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Nonazeotropy in the System Methyl Ethanoate + 1,2-Epoxybutane

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New vapor−liquid equilibrium data for the binary system methyl ethanoate + 1,2-epoxybutane are reported at 35 and 101.3 kPa and at 298.15 K. It is shown that no azeotropes are present in the system, in disagreement with data reported by others who claim that two azeotropes are present at 298.15 K. We claim that previously reported data are in error because of impurities in the reagents and experimental errors. According to our results, the system methyl ethanoate + 1,2-epoxybutane behaves like a regular solution and its vapor phase can be considered practically ideal so that it cannot fulfill the necessary conditions for multiple azeotropy. The data were satisfactorily correlated using the regular model and the Wisniak−Tamir equation.

Introduction

Binary polyazeotropy, i.e., the condition for which more than one stable azeotrope exists at a given temperature or pressure, was discovered experimentally by Gaw and Swinton (1968) for the system benzene + hexafluorobenzene. Since then it has been reported experimentally for the five organic systems benzene + hexafluorobenzene (Aucejo et al., 1996), diethylamine + methanol (Srivastava and Smith, 1985; Aucejo et al., 1997), 1,2-epoxybutane + methyl ethanoate (Leu and Robinson, 1991), ethanoic acid + 2-methylpropyl ethanoate (Christensen and Olson, 1992; Burguet et al., 1996) and ammonia + 1,1,2,2,2-pentafluoroethane (Chai Kao et al., 1997). The latter system is unusual in that the two azeotropes occur at temperatures for which the vapor pressure of the two components are notably different. The thermodynamic aspects of azeotropy and polyazeotropy for associating and nonassociating mixtures have been analyzed by Wisniak et al. (1996) and Segura et al. (1996). Vapor−liquid data for the system methyl ethanoate + 1,2-epoxybutane have been measured at 298.15 and 348.15 K (28 to 145 kPa) by Leu and Robinson (1991) using a static equilibrium cell. On the basis of their results, the authors claimed that the system presents two azeotropes at 298.15 K and no azeotrope at 348.15 K. The publication of Leu and Robinson includes also the measurement of vapor−liquid equilibrium (VLE) for the systems 1,2-epoxybutane + 2,2-dimethyloxirane, ethanal + 2-propanone, and ethanal + 2-methyloxirane, at the same two temperature levels. Inspection of the results reported indicates substantial differences between the properties of the pure components. For example, for the system methyl ethanoate + 1,2-epoxybutane, the vapor pressure of pure 1,2-epoxybutane is reported as 27.0 kPa at 298.15 K and 145 kPa at 348.15 K. For the system 1,2-epoxybutane + 2,2-dimethyloxirane, the pertinent vapor pressures are now 31.6 and 142 kPa. The same discrepancy is observed for the vapor pressure of ethanal in the two other systems. The purity of 1,2-epoxybutane is reported as that given by the provider (Aldrich Chemical), and no indication is given of its actual concentration, as measured by gas chromatography. Osborn and Scott (1980) have measured the vapor pressure of 1,2-epoxybutane, purified by preparative to 99.934 mass %, in the range 294 to 369 K and reported the pertinent Antoine constants. The normal boiling point of the purified compound was measured as 336.574 K.

Within our program of systematic experimental research of polyazeotropic systems, it is the purpose of this work to measure again the data reported by Leu and Robinson, to verify the claim that two azeotropes are present, and to study the variation of azeotropic composition with pressure. Preliminary measurements of the isobars of the title system were made at 35 and 101.3 kPa, in order to determine the variation of the azeotropes with pressure; however, no azeotrope was found under these conditions. In addition, analysis of all the data by the criteria for polyazeotropy discussed by Wisniak et al. (1996) and Segura et al. (1996), indicating that the system did not fulfill the necessary conditions for polyazeotropy. Thus a careful experimental study was carried at 298.15 K, condition at which again no azeotropic behavior was found, in opposition to the VLE data reported by Leu and Robinson at the same temperature. In the present work, we offer both experimental and theoretical evidence that seems to indicate that the classification of the system methyl ethanoate (1) + 1,2-epoxybutane (2) at 298.15 K as polyazeotropic is in error.

Experimental Section

Chemicals. Methyl ethanoate anhydrous (>99.5%) was purchased from Aldrich, and 1,2-epoxibutane (>99%) was purchased from Fluka. The actual purity, as checked by gas chromatography, was methyl ethanoate, 99.9 mass %, and 1,2-epoxybutane, 99.9 mass %. The reagents were used without further purification. The experimental densities, refractive indexes, and normal boiling points are given in Table 1 and shown to be in good agreement with the corresponding values reported in the literature.

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Table 1. Properties of Pure Compounds

	d(298.15)/ g·cm^{-3}		n(D,298.15 K)		T_b (101.3 kPa)/K	
components	exptl[a]	lit.	exptl[a]	lit.	exptl[a]	lit.[a]
methyl ethanoate	0.926 84	0.9273[b]	1.3588	1.3589[b]	329.7	329.09[b]
1,2-epoxybutane	0.824 45	0.824[d]	1.3812	1.381[d]	336.3	336.574[c]

[a] Measured. [b] TRC Tables, a-5560. [c] Osborn and Scott (1980). [d] Riddick et al. (1986).

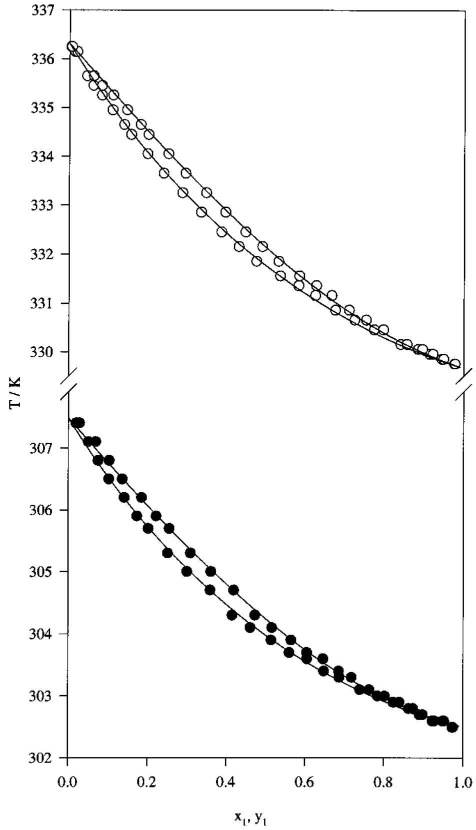

Figure 1. Experimental data for the system methyl ethanoate (1) + 1,2-epoxybutane (2) at 35 and 101.3 kPa: experimental data at 35 kPa (●); experimental data at 101.3 kPa (○); smoothed data using the regular model, eq 4 (—).

Apparatus and Procedure. The equilibrium vessel was an all-glass, dynamic-recirculating still described by Walas (1985), equipped with a Cottrell circulation pump. The still (Labodest model), manufactured by Fischer Labor und Verfahrenstechnik (Germany), is capable of handling pressures from 0.25 to 150 kPa and temperatures up to 523.15 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature sensing element. The equilibrium temperature was measured with a Fisher digital thermometer with an accuracy of ±0.1 K, and the pressure with a digital manometer with an accuracy of ±0.01 kPa. The temperature probe was calibrated against the ice and steam points of distilled water. The manometer was calibrated using the vapor pressure of high-purity hexane (>99.9 mass %). The still was operated under constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 30 min or longer. At this time, samples of liquid and condensate were taken for analysis. The sample extractions were carried out with special syringes (Hamilton, RSN 1001), which allowed withdrawal of small-volume samples (0.1 mL) in a system under partial vacuum.

Table 2. Experimental Vapor−Liquid Equilibrium Data for Methyl Ethanoate (1) + 1,2-Epoxybutane (2) at 35 kPa

T/K	x_1	y_1	γ_1	γ_2	ϕ_1	ϕ_2	G^E/J·mol^{-1}
302.5	1.000	1.000	1.000				0.00
302.5	0.973	0.974	1.001	1.182	0.985	0.981	14.23
302.6	0.949	0.952	0.999	1.151	0.985	0.981	15.60
302.6	0.923	0.928	1.001	1.143	0.985	0.981	28.80
302.7	0.890	0.898	1.001	1.129	0.985	0.981	34.64
302.8	0.863	0.873	0.999	1.124	0.985	0.981	37.56
302.9	0.824	0.839	1.001	1.104	0.985	0.981	46.05
303.0	0.784	0.802	1.001	1.102	0.985	0.981	55.54
303.1	0.739	0.763	1.006	1.087	0.985	0.981	66.69
303.3	0.687	0.718	1.010	1.070	0.985	0.981	70.33
303.4	0.648	0.686	1.019	1.055	0.985	0.981	77.50
303.6	0.605	0.646	1.019	1.051	0.985	0.981	77.69
303.7	0.560	0.605	1.026	1.048	0.985	0.981	89.03
303.9	0.514	0.565	1.035	1.036	0.985	0.981	89.12
304.1	0.461	0.516	1.045	1.031	0.985	0.981	93.61
304.3	0.415	0.473	1.056	1.026	0.986	0.981	94.65
304.7	0.359	0.419	1.063	1.015	0.986	0.981	80.04
305.0	0.300	0.361	1.082	1.010	0.986	0.982	77.59
305.3	0.251	0.309	1.093	1.008	0.986	0.982	72.25
305.7	0.202	0.255	1.102	1.004	0.986	0.982	57.44
305.9	0.173	0.222	1.111	1.003	0.986	0.982	52.98
306.2	0.141	0.185	1.122	0.999	0.986	0.982	40.02
306.5	0.102	0.136	1.126	1.001	0.986	0.982	33.59
306.8	0.075	0.103	1.145	0.997	0.986	0.982	18.63
307.1	0.050	0.069	1.137	0.995	0.986	0.982	4.94
307.4	0.019	0.028	1.199	0.994	0.986	0.982	−5.81
307.5	0.000	0.000		1.000			0.00
γ_i^{∞} [a]			1.17	1.18			

[a] Extrapolated from present VLE data according to the method of Wisniak et al. (1996).

Analysis. Compositions of the sampled liquid and condensed vapor phases were determined using a Hewlett-Packard 5890 S-II gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 60 m, 0.2 mm i.d., fused silica capillary column, SUPERCOWAX 10. The column and detector temperatures were 333 and 523 K, respectively. The GC response peaks were integrated with a Hewlett-Packard 3396 integrator. At least two analyses were made of each vapor composition; the standard deviation of composition analysis was usually less than 0.001 mole fraction.

Results and Discussion

The temperature T and the liquid-phase x_i, and vapor-phase y_i mole fractions at P = 35 and 101.3 kPa are reported in Figure 1 and Tables 2 and 3. The pressure P and equilibrium compositions at T = 298.15 K are reported in Figure 2 and Table 4. Figures 3 and 4 show the activity coefficients γ_i that were calculated from the following equation (Van Ness and Abbott, 1982)

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^L)(P - P_i^0)}{RT} + y_j^2 \frac{\delta_{ij} P}{RT} \qquad (1)$$

where T and P are the boiling point and the total pressure, V_i^L is the molar liquid volume of component i, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, P_i^0 is the vapor pressure, B_{ij} is the cross second virial coefficient, and

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \qquad (2)$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation 1 is valid at low and moderate pressures when the virial equation of state truncated after

Table 3. Experimental Vapor–Liquid Equilibrium Data for Methyl Ethanoate (1) + 1,2-Epoxybutane (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2	ϕ_1	ϕ_2	G^E/J·mol^{-1}
329.7	1.000	1.000	1.000				0.00
329.8	0.977	0.979	0.999	1.149	0.969	0.961	5.38
329.9	0.945	0.950	0.999	1.128	0.969	0.961	14.79
330.0	0.915	0.922	0.999	1.121	0.969	0.961	23.07
330.1	0.885	0.896	0.999	1.109	0.969	0.961	30.94
330.2	0.841	0.857	1.002	1.101	0.969	0.961	47.12
330.5	0.774	0.797	1.003	1.086	0.969	0.961	57.81
330.7	0.724	0.754	1.006	1.076	0.969	0.961	67.45
330.9	0.675	0.710	1.010	1.067	0.969	0.961	76.77
331.2	0.625	0.666	1.014	1.052	0.969	0.961	77.28
331.4	0.582	0.627	1.018	1.049	0.969	0.961	83.17
331.6	0.535	0.584	1.024	1.045	0.969	0.961	91.47
331.9	0.475	0.531	1.040	1.032	0.969	0.962	96.39
332.2	0.430	0.490	1.048	1.024	0.970	0.962	93.73
332.5	0.386	0.447	1.056	1.020	0.970	0.962	91.81
332.9	0.334	0.396	1.065	1.015	0.970	0.962	85.33
333.3	0.286	0.347	1.075	1.010	0.970	0.962	77.56
333.7	0.239	0.294	1.080	1.010	0.970	0.962	71.88
334.1	0.198	0.251	1.096	1.005	0.970	0.962	60.31
334.5	0.156	0.200	1.094	1.006	0.971	0.962	53.67
334.7	0.138	0.180	1.104	1.004	0.971	0.963	46.65
335.0	0.109	0.145	1.120	1.002	0.971	0.963	39.24
335.3	0.082	0.111	1.120	1.003	0.971	0.963	32.33
335.5	0.060	0.082	1.125	1.004	0.971	0.963	30.61
335.7	0.045	0.061	1.125	1.004	0.971	0.963	24.64
336.2	0.014	0.019	1.134	1.000	0.971	0.963	3.64
336.3	0.004	0.006	1.123	1.000	0.971	0.963	2.16
336.3	0.000	0.000		1.000			0.00
γ_i^{∞} [a]			1.15	1.14			

[a] Extrapolated from present VLE data according to the method of Wisniak et al. (1996).

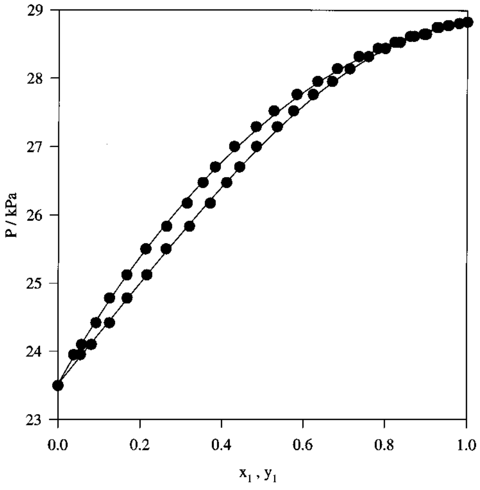

Figure 2. Experimental data for the system methyl ethanoate (1) + 1,2-epoxybutane (2) at 298.15 K: experimental data (●); smoothed data using the regular model, eq 4 (—).

the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration. The pure component vapor pressures P_i^0 were determined experimentally as a function of the temperature, using the same equipment as that for obtaining the VLE data, the pertinent results appear in Table 5. The measured vapor pressures were correlated using the Antoine equation

$$\log(P_i^0/\mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) - C_i} \qquad (3)$$

where the Antoine constants A_i, B_i, and C_i are reported in Table 6. The vapor pressures were correlated with a MADP of 0.07% for methyl ethanoate and 0.04% for 1,2-epoxybutane. The parameters presented in Table 6 predict very well the experimental vapor pressures measured by

Table 4. Experimental Vapor–Liquid Equilibrium Data for Methyl Ethanoate (1) + 1,2-Epoxybutane (2) at 298.15 K

P/kPa	x_1	y_1	γ_1	γ_2	ϕ_1	ϕ_2	G^E/J·mol^{-1}
28.82	1.000	1.000	1.000				0.00
28.81	0.980	0.980	1.000	1.221	0.987	0.984	8.99
28.78	0.953	0.955	1.001	1.168	0.987	0.984	19.74
28.75	0.926	0.930	1.002	1.153	0.987	0.984	30.42
28.65	0.894	0.900	1.001	1.146	0.987	0.984	37.61
28.62	0.861	0.871	1.005	1.126	0.987	0.984	50.85
28.53	0.823	0.836	1.006	1.121	0.987	0.984	61.60
28.44	0.782	0.800	1.010	1.106	0.987	0.984	73.28
28.32	0.735	0.759	1.015	1.092	0.987	0.984	84.88
28.14	0.682	0.713	1.021	1.077	0.987	0.984	93.76
27.95	0.634	0.670	1.025	1.069	0.987	0.984	99.57
27.76	0.583	0.623	1.030	1.065	0.988	0.984	107.03
27.52	0.527	0.575	1.043	1.049	0.988	0.984	110.36
27.29	0.483	0.535	1.050	1.041	0.988	0.984	109.87
27.00	0.430	0.484	1.055	1.037	0.988	0.984	108.94
26.70	0.383	0.443	1.073	1.023	0.988	0.985	101.22
26.47	0.353	0.411	1.071	1.023	0.988	0.985	95.73
26.17	0.314	0.371	1.074	1.019	0.988	0.985	87.09
25.83	0.264	0.320	1.088	1.013	0.989	0.985	79.18
25.50	0.213	0.263	1.094	1.014	0.989	0.985	74.84
25.12	0.167	0.216	1.129	1.004	0.989	0.986	59.04
24.78	0.125	0.168	1.158	1.001	0.989	0.986	47.58
24.42	0.092	0.125	1.154	1.000	0.989	0.986	32.49
24.10	0.057	0.081	1.191	0.998	0.989	0.986	20.45
23.95	0.038	0.054	1.184	1.001	0.989	0.986	18.35
23.52	0.000	0.000		1.000			0.00
γ_i^{∞} [a]			1.19	1.18			

[a] Extrapolated from present VLE data according to the method of Wisniak et al. (1996).

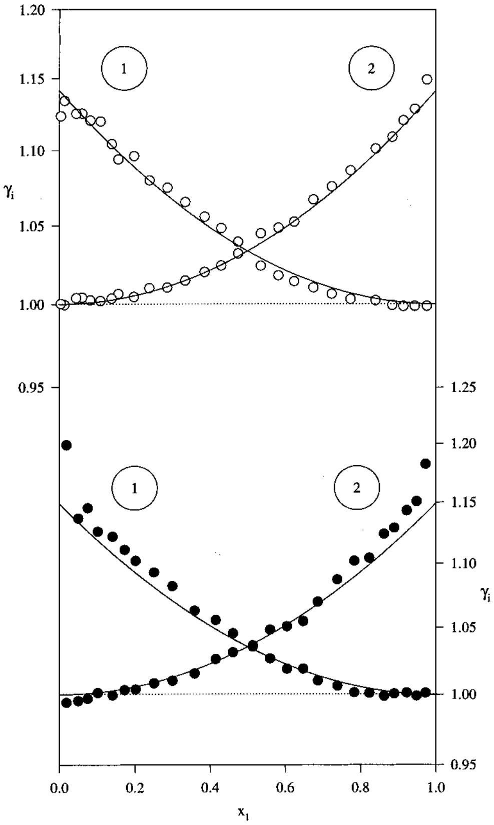

Figure 3. Activity coefficient plots of the system methyl ethanoate (1) + 1,2-epoxybutane (2) at 35 and 101.3 kPa, calculated from experimental data: experimental data at 35 kPa (●); experimental data at 101.3 kPa (○); smoothed data using the regular model, eq 4 (—).

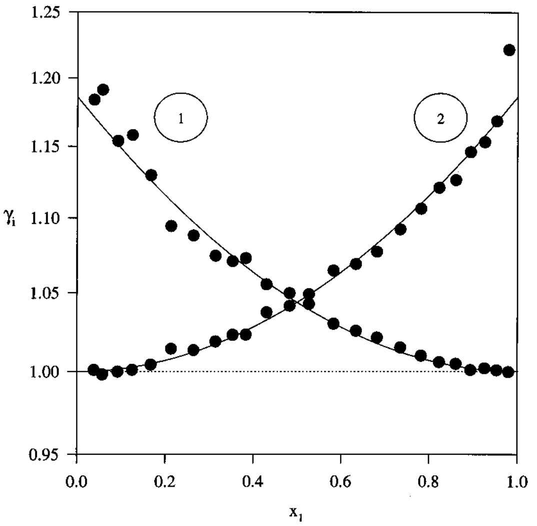

Figure 4. Activity coefficient plot of the system methyl ethanoate (1) + 1,2-epoxybutane (2) at 298.15 K, calculated from experimental data: experimental data (●); smoothed data using the regular model, eq 4 (—).

Table 5. Vapor Pressure of Methyl Ethanoate and 1,2-Epoxybutane as a Function of Temperature

methyl ethanoate		1,2-epoxybutane	
T/K	P^0/kPa	*T*/K	P^0/kPa
296.3	26.48	296.5	21.85
298.2	28.84	298.2	23.50
301.8	33.94	305.3	31.94
305.6	39.95	307.5	35.00
308.4	44.94	309.2	37.53
312.0	51.95	311.4	40.93
315.5	59.85	313.8	44.97
318.7	67.75	316.4	49.78
321.3	74.89	319.9	56.93
323.1	79.86	323.1	63.92
324.7	84.90	323.2	64.11
326.0	88.88	325.6	69.91
327.5	93.94	328.3	76.89
328.7	97.91	330.5	83.26
329.8	101.63	332.8	89.86
331.7	108.87	334.8	96.40
333.2	114.58	336.7	102.66
335.1	122.02	336.8	102.80
336.7	128.92	338.8	109.97
336.8	128.95	341.4	119.38
338.1	134.60	343.5	127.87
339.8	142.30	343.5	127.90
341.4	149.90	345.9	137.80
342.9	157.40	347.7	145.70
344.9	167.50	349.8	155.00
346.6	176.30	351.6	163.60
348.2	185.40	353.2	171.60
349.8	194.80	354.8	180.20
351.5	204.40	356.6	189.40
353.1	214.80	356.5	189.30
		358.2	198.40
		360.0	208.90
		361.5	218.10

Table 6. Antoine Coefficients, Eq 3[a]

compound	A_i	B_i	C_i
methyl ethanoate	5.907 60	1001.580	72.969
1,2-epoxybutane	6.104 27	1167.133	51.545

[a] Determined from experimental information using the equilibrium cell and the component used in this work.

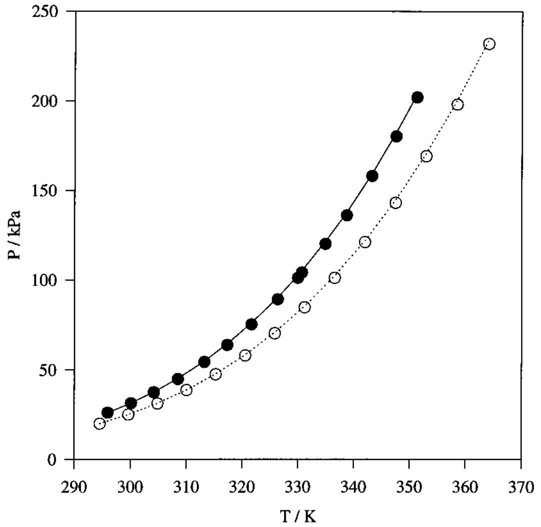

Figure 5. Comparison of correlated vapor pressures with other references: experimental data of Ambrose et al. (1981) for methyl ethanoate (●); experimental data of Osborn and Scott (1980) for 1,2-epoxybutane (○); predicted by eq 3 and parameters in Table 6 for methyl ethanoate (—) and for 1,2-epoxybutane (···).

Table 7. Consistency Test for the Various Experimental Conditions Considered in VLE Measurements, System Methyl Ethanoate (1) + 1,2-Epoxybutane (2)

conditions		A^a	100 × MADy_1^b	MADP^c/kPa
P	101.3 kPa	0.1322	0.079	0.176
	35 kPa	0.1390	0.144	0.061
T	298.15 K	0.1707	0.120	0.026

[a] Zeroth order Legendre polynomial (or Porter model) parameter in eq 4. [b] Average absolute deviation in vapor-phase composition. [c] Average Absolute deviation in pressure.

Ambrose et al. (1981) for methyl ethanoante (MADP = 0.92%) and by Osborn and Scott (1980) for 1,2-epoxybutane (MADP = 0.75%), as can be confirmed in Figure 5. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of Hayden and O'Connell (1975) assuming the association parameter η to be zero. Critical properties of both components were taken from DIPPR (Daubert and Danner, 1989). The last two terms in eq 1, particularly the second one that expresses the correction due to the nonideal behavior of the vapor phase, contributed less than 4% at the higher pressure considered in this work (101.3 kPa); in general, their influence was important only at very dilute concentrations in the higher pressure range. The calculated activity coefficients reported in Tables 2, 3, and 4 are estimated accurate to within ±3%. Tables 2, 3, and 4 contain also the activity coefficients at infinite dilution γ_i^∞ estimated from experimental data using the method suggested by Wisniak et al. (1996). The results reported in these tables indicate that both systems exhibit moderate positive deviations from ideal behavior and that *no azeotrope is present.*

The vapor–liquid equilibria data reported in Tables 2, 3, and 4 were found to be thermodynamically consistent by the point-to-point method of Van Ness et al. (1973), as modified by Fredenslund et al. (1977). Consistency was achieved using a one-parameter Legendre polynomial, or regular model, which reduces the functionality of the excess Gibbs energy G^E to the following symmetric relation

$$G^E = Ax_1x_2 \tag{4}$$

The parameter *A* in eq 4 together with the pertinent statistics required by the Fredenslund's test are shown in Table 7 for the different conditions of temperature and pressure considered in this work. From Table 7 it is concluded that the assumed model gives an excellent fit of

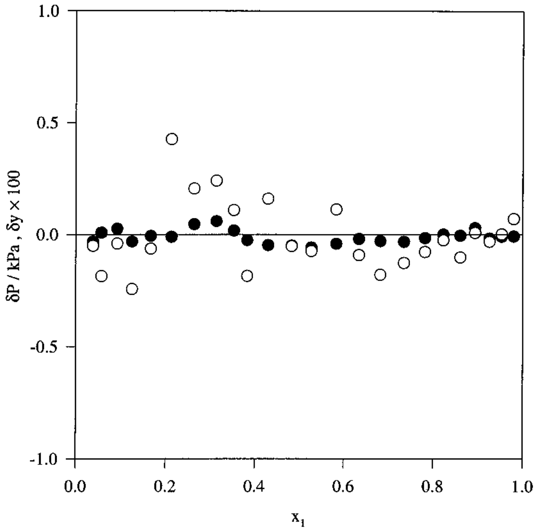

Figure 6. Residuals of consistency analysis for the system methyl ethanoate (1) + 1,2-epoxybutane (2) at 298.15 K: vapor-phase composition residuals 100 × δy (○); vapor pressure residuals δP/kPa (●).

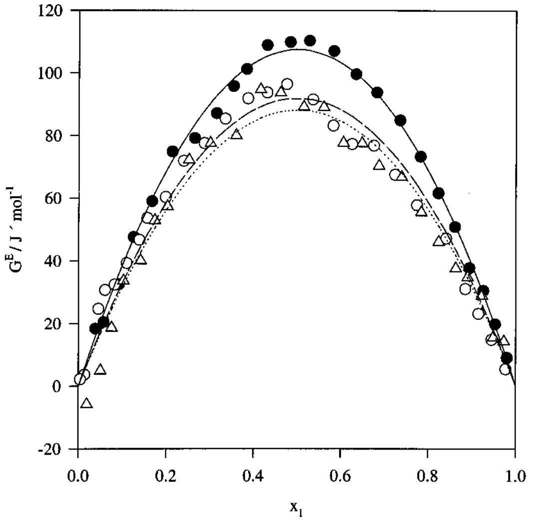

Figure 7. Excess Gibbs energy for the system methyl ethanoate (1) + 1,2-epoxybutane (2) at 35 and 101.3 kPa and at 298.15 K, calculated from experimental data: T = 298.15 K (●); P = 35 kPa (○); P = 101.3 kPa (△). Data smoothed using the regular model at T = 298.15 K (—), P = 35 kPa (···), and P = 101.3 kPa (- - -).

the data. For all the experimental pressures and temperatures the residuals of the Fredenslund test were reasonably distributed, as measured by the Durbin−Watson statistic. This fact is illustrated in Figure 6, which shows the residuals of both the pressure and vapor phase composition of the system at 25 °C.

The variation of the excess Gibbs function G^E with composition appears in Tables 2, 3, and 4 and Figure 7. Inspection of these tables indicates that the maximum value of G^E appears in the neighborhood of composition x_1 = 0.5 and that the estimated γ_i^∞ are approximately equal for both components. In addition, from Figure 7, it is clear that the excess energy behaves symmetrically about the composition $x_1 = 0.5$, the same composition at which the activity coefficients curves intersect, as shown in Figures 3 and 4. Thus according to the present experimental data, and its pertinent consistency test, we can conclude that the system can be satisfactorily explained by a regular solution behavior (Porter equation).

Table 8. Vapor Pressures of Pure Components at 298.15 and 348.15 K According to Various References

component	T/K	P^a/kPa	P^b/kPa	P^c/kPa	P^d/kPa
methyl ethanoate	298.15	28.6	28.83		28.82
	348.15	179.0	183.64		185.30
1,2-epoxybutane	298.15	27.0 (31.6)		23.45	23.52
	348.15	145.0 (142.0)		146.30	147.67

[a] Leu and Robinson (1991). [b] Ambrose et al. (1981). [c] Osborn and Scott (1980). [d] This work.

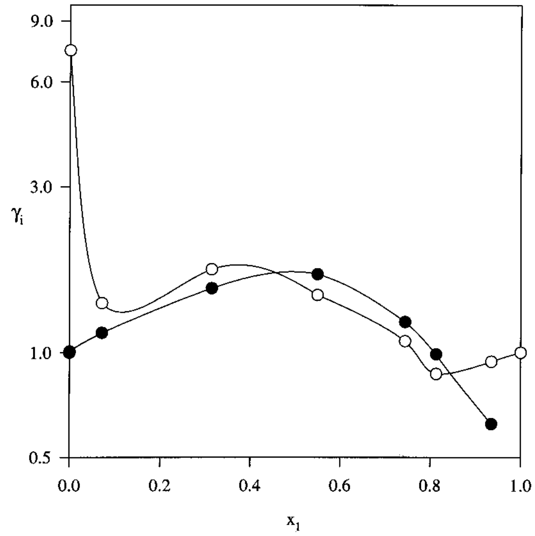

Figure 8. Activity coefficient plot of the system methyl ethanoate (1) + 1,2-epoxybutane (2) at 298.15 K: experimental data from Leu and Robinson (1991) γ_2 (●), γ_1 (○); smoothed data, using a spline fit (—).

As pointed by Wisniak et al. (1996) and Segura et al. (1996), when fugacity coefficients of the vapor phase are weakly dependent on the vapor phase concentration (as observed in Tables 2 to 4), then a necessary condition of polyazeotropy is the inflection of the liquid phase excess energy on composition. However, no inflection can be seen in the data shown in Figure 7. In addition, the regular behavior of the system (given mathematically by eq 4) does not allow compositional inflections of the excess energy. Hence it can be concluded that the system methyl ethanoate (1) + 1,2-epoxybutane (2) *does not match the necessary conditions of polyazeotropy* in the pressure and temperature range under consideration.

Errors on the data of Leu and Robinson (1991) become evident when considering the vapor pressure of the pure species, as measured in their static equilibrium cell. In Table 8, vapor pressures at the experimental conditions considered by Leu and Robinson (298.15 and 348.15 K) are compared with data from different sources. The main difference can be observed in the experimental value of 1,2-epoxybutane at 298.15 K, where the vapor pressure is overestimated, probably due to an insufficient degasification of the liquid. In addition, Figure 8 illustrates the activity coefficient plot obtained from the data of Leu and Robinson: the variation of the activity coefficients with composition does not satisfy the constrained Gibbs-Duhem equation (Van Ness and Abbott, 1982)

$$x_1 \frac{\mathrm{d} \ln \gamma_1}{\mathrm{d}x_1} + x_2 \frac{\mathrm{d} \ln \gamma_2}{\mathrm{d}x_1} \equiv 0 \qquad (5)$$

applicable to isothermal VLE data, because *the compositional derivatives of both activity coefficients show the same sign* in a wide range of concentrations, indicating strong internal inconsistency of these data.

The boiling point temperatures of the solution at 35 and 101.3 kPa were correlated with its composition by the

Table 9. Coefficients in Correlation of Boiling Points, Eqs 6 and 7, System Methyl Ethanoate (1) + 1,2-Epoxybutane (2). Average Deviation and Root Mean Square Deviations in Temperature, rmsd

P/kPa	C_0	C_1	C_2	max dev[a]/K	avg dev[b]/K	rmsd[c]/K
35.0	−4.39	0.03	1.27	0.17	0.08	0.02
101.3	−5.52	1.25	3.32	0.23	0.10	0.02

T/K	C_0	C_1	C_2	max dev[a]/kPa	avg dev[b]/kPa	rmsd[c]/kPa
298.15	4.76	−0.35	0.00	0.07	0.02	0.01

[a] Maximum deviation. [b] Average deviation. [c] Root mean square deviation.

equation proposed by Wisniak and Tamir (1976):

$$T/\mathrm{K} = x_1 T_1^0 + x_2 T_2^0 + x_1 x_2 \sum_{k=1}^{m} C_k (x_1 - x_2)^k \qquad (6)$$

In this equation T_i^0/K is the boiling point of the pure component i and m are the number of terms in the series expansion of $(x_1 - x_2)$. A similar equation was used for the correlation of boiling point pressures at 298.15 K, but now based on the vapor pressures P_i^0/kPa of pure constituents

$$P/\mathrm{kPa} = x_1 P_1^0 + x_2 P_2^0 + x_1 x_2 \sum_{k=1}^{m} C_k (x_1 - x_2)^k \qquad (7)$$

The various constants of eqs 6 and 7 are reported in Table 9, which also contains information indicating the degree of goodness of the correlation.

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