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Polyazeotropy in Associating Systems: The 2-Methylpropyl Ethanoate + Ethanoic Acid System

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Polyazeotropy in binary systems is a singular case of vapor−liquid equilibrium (VLE) where, at a given pressure or temperature, various azeotropes of alternating deviations from ideality are observed. Multiple azeotropy can be observed in systems which strongly associate in the vapor phase. Vapor−liquid equilibrium was measured for the 2-methylpropyl ethanoate (1) + ethanoic acid (2) system at 390.15 K and 353.15 K. The system presents two azeotropes at 390.15 K and none at 353.15 K, the polyazeotropic behavior at the higher temperature can be explained in terms of dimerization of ethanoic acid. The data were satisfactorily correlated using excess models for associating mixtures and chemical theory for the treatment of the vapor phase.

Introduction

Polyazeotropy in binary systems is a singular case of vapor−liquid equilibrium (VLE) where at a given pressure or temperature various azeotropes of alternating deviations from ideality are observed. At low pressures these deviations are generally caused by the liquid phase nonidealities because the vapor phase usually behaves as an ideal vapor mixture (Wisniak et al., 1996), but in associated systems, even at low pressures, the vapor phase nonidealities are significant and can induce polyazeotropic behavior (Christensen and Olson, 1992; Segura et al., 1996). Numerous papers have dealt with association effects present in carboxylic acid systems (Sebastiani and Lacquaniti, 1967; Barton and Hsu, 1969; Francesconi et al., 1974; Seaton, 1993), the general agreement being that the acid undergoes partial dimerization end even higher polymerizations both in the liquid and in the vapor phase. As pointed out by Prausnitz et al. (1986), for a given acid, the degree of association depends on the temperature, the pressure, and the interactions with other components present in the mixture; in phase equilibrium, the association behavior is reflected in positive and/or negative deviations from ideality. Ethanoic acid is well-known to dimerize in the vapor phase, giving highly nonideal vapor behavior (Tsonopoulos and Prausnitz, 1970), and association evidence of ethanoic acid in the liquid phase has been reported by Seaton (1993). Christensen and Olson (1992) suggested a class of polyazeotropy that can be achieved by a combination of nonidealities in the vapor and in the liquid phases, where the first is a consequence of chemical interactions at low pressures (association). In their study of the 2-methylpropyl ethanoate (1) + ethanoic acid (2) system, Christensen and Olson applied the correlation of Hayden and O'Connell (1975), for the treatment of association in the vapor phase, and the UNIFAC group contribution method (Fredenslund et al., 1977; Hansen at al, 1991) to predict the existence of two azeotropes at 390.15 K. Their prediction of polyazeotropy was confirmed from batch distillation experiments at atmospheric pressure, but neither the exact azeotropic compositions nor their temperatures were indicated. Experimental evidence indicates that ethanoic acid and 2-methylpropyl ethanoate have near identical vapor pressures in the entire range of temperatures, a condition usually observed in polyazeotropic behavior (Wisniak et al., 1996).

Table 1. Properties of the Pure Compounds

	d(293.15)/g·cm^{-3}		n(D,298.15 K)		T_b(101.3 kPa)/K	
components	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]
2-methylpropyl ethanoate	0.866 12	0.867 70	1.3876	1.3880	389.85	389.8
ethanoic acid	1.043 65	1.043 66	1.3691	1.3698	391.15	391.12

[a] *TRC* (1996).

Table 2. Vapor Pressure of 2-Methylpropyl Ethanoate as a Function of the Temperature

T/K	$P°$/kPa	T/K	$P°$/kPa
325.86	9.69	376.90	67.49
335.29	14.64	378.42	71.56
341.05	18.54	380.33	75.72
346.16	22.72	382.28	80.42
350.81	27.10	384.20	85.33
354.74	31.42	385.14	87.58
358.17	35.63	386.68	91.92
361.37	39.95	388.23	96.38
364.87	45.17	389.74	100.80
367.66	49.69	390.15	102.03
370.52	54.88	391.73	106.75
374.02	61.67	393.05	110.96
373.98	61.65		

The purpose of this contribution is to determine the polyazeotropic behavior of the 2-methylpropyl ethanoate (1) + ethanoic acid (2) system, by making a complete set of VLE measurements.

Experimental Section

Chemicals. 2-Methylpropyl ethanoate (99%, analytical grade) and ethanoic acid (99.8%, analytical grade) were purchased from Aldrich. The ethanoic acid was used without further purification, and 2-methylpropyl ethanoate was purified by batch distillation in a Fisher SPALTROHR-columm HMS-500, controlled by a Fisher System D301-C, until gas chromatography analysis failed to show any significant impurities (none higher than 0.2%). The experimental densities, refractive indexes, and normal boiling

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Table 3. Vapor−Liquid Equilibria for the System 2-Methylpropyl Ethanoate (1) + Ethanoic Acid (2) at 390.15 K

x_1	y_1	P/kPa	$\hat{\phi}_1$	$\hat{\phi}_2$	γ_1	γ_2
0.0000	0.0000	98.50	1.5960	0.4040		1.0000
0.0231	0.0262	98.84	1.5659	0.4036	1.7205	0.9992
0.0500	0.0557	99.28	1.5337	0.4033	1.6625	1.0001
0.0827	0.0888	99.72	1.4993	0.4034	1.5734	1.0040
0.1063	0.1137	99.95	1.4745	0.4038	1.5450	1.0057
0.1357	0.1428	100.32	1.4468	0.4044	1.4969	1.0110
0.1703	0.1767	100.58	1.4158	0.4057	1.4482	1.0173
0.2075	0.2126	100.81	1.3847	0.4075	1.4018	1.0256
0.2488	0.2529	101.00	1.3517	0.4103	1.3601	1.0355
0.2457	0.2493	100.98	1.3545	0.4100	1.3602	1.0353
0.2639	0.2668	101.10	1.3407	0.4113	1.3431	1.0407
0.2806	0.2833	101.16	1.3280	0.4127	1.3293	1.0451
0.3039	0.3062	101.23	1.3108	0.4149	1.3104	1.0517
0.3264	0.3272	101.31	1.2955	0.4170	1.2895	1.0602
0.3509	0.3515	101.32	1.2784	0.4199	1.2716	1.0679
0.3807	0.3811	101.33	1.2582	0.4237	1.2509	1.0781
0.4233	0.4225	101.30	1.2314	0.4299	1.2203	1.0958
0.4640	0.4623	101.26	1.2071	0.4369	1.1936	1.1150
0.5251	0.5232	101.22	1.1723	0.4495	1.1588	1.1478
0.5696	0.5674	101.22	1.1489	0.4605	1.1354	1.1773
0.6253	0.6233	101.18	1.1213	0.4774	1.1084	1.2202
0.6799	0.6787	101.16	1.0960	0.4982	1.0848	1.2710
0.7032	0.7021	101.15	1.0860	0.5085	1.0750	1.2972
0.7638	0.7636	101.10	1.0614	0.5417	1.0515	1.3772
0.8220	0.8235	101.17	1.0401	0.5858	1.0332	1.4767
0.8677	0.8696	101.25	1.0256	0.6332	1.0200	1.5878
0.8879	0.8900	101.39	1.0198	0.6599	1.0158	1.6495
0.9125	0.9145	101.50	1.0134	0.6991	1.0104	1.7421
0.9499	0.9516	101.68	1.0054	0.7822	1.0037	1.9306
0.9811	0.9814	101.86	1.0010	0.8898	0.9997	2.2413
1.0000	1.0000	102.03	1.0000	1.0000	1.0000	

Table 4. Vapor−Liquid Equilibria for the System 2-Methylpropyl Ethanoate (1) + Ethanoic Acid (2) at 353.15 K

x_1	y_1	P/kPa	$\hat{\phi}_1$	$\hat{\phi}_2$	γ_1	γ_2
0.0000	0.0000	27.54	1.6909	0.3091		1.0000
0.0484	0.0528	27.60	1.6215	0.3092	1.6444	0.9978
0.0647	0.0704	27.65	1.5999	0.3093	1.6212	0.9983
0.0868	0.0935	27.67	1.5723	0.3097	1.5784	0.9990
0.1174	0.1251	27.70	1.5362	0.3104	1.5273	1.0011
0.1416	0.1476	27.74	1.5118	0.3110	1.4723	1.0063
0.1730	0.1792	27.77	1.4787	0.3122	1.4327	1.0108
0.2176	0.2245	27.84	1.4342	0.3143	1.3875	1.0188
0.2516	0.2581	27.87	1.4031	0.3164	1.3511	1.0268
0.2805	0.2872	27.91	1.3774	0.3184	1.3258	1.0342
0.3287	0.3372	27.95	1.3357	0.3227	1.2899	1.0461
0.3680	0.3789	27.98	1.3031	0.3271	1.2644	1.0564
0.4058	0.4175	28.04	1.2747	0.3316	1.2385	1.0707
0.4431	0.4584	28.10	1.2461	0.3373	1.2201	1.0826
0.4874	0.5020	28.15	1.2174	0.3444	1.1888	1.1063
0.5385	0.5557	28.21	1.1842	0.3550	1.1611	1.1324
0.5976	0.6159	28.28	1.1498	0.3698	1.1287	1.1726
0.6491	0.6704	28.40	1.1210	0.3866	1.1075	1.2113
0.6947	0.7182	28.48	1.0975	0.4053	1.0884	1.2515
0.7499	0.7737	28.56	1.0722	0.4338	1.0642	1.3167
0.7851	0.8144	28.66	1.0551	0.4612	1.0565	1.3408
0.8483	0.8693	28.85	1.0340	0.5130	1.0297	1.4978
0.8933	0.9108	29.04	1.0199	0.5732	1.0171	1.6344
0.9127	0.9297	29.11	1.0141	0.6119	1.0128	1.6848
0.9501	0.9615	29.28	1.0057	0.7086	1.0037	1.8802
0.9783	0.9834	29.48	1.0015	0.8261	0.9996	2.1883
1.0000	1.0000	29.69	1.0000	1.0000	1.0000	

points are given in Table 1 and shown to be in good agreement with the corresponding values reported in the literature.

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 Labon/Ditel digital thermometer with an accuracy of ±0.01 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 one to withdraw small volume samples (0.1 mL) in a system under partial vacuum.

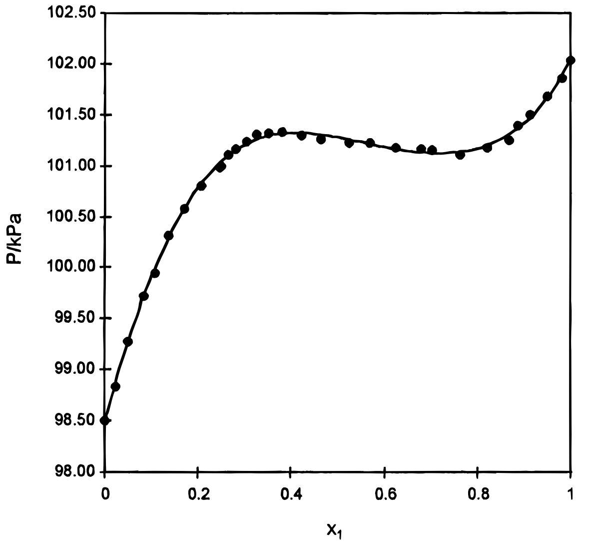

Figure 1. $P-x_1$ diagram for the 2-methylpropyl ethanoate (1) + ethanoic acid (2) system at 390.15 K: experimental data of the liquid phase (●); splined curve (—).

Analysis. Compositions of the sampled liquid and condensed vapor phases were analyzed using a Varian STAR 3400 CX gas chromatograph (GC) with a thermal conductivity detector, and the response was treated with a Star Chromatography Station. The chromatographic column (2 m × $^1/_8$ in.) was packed with Porapak P. The gas carrier was helium flowing at 50 $cm^3 \cdot min^{-1}$, and the column temperature was 423 K. The calibration was carefully carried out with gravimetrically prepared standard solutions. The accuracy of meassured liquid and vapor compositions was usually less than 5×10^{-4} mole fraction.

Results and Discussion

The vapor pressure of 2-methylpropyl ethanoate has been measured in the temperature range 323 K to 393 K, and the experimental results are reported in Table 2. The experimental data were adjusted to the Antoine equation

$$\ln(P_1^0/\mathrm{kPa}) = A + \frac{B}{(T/\mathrm{K}) + C} \tag{1}$$

with $A = 15.0090$, $B = -3611.88$, and $C = -42.3072$. The vapor pressure of ethanoic acid was not measured because very good data are available in the literature (TRC, 1994). Vapor−liquid equilibrium measurements were made at 390.15 K and 353.15 K and are presented in Tables 3 and 4. Figures 1 and 2 show the pressure composition ($P-x_1$)

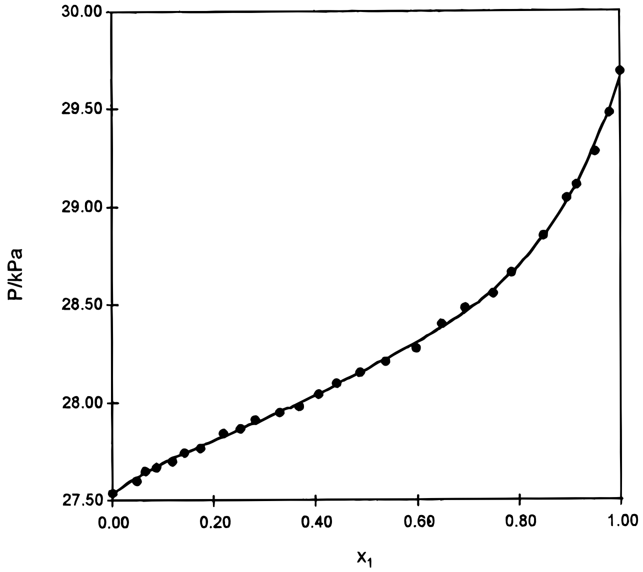

Figure 2. $P-x_1$ diagram for the 2-methylpropyl ethanoate (1) + ethanoic acid (2) system at 353.15 K: experimental data of the liquid phase (●); splined curve (—).

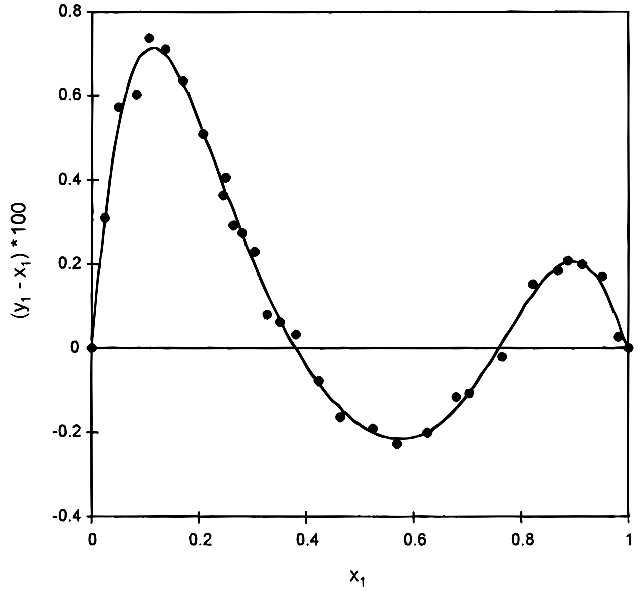

Figure 3. Representation of the function $(y_1 - x_1) \times 100 = f(x_1)$ for the 2-methylpropyl ethanoate (1) + ethanoic acid (2) system at 390.15 K.

curves at 390.15 K and 353.15 K. It can be observed that this system presents two local extrema (two azeotropes) in the $P-x_1$ plot at 390.15 K, whereas at 353.15 K no local extrema in the $P-x_1$ curve can be observed.

Figure 3 shows the two azeotropic points at 390.15 K. Composition and pressure for both azeotropes are $x_1 = 0.3797$, $P = 101.32$ kPa (maximum pressure or positive deviation azeotrope) and $x_1 = 0.7582$, $P = 101.13$ kPa (minimum pressure or negative deviation azeotrope). Azeotropic compositions were obtained by determining the x_1 values that make zero the best polynomial fit of the function $(y_1 - x_1) \times 100 = f(x_1)$.

On the basis of the reasoning of Marek and Standart (1954) for associated systems, activity coefficients were calculated from the following equation:

$$\gamma_i = \frac{y_i\hat{\phi}_i P}{x_i\phi_i P_i^0} \qquad i = 1, 2 \tag{2}$$

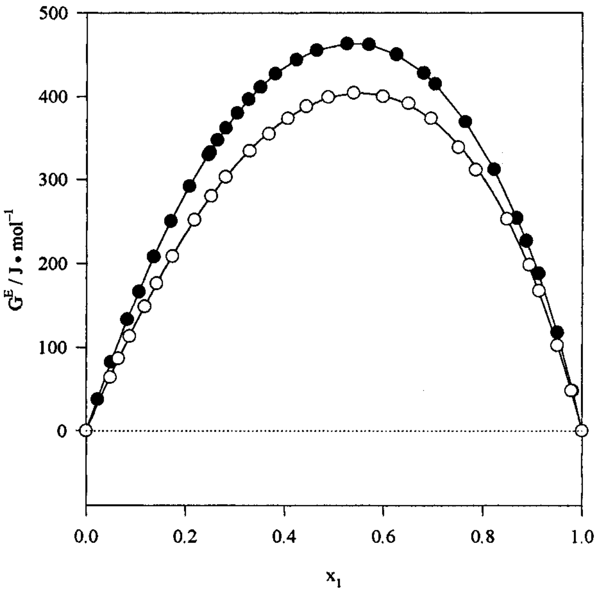

Figure 4. Excess energy function for the 2-methylpropyl ethanoate (1) + ethanoic acid (2) system (calculated as $\tilde{G}^E = RT\Sigma_i x_i \ln \gamma_i$): splined curves (—); $T = 390.15$ K (●); $T = 353.15$ K (○).

where $\hat{\phi}_i$ is the effective fugacity coefficient and ϕ_i is the pure fugacity coefficient for apparent species, whose concentrations are given by the molar fractions x_i and y_i. Fugacity coefficients were estimated by assuming dimerization of the ethanoic acid in an ideal vapor mixture of monomer, dimer, and inert component. According to these assumptions, and using the chemical theory (Prausnitz et al., 1986) for the treatment of the vapor phase, the following relations for the mechanism of ideal dimerization can be deduced (Segura et al., 1996):

$$\hat{\phi}_1 = \left(1 - \frac{1 + 4K^vPy_2 - \sqrt{(1 + 4K^vPy_2)^2 - 4K^vPy_2{}^2(1 + 4K^vP)}}{2(1 + 4K^vP)}\right)^{-1} \tag{3}$$

$$\hat{\phi}_2 = \hat{\phi}_1\left(1 - \frac{1 + 4K^vPy_2 - \sqrt{(1 + 4K^vPy_2)^2 - 4K^vPy_2{}^2(1 + 4K^vP)}}{(1 + 4K^vP)}\right) \tag{4}$$

$$\phi_1 = \lim_{y_2 \to 0} \hat{\phi}_1 = 1 \tag{5}$$

$$\phi_2 = \lim_{y_2 \to 1} \hat{\phi}_2 = \frac{2}{1 + \sqrt{1 + 4K^vP_2^0}} \tag{6}$$

In eqs 3–6, K^v is the dimerization constant for ethanoic acid, taken from the work of Fu et al. (1995).

$$\ln(K^v/\mathrm{atm}^{-1}) = -17.362 + \frac{7290}{(T/\mathrm{K})} \tag{7}$$

Figure 4 shows the excess Gibbs energy for the liquid phase at 390.15 K and 353.15 K, from the which it is concluded that only positive deviations from ideality are present in the liquid phase. According to Prausnitz et al. (1986), positive deviations in the liquid phase are expected when one of the components shows a tendency toward association; this is the case of the carboxylic acid in the 2-methylpropyl ethanoate (1) + ethanoic acid (2) system. These results show the critical role of nonidealities in the

Table 5. Binary VLE Correlation and Parameters Using the Associated Margules Model (Eqs 8−14)

T/K	A_{12}	A_{21}	ΔP/%[a]	$10^2\Delta y_1$[b]	$(\Delta P)_{max}$/%	$10^2(\Delta y_1)_{max}$
390.15	−0.1580	0.0402	0.15	0.26	0.58	0.54
353.15	−0.5119	−0.3388	0.11	0.27	0.21	1.01

[a] ΔP/%: average percent error in bubble pressure. [b] Δy_1: average absolute error in vapor phase composition.

vapor phase, because the negative azeotrope observed at 390.15 K cannot be explained in terms of the deviation of the liquid phase alone.

Both isothermal sets of data were tested for thermodynamic consistency according to the method of Fredenslund et al. (1977), with nonidealities in the vapor phase taken into account as explained above. The data were found to be consistent for a second-order Legendre polynomial, a decreasing succession of coefficients was observed for higher order polynomials.

Data Correlation. As pointed out by Prausnitz et al. (1986), the excess energy of associated solutions in the liquid phase, $\tilde{G}^E$, can be considered as an additive contribution of chemical and physical effects:

$$\tilde{G}^E = \tilde{G}^E_{chem} + \tilde{G}^E_{phys} \tag{8}$$

The excess energy, $\tilde{G}^E_{chem}$, due to the mixing of dimers and monomers plus chemical effects can be modeled from Flory's theory as a unique chemical contribution induced by dimerization:

$$\frac{\tilde{G}^E_{chem}}{RT} = x_1 \ln \frac{\Phi_1^0}{x_1} + x_2 \ln \frac{\Phi_2}{\Phi_2^* x_2} + K^L x_2(\Phi_2 - \Phi_2^*) \tag{9}$$

where Φ_2 is the true volume fraction of the monomer, Φ_2^* is the true volumetric fraction in a mixture that contains only the associating component 2, and Φ_i^0 is the apparent volumetric fraction. These parameters were calculated from the following expressions (Prausnitz, 1986):

$$\Phi_2 = \frac{1 + 2K^L\Phi_2^0 - \sqrt{1 + 4K^L\Phi_2^0}}{2(K^L)^2\Phi_2^0} \tag{10}$$

$$\Phi_2^* = \frac{1 + 2K^L - \sqrt{1 + 4K^L}}{2(K^L)^2} \tag{11}$$

$$\Phi_i^0 = \frac{x_i\tilde{v}_i}{\sum_j x_j\tilde{v}_j} \tag{12}$$

where the liquid association constant K^L was calculated using the equation suggested by Segura et al. (1996)

$$\ln K^L = -7.400 + \frac{3177}{(T/\mathrm{K})} \tag{13}$$

The physical contribution to the Gibbs excess energy, $\tilde{G}^E_{phys}$, was modeled with the Margules equation:

$$\frac{\tilde{G}^E_{phys}}{RT} = x_1x_2(A_{12}x_2 + A_{21}x_1) \tag{14}$$

Parameters and correlation statistics of the model are reported in Table 5, from where it is seen that the suggested model gives an excellent fit of the measured data, although the negative values of the Margules parameters indicate that the physical contributions to the excess Gibbs energy are negative. Generally, physical contributions to the excess energy are positive, this fact was pointed out by Prausnitz et al. (1996) who recommend a Scatchard−Hildebrand model for $\tilde{G}^E_{phys}$ in alcoholic systems. The Scatchard−Hildebrand model, however, does not give a good representation of the experimental data. In Figure 5 are shown the chemical and the physical contributions to the excess energy, where the chemical contribution was calculated from eqs 9−13 and the physical contribution was calculated from the difference between the experimental excess data and the chemical contribution. From the figure it is concluded that the physical contribution is negative in the compositional range $0 < x_1 < 0.7$, and the figure suggests also that the experimental excess data are overestimated by the chemical contribution. As pointed out by Prausnitz et al. (1986), the distinction between chemical

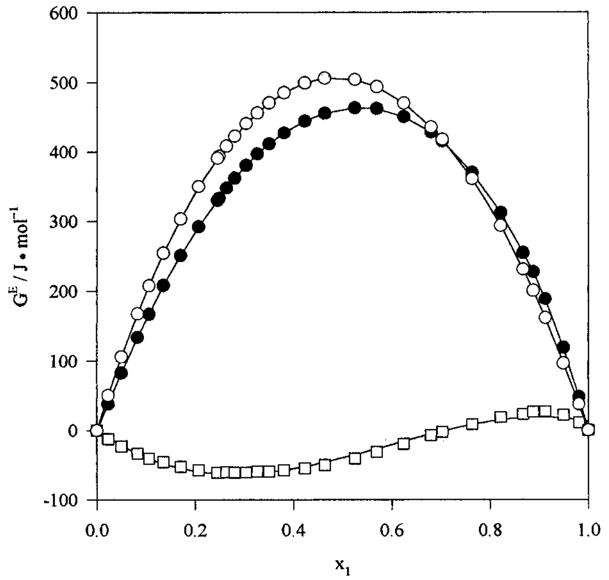

Figure 5. Chemical and physical contributions to the Gibbs excess energy: $\tilde{G}^E$ calculated from experimental data at 390.15 K (●); $\tilde{G}^E_{chem}$ calculated from eqs 9−13 (○); $\tilde{G}^E_{phys}$ (□).

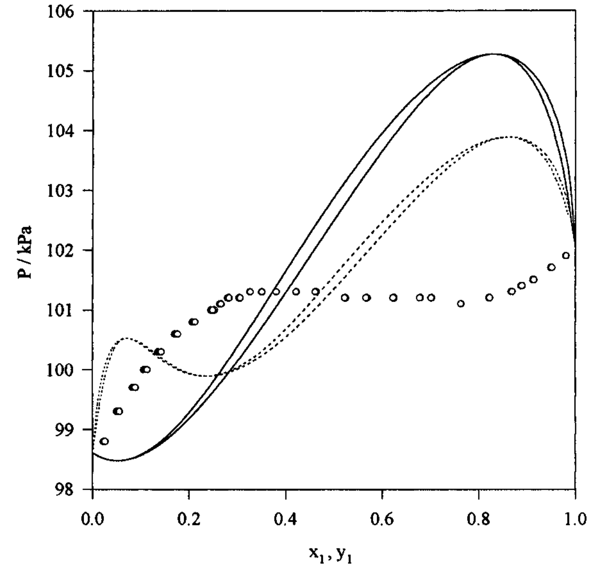

Figure 6. Interpolation of the 2-methylpropyl ethanoate (1) + ethanoic acid (2) system at 390.15 K using the UNIQUAC-A model (Fu et al., 1995) with the original self-association parameter for acetic acid and new optimum parameters U_{ij}. Case 1 (—): U_{12} = −3.74 K, U_{21} = −24.69 K. Case 2 (···): U_{12} = −427.79 K; U_{21} = 632.97 K. Experimental data (●, ○).

Table 6. Binary VLE Correlation and Parameters Using the UNIQUAC-A Model (Fu et al., 1995)

T/K	U_{12}/K	U_{21}/K	ln $\alpha^{A_2A_2}$	[ln $\alpha^{A_2A_2}$][a]	ΔP/%[b]	$10^2\Delta y_1$[c]	ΔP_{max}/%	$10^2\Delta y_{1,max}$
390.15	−231.36	263.08	3.2745	5.5306	0.27	0.10	1.50	0.21
353.15	−231.36	263.08	3.4308	6.2445	0.17	0.29	0.36	0.89

[a] As suggested, for ethanoic acid, by Fu et al. (1995). [b] ΔP/%: average perecent error in bubble pressure. [c] Δy_1: average absolute error in vapor phase composition.

and physical contributions to the excess leads to an arbitrary and, perhaps, artificial approach to associated solutions in the liquid phase but provides a reasonable and useful treatment for highly nonideal solutions.

The data were also correlated using the recent modification of the UNIQUAC model for associated solutions (UNIQUAC-A) developed by Fu et al. (1995) and based also on eq 9. The physical contribution is modeled using the UNIQUAC model (Abrams and Prausnitz, 1975), while an approximation of the Wertheim (1984a,b, 1986a,b) theory of association is used for the chemical contribution. The pertinent results appear in Figure 6. It is seen that the ethanoic acid self-association parameter ($\alpha^{A_2A_2}$) given by Fu et al. is not appropiate for the correlation of the data, because the UNIQUAC-A model does not predict the correct deviation of the azeotropes; the predicted behavior is exactly inverse of the experimental one. Furthermore, it should be realized that the optimum parameters obtained by using the original self-association parameter are not unique; multiple roots are possible, and none of them gives a satisfactory representation of the data at 390.15 K. Two of the possible solutions are shown in Figure 6. For correlation purposes, we have re-estimated the self-association parameter for the 2-methylpropyl ethanoate (1) + ethanoic acid (2) system. An excellent representation of the data is obtained, as can be seen in Table 6.

Conclusions

In this work, consistent experimental data for the isothermal VLE of the 2-methylpropyl ethanoate (1) + ethanoic acid (2) system have been determined at 353.15 K and 390.15 K. Double azeotropy is observed only at 390.15 K and can be explained in terms of association of ethanoic acid, in both the liquid and the vapor phase.

Literature Cited

Abrams, D.; Prausnitz, J. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly and Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116−128.

Barton, J. R.; Hsu, C. C. P-V-T-x Properties of Associated Vapors of Formic and Acetic Acid. *J. Chem. Eng. Data* **1969**, *14*, 184−187.

Christensen, S.; Olson, J. Phase Equilibria and Multiple Azeotropy of the Acetic Acid − Isobutyl Acetate System. *Fluid Phase Equilib.* **1992**, *79*, 187−199.

Francesconi, R.; Comelli, F.; Canepa, B. Liquid-Vapour Equilibrium with Association of Components. The Acetic Acid − Acetone and Water − Pyridine Mixtures. *Chim. Ind.* **1974**, *56*, 485−491.

Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC. A Group Contribution Method*; Elsevier: Amsterdam, 1977; pp 68−74.

Fu, Y.; Sandler, S.; Orbey, H. A Modified UNIQUAC Model That Includes Hydrogen Bonding. *Ind. Eng. Chem. Res.* **1995**, *34*, 4351−4363.

Hansen, H.; Rasmussen, P.; Fredenslund, Aa. Vapor Liquid Equilibrium by Using UNIFAC Group Contribution. 5. Revision and Extension. *Ind. Eng. Chem. Res.* **1991**, *30*, 2352−2355.

Hayden, J.; O'Connell, J. A Generalized Method for Predicting Second Virial Coefficients. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209−216.

Marek, J.; Standart, G. Effect of Association on Liquid-Vapor Equilibria. I. Equilibrium Relations for Systems Involving an Associating Component. *Collect. Czech. Chem. Commun.* **1954**, *19*, 1074−1084.

Prausnitz, J.; Lichtenthaler, R.; Azevedo, E. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice-Hall: Englewood Cliffs: NJ, 1986; pp 137−142, 333−348.

Seaton, W. Acetic Acid. *Chem. Week* **1993**, *49*, 73−100.

Sebastiani, E.; Lacquaniti, L. Acetic Acid − Water System Thermodynamical Correlation of Vapor-Liquid Equilibrium Data. *Chem. Eng. Sci.* **1967**, *22*, 1155−1162.

Segura, H.; Wisniak, J.; Aucejo, A.; Montón, J. B.; Muñoz, R. Polyazeotropy in Associated Binary Systems. *Ind. Eng. Chem. Res.* **1996**, submitted for publication.

TRC Thermodynamic Tables Hydrocarbons; Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1994.

Tsonopoulos, C.; Prausnitz, J. Fugacity Coefficients in Vapor-Phase Mixtures of Water and Carboxylic Acids. *Chem. Eng. J.* **1970**, *1*, 273−278.

Walas, S. M. *Phase Equilibria in Chemical Engineering*; Butterworth: London, 1985; pp 534−538.

Wertheim, M. S. Fluids with Highly Directional Attractive Forces. I. Statistical Thermodynamics. *J. Stat. Phys.* **1984a**, *35*, 19−34.

Wertheim, M. S. Fluids with Highly Directional Attractive Forces. II. Thermodynamic Perturbation Theory and Integral Equations. *J. Stat. Phys.* **1984b**, *35*, 35−47.

Wertheim, M. S. Fluids with Highly Directional Attractive Forces. III. Multiple Attraction Sites. *J. Stat. Phys.* **1986a**, *42*, 459−476.

Wertheim, M. S. Fluids with Highly Directional Attractive Forces. IV. Equilibrium Polymerization. *J. Stat. Phys.* **1986b**, *42*, 477−492.

Wisniak, J.; Segura, H.; Reich, R. Polyazeotropy in Binary Systems. *Ind. Eng. Chem. Res.* **1996**, in press.

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