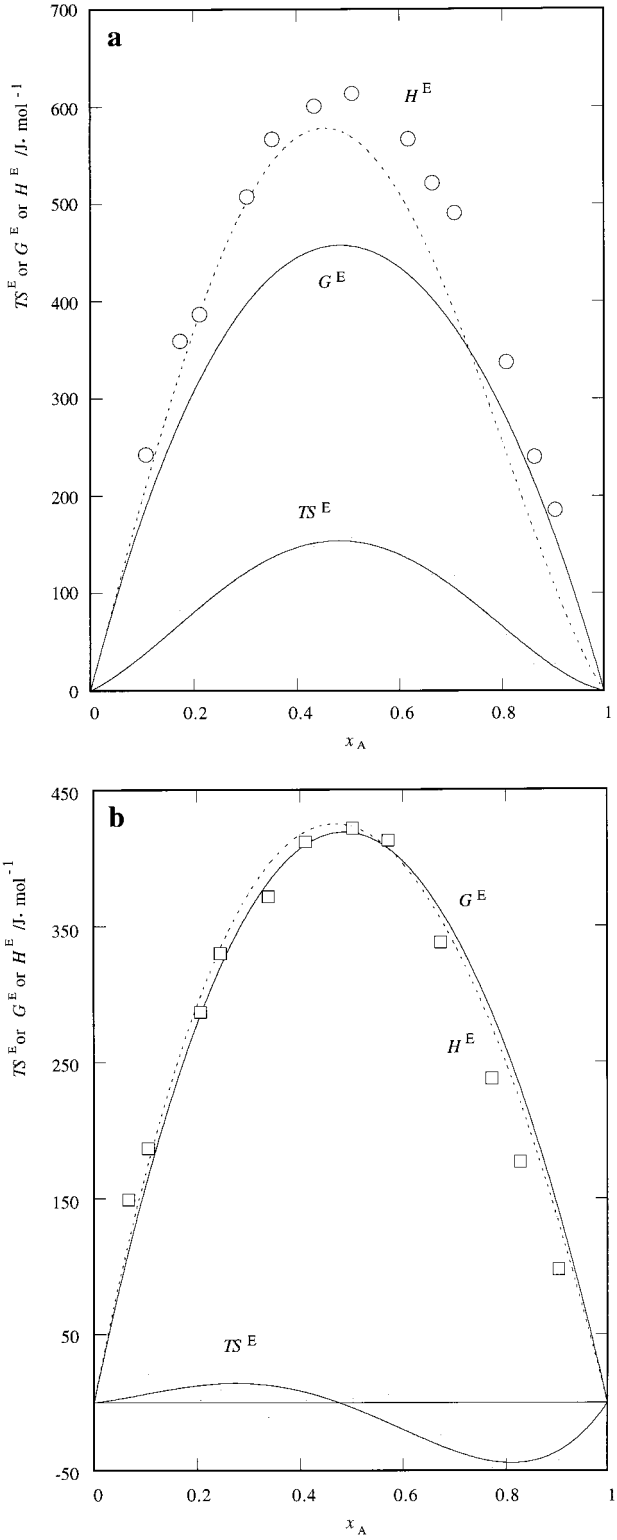

Figure 2. Thermal excess molar functions, at $T = 298.15$ K: (a) {x_A butanone + x_B *n*-propyl ether} (○) experimental H^E; (b) {x_A butanone + x_B isopropyl ether} (□) experimental H^E, (···) Gibbs–Helmholtz H^E, and (—) G^E and TS^E.

pure substance

$$\ln(P_z/\mathrm{Pa}) = A + B(T/\mathrm{K})^{-1} \qquad (13)$$

For butanone + *n*-propyl ether $A = 16.60$ and $B = -4194$ K, and for butanone + isopropyl ether $A = 16.21$ and $B = -3940$ K. Experimental and calculated (from eqs 11 and 13) azeotropic compositions and pressures are compared in Table 6 and plotted in Figure 4. From eqs 12 and 13, the molar enthalpy of azeotropic vaporization for the system containing *n*-propyl ether is $\Delta_{vap}H_z = 34.9$ kJ·mol^{-1}, and with isopropyl ether $\Delta_{vap}H_z = 32.8$ kJ·mol^{-1}. By using the azeotropic compositions together with the vaporization enthalpies for the pure compounds (Riddick et al., 1986), butanone ($\Delta_{vap}H_A° = 34.5$ kJ·mol^{-1}), *n*-propyl ether

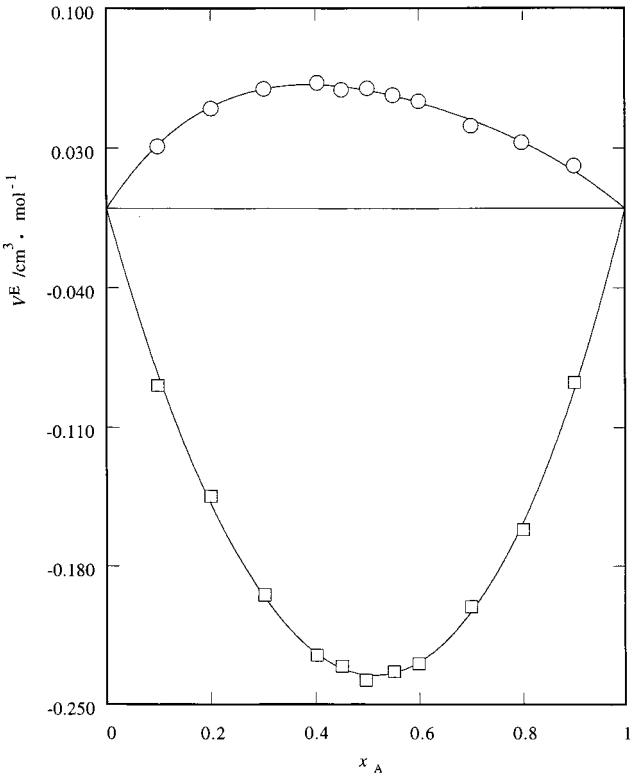

Figure 3. Excess molar volumes V^E, at $T = 298.15$ K: (○) {x_A butanone + x_B *n*-propyl ether}; (□) {x_A butanone + x_B isopropyl ether}.

Table 3. Parameters and Standard Deviations $\sigma(P)$, of Equations 3, 4, and 9

	butanone (A) + *n*-propyl ether (B)				butanone (A) + iso propyl ether (B)			
T/K	A_0	A_1	A_2	σ/Pa	A_0	A_1	A_2	σ/Pa
288.15	0.7738	0.0419	0.0264	14	0.7043	0.0263	0.0328	16
293.15	0.7534	0.0429	0.0231	23	0.6901	0.0279	0.0037	30
298.15	0.7380	0.0431	0.0382	25	0.6759	0.0390	0.0109	18
303.15	0.7228	0.0267	0.0434	37	0.6610	0.0289	0.0376	32
308.15	0.7115	0.0249	0.0117	16	0.6534	0.0421	0.0229	25
313.15	0.6904	0.0288	0.0747	36	0.6431	0.0385	0.0288	32
323.15	0.6643	0.0156	0.0644	28	0.6236	0.0079	0.0177	52

Table 4. Experimental Molar Excess Enthalpies and Volumes at 298.15 K

x_A	H^E/(J·mol^{-1})	x_A	H^E/(J·mol^{-1})	x_A	V^E/(cm^3·mol^{-1})	x_A	V^E/(cm^3·mol^{-1})
Butanone (A) + *n*-Propyl Ether (B)							
0.1069	243	0.6167	567	0.0982	0.031	0.5500	0.057
0.1729	360	0.6635	522	0.1999	0.050	0.5994	0.054
0.2109	387	0.7068	491	0.3004	0.060	0.7003	0.041
0.3025	508	0.8071	338	0.4032	0.063	0.7972	0.033
0.3517	567	0.8622	241	0.4503	0.060	0.8990	0.021
0.4333	601	0.9028	186	0.5004	0.060		
0.5071	614						
Butanone (A) + Isopropyl Ether (B)							
0.0673	149	0.5027	422	0.0984	−0.089	0.5514	−0.233
0.1052	187	0.5718	413	0.1999	−0.145	0.5991	−0.229
0.2062	287	0.6737	338	0.3017	−0.194	0.7003	−0.200
0.2452	330	0.7732	238	0.4021	−0.225	0.8000	−0.161
0.3382	372	0.8282	177	0.4510	−0.230	0.9000	−0.087
0.4109	412	0.9038	98	0.4971	−0.238		

($\Delta_{vap}H_B° = 35.7$ kJ·mol^{-1}), and isopropyl ether ($\Delta_{vap}H_B° = 32.0$ kJ·mol^{-1}), the equation

$$\Delta_{vap}H_z = z_A\Delta_{vap}H_A° + z_B\Delta_{vap}H_B° \qquad (14)$$

is satisfied.

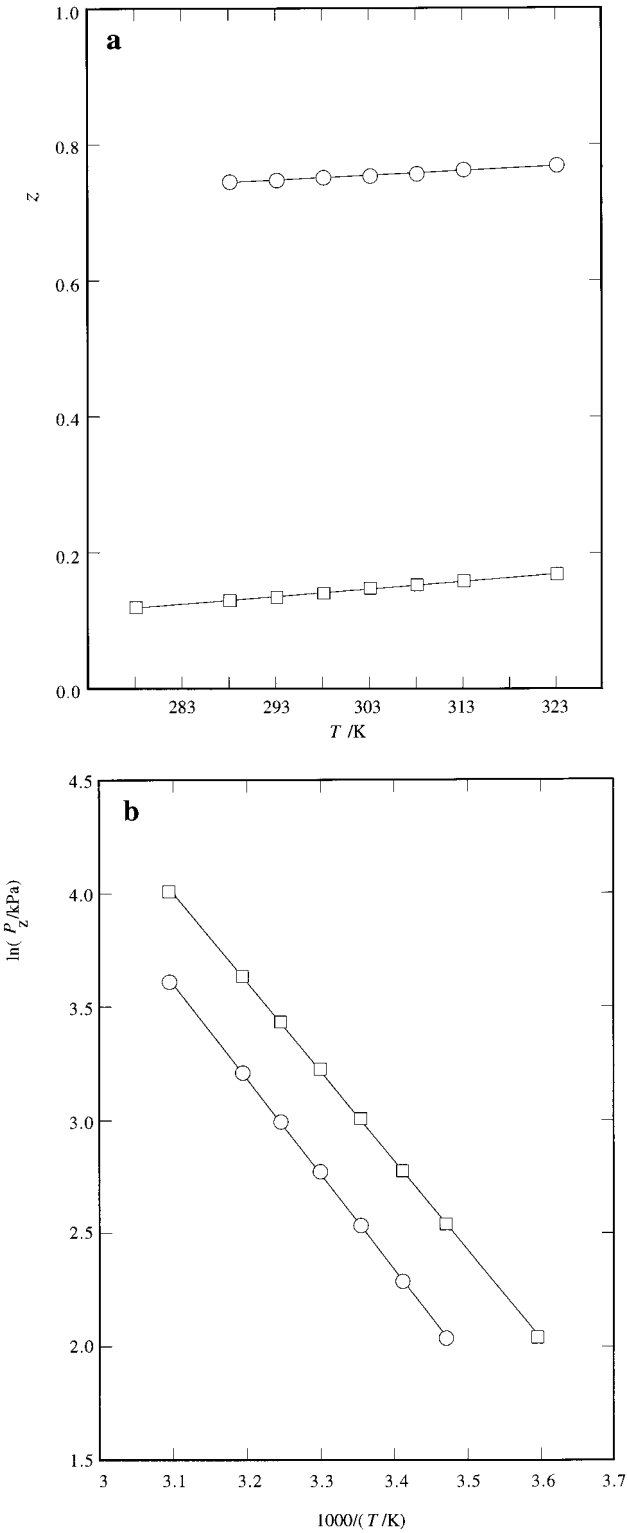

Figure 4. (a) Azeotropic mole fractions and (b) azeotropic vapor pressures for the following: (○) {x_A butanone + x_B *n*-propyl ether}; (□) {x_A butanone + x_B isopropyl ether}.

Since *n*-propyl ether is a strong polar solvent (dipole moment $\mu = 1.1 \times 10^{-29}$ C·m) (McClelland, 1963), strong solvent−solvent and oxygen (ether)−solvent interactions come into play. In mixtures of *n*-propyl ether with butanone, the excess molar enthalpies and volumes, at $T = 298.15$ K, are much lower than those for mixtures in which *n*-heptane takes the place of *n*-propyl ether.

The apparent contribution to the excess molar enthalpies and volumes due to the effect of the specific interaction

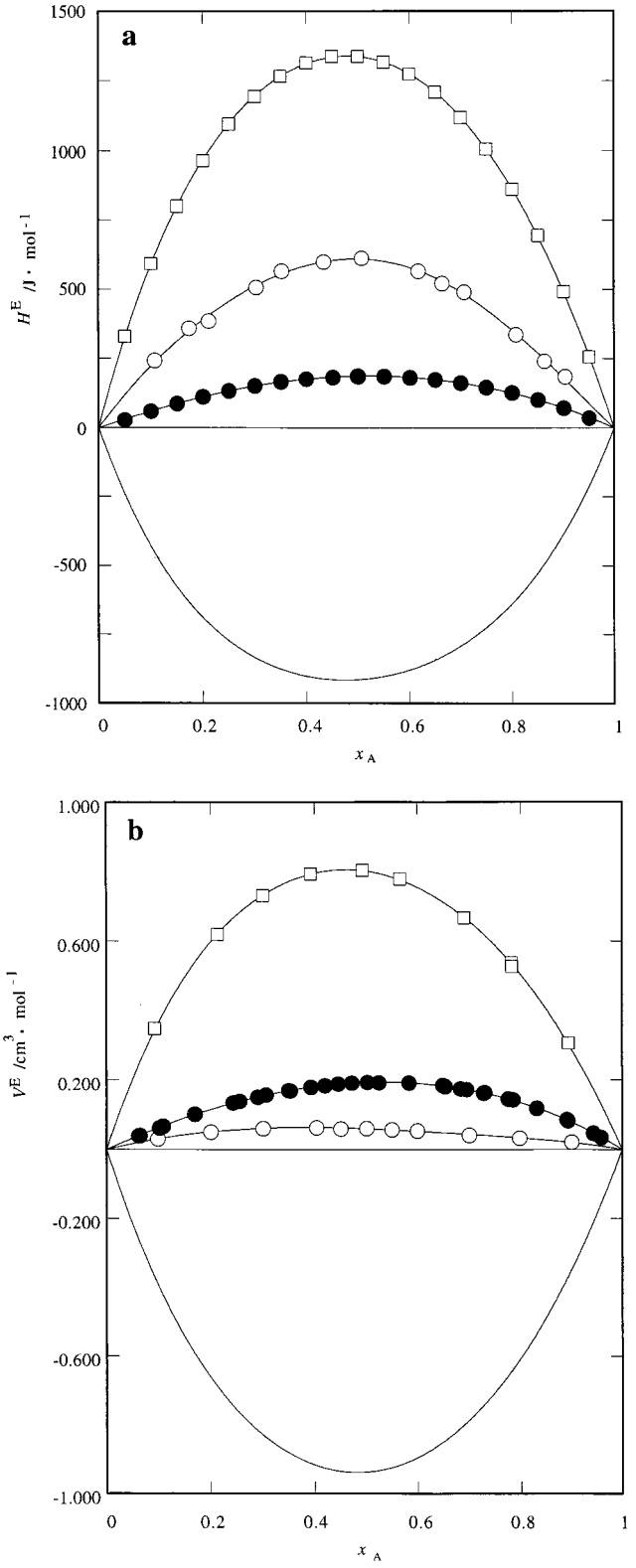

Figure 5. (a) Excess molar enthalpies H^E and (b) volumes V^E, at $T = 298.15$ K, for the following: (○) {x_A butanone + x_B *n*-propyl ether}; (●) {x_A *n*-hexane + x_B *n*-propyl ether} (Wang et al., 1988, 1989); (□) {x_A butanone + x_B *n*-heptane} (Kiyohara et al., 1979; Grolier and Benson, 1987); (—) apparent contribution to the excess properties.

between the oxygen (ether) and the oxygen of the carbonyl group in mixtures (butanone + *n*-propyl ether) can be obtained by subtracting the corresponding H^E and V^E of (butanone + *n*-heptane) and (*n*-hexane + *n*-propyl ether). These strongly negative contributions are plotted in Figure 5. Presumably, the specific interaction between the oxygen of the ether and the oxygen of the carbonyl group may be of the donor−acceptor type.

In mixtures of butanone with isopropyl ether in place of *n*-propyl ether, a less positive excess enthalpy is observed. On the other hand, the excess volume is negative over the whole composition range.

Table 5. Coefficients A_j and Standard Deviations $\sigma(Q^E)$ for Least-Squares Representation by Equation 10 of H^E and V^E, at 298.15 K

mixture	Q^E	A_0	A_1	A_2	A_3	$\sigma(Q^E)$
x_A butanone + x_B *n*-propyl ether	H^E/(J· mol^{-1})	2429	229.0	−255.2		13
	V^E/(cm^3·mol^{-1})	0.237	0.110	0.070	−0.053	0.002
+ x_B isopropyl ether	H^E/(J· mol^{-1})	1669	83.34	−245.9	882.5	11
	V^E/(cm^3·mol^{-1})	−0.940	0.076	−0.049	−0.091	0.003

Table 6. Azeotropic Pressures and Mole Fractions

	butanone + *n*-propyl ether				butanone + isopropyl ether			
T/K	z exptl	P_z/kPa exptl	z calcd, eq 11	P_z/kPa calcd, eq 13	z exptl	P_z/kPa exptl	z calcd, eq 11	P_z/kPa calcd, eq 13
288.15	0.746	7.677	0.745	7.725	0.130	12.690	0.130	12.698
293.15	0.748	9.866	0.748	9.902	0.135	16.054	0.136	16.033
298.15	0.752	12.614	0.752	12.586	0.141	20.229	0.142	20.086
303.15	0.754	16.012	0.755	15.873	0.148	25.166	0.147	24.977
308.15	0.757	19.980	0.758	19.867	0.153	30.991	0.153	30.841
313.15	0.763	24.761	0.762	24.689	0.159	37.911	0.158	37.820
323.15	0.769	37.009	0.769	37.367	0.169	55.081	0.169	55.831

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