Liquid + Liquid Equilibrium in the Ternary Systems Water + Ethanol + Dialkyl Phthalate (Dimethyl, Diethyl, and Dibutyl Phthalate) at 298.15 K

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Liquid + liquid equilibrium was determined for three ternary systems water + ethanol + dialkyl phthalates (dimethyl, diethyl, and dibutyl phthalate) at 298.15 K. The turbidimetry titration method was used to obtain the binodal curves. Direct analytical methods were used to determine the composition of coexisting phases. The critical point composition was extrapolated from equilibrium data for each of the ternary systems using the Coolidge method. Excess enthalpy data were obtained for the system dimethyl phthalate + ethanol at 298.15 K. These, along with ternary and literature binary data, allowed a thorough thermodynamic description of the system water + ethanol + dimethyl phthalate. The modified Wilson equation was employed for this purpose.

Introduction

Esters of the phthalic acid are widely used as plasticizers for cellulosic resins and some vinyl ester resins. Phthalates are considerable pollutants; they are not chemically bonded in the plastic and can therefore easily be released into the environment and materials with which they come in contact.

The present paper complements a previous work in which liquid + liquid equilibria in the binary systems water + dialkyl phthalate were studied.[1] The aim of this work was to determine liquid + liquid equilibria in three ternary systems water + ethanol + dialkyl phthalates (dimethyl, diethyl, and dibutyl phthalate) at 298.15 K. The turbidimetry titration method has been used to determine binodal curves. Direct analytical methods allowed determination of the tie lines. Garcia et al.[2] published data on liquid + liquid equilibria in the ternary systems water + ethanol + diethyl phthalate and water + ethanol + dibutyl phthalate, but these were obtained by other experimental methods (refractive index measurement). Their data are, in addition, inadequately rounded off to three decimal places only (the mole fraction of dibutyl phthalate in four tie lines is given equal to zero). Data for the system water + ethanol + dimethyl phthalate have not been found in the literature.

Another goal of this work was to determine the excess enthalpy for the system dimethyl phthalate + ethanol. This brought out some complementary information on the system and allowed us to describe thermodynamically the ternary system water + ethanol + dimethyl phthalate. Describing and predicting liquid + liquid equilibrium in systems containing components differing in molecule size often fail. Data published in this work together with those published recently (i.e., for the binary systems water + dimethyl phthalate[1] and water + ethanol[3]) can thus be utilized to test the reliability of some thermodynamic models. In this work, the experimental data obtained for the system water + ethanol + dimethyl phthalate were correlated with the modified Wilson equation.

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Experimental Section

The esters used were supplied by Sigma-Aldrich. Dimethyl phthalate [$C_{10}H_{10}O_4$ (DMP)] was used without any additional treatment, diethyl [$C_{12}H_{14}O_4$ (DEP)] and dibutyl phthalate [$C_{16}H_{22}O_4$ (DBP)] were purified by extraction with water to remove polar impurities that would affect the equilibrium. Ethanol (Merck) was used as delivered (gradient grade for the liquid chromatography), and water was deionized with a Milli-Q RG water purification system (Millipore) to achieve its resistivity of 18 MΩ cm. Purities declared by the manufacturer and the water contents in substances used in the experiments are given in Table 1. Other chemicals used were methanol (Merck, GC purity = 99%) as GC solvent and 1-propanol (HPLC grade, 99.9%, water content = 0.03 mass %) as the internal standard for the quantitative GC analysis of ethanol and as solvent for the Karl Fischer titration. 1-Decanol (98%) and methyl benzoate (99%) were used as internal standards for the quantitative GC analysis of dimethyl phthalate and diethyl phthalate, respectively. The Karl Fischer reagent was supplied by Lachema and Sigma-Aldrich.

To check the purity of the chemicals, their densities at 298.15 K were measured using an Anton Paar DMA 5000 densitometer. The densities measured were compared to literature values and are listed in Table 1.

The first step to determining the liquid + liquid equilibrium was establishing the binodal curve in the critical region using the turbidimetry titration method. Homogeneous mixtures of the respective phthalate with ethanol were prepared and then titrated with water until permanent turbidity appeared. The titration was carried out and monitored using a Metrohm DMS-Titrino 716 titrator. The method consists of measuring the transparency of the titrated mixture and in monitoring the course of the titration using a PC.

To determine the tie lines, samples of the two conjugated phases were analyzed. Phthalate and ethanol were determined in the aqueous phase and water and ethanol in the organic phase. Capillary gas chromatography was employed to determine concentrations of phthalate and etha-

Table 1. Purity, Water Content, and Density of the Measured Compounds

compd	purity[a] %	water content mass %	ρ/g·cm^{-3} this work	lit. data
DMP	99.0	0.05	1.1869	1.18675 (ref 4)
DEP	99.0	0.05	1.1137	1.1137 (ref 5)
				1.11381 (ref 6)
DBP	99.0	0.04	1.0421	1.0423 (ref 5)
ethanol	99.9	0.06	0.7853	0.78509 (ref 7)

[a] As provided by the manufacturer.

Table 2. Binodal Curve Mole Fractions for the Systems Water (1) + Ethanol (2) + Dialkyl Phthalate (3) at 298.15 K

x_1	x_2	x_3	x_1	x_2	x_3
Water (1) + Ethanol (2) + Dimethyl Phthalate (3)					
0.4211	0.2589	0.3200	0.6052	0.2650	0.1298
0.4831	0.2766	0.2403	0.6699	0.2508	0.0793
0.5132	0.2857	0.2012	0.7218	0.2266	0.0516
0.5839	0.2710	0.1451	0.7246	0.2247	0.0507
0.6044	0.2650	0.1306	0.7606	0.2064	0.0329
Water (1) + Ethanol (2) + Diethyl Phthalate (3)					
0.4117	0.3840	0.2043	0.5997	0.3298	0.0705
0.4890	0.3706	0.1404	0.6759	0.2865	0.0376
0.5277	0.3569	0.1154	0.6858	0.2808	0.0334
0.5812	0.3370	0.0818	0.6931	0.2765	0.0304
Water (1) + Ethanol (2) + Dibutyl Phthalate (3)					
0.2806	0.4747	0.2447	0.4348	0.4845	0.0807
0.3323	0.4903	0.1774	0.4539	0.4728	0.0733
0.3738	0.4732	0.1530	0.4660	0.4699	0.0641
0.4062	0.4893	0.1045	0.4779	0.4669	0.0552
0.4249	0.4769	0.0982	0.4862	0.4661	0.0477

nol, and Karl Fischer titration permitted the concentration of water to be obtained. Water content in the aqueous phase and phthalate content in the organic phase can be calculated to make up the mole fraction equal to 1.

Heterogeneous mixtures for sampling were prepared in a thermostated equilibrium cell.[8] The liquid mixture was thermostated to 298.15 K, agitated for at least 8 h, and then allowed to stand for at least 24 h to allow the two phases to separate. Samples of each phase were then analyzed. As the composition of the phases approached the critical point, sampling became more difficult. Samples tended to split into two phases in the sampling pipet due to a temperature change. This prevented measurements in the immediate vicinity of the critical point.

An HP 6890 gas chromatograph was utilized for the GC analysis. The parameters of analyses were reported in a previous work.[9] The chromatograph was calibrated with methanol solutions of known concentrations of both substances (dialkyl phthalate and ethanol) and their corresponding internal standards, and the acquired data were fit to a calibration equation. Samples were then diluted with methanol to adjust their compositions approximately to those of calibration mixtures. Samples for the determination of the water content were diluted with 1-propanol of known water content to prevent phase separation due to the temperature changes.

Excess enthalpies for the system dimethyl phthalate + ethanol were determined at 298.15 K using a Hart 4410 microcalorimeter with continuous-flow mixing cells (model 4442) and modified high-pressure HPP 5001 pumps from Laboratorní přístroje. Calibration of the calorimeter was carried out by measuring the excess enthalpy for the reference systems hexane + cyclohexane and methanol + water. The accuracy of the apparatus was found to be ~1%. Excess enthalpies in the remaining two binary systems

Table 3. Conjugated Phases Mole Fractions for the Systems Water (1) + Ethanol (2) + Dialkyl Phthalate (3) at 298.15 K

aqueous phase		organic phase	
x_2'	x_3'	x_1''	x_2''
Water (1) + Ethanol (2) + Dimethyl Phthalate (3)			
0.0211	5.59×10^{-4}	0.1611	0.0315
0.0325	6.22×10^{-4}	0.1648	0.0498
0.0501	8.12×10^{-4}	0.1898	0.0785
0.0763	1.35×10^{-3}	0.2193	0.1258
0.0981	2.32×10^{-3}	0.2667	0.1669
0.1228	3.94×10^{-3}	0.3186	0.2140
0.1292	4.45×10^{-3}	0.3304	0.2196
0.1492	7.63×10^{-3}	0.3590	0.2361
0.1753	1.48×10^{-2}	0.4525	0.2727
0.2272	4.90×10^{-2}	0.6112	0.2611
0.2278	4.89×10^{-2}	0.5979	0.2690
0.2377	6.10×10^{-2}	0.6612	0.2425
Water (1) + Ethanol (2) + Diethyl Phthalate (3)			
0.0307	1.51×10^{-4}	0.1205	0.0518
0.0520	1.95×10^{-4}	0.1262	0.0827
0.0529	2.07×10^{-4}	0.1332	0.0915
0.0811	3.88×10^{-4}	0.1567	0.1346
0.0931	3.77×10^{-4}	0.1688	0.1555
0.1170	7.71×10^{-4}	0.2044	0.2190
0.1459	1.59×10^{-3}	0.2339	0.2601
0.1499	1.94×10^{-3}	0.2522	0.2727
0.1709	3.00×10^{-3}	0.2726	0.3025
0.1970	5.48×10^{-3}	0.3122	0.3331
0.2222	9.57×10^{-3}	0.3392	0.3650
0.2393	1.26×10^{-2}	0.4030	0.3612
0.2442	1.43×10^{-2}	0.4160	0.3590
0.2806	3.09×10^{-2}	0.5150	0.3452
Water (1) + Ethanol (2) + Dibutyl Phthalate (3)			
6.73×10^{-3}	1.12×10^{-6}	0.0659	0.00938
7.51×10^{-3}	3.80×10^{-6}	0.0673	0.0115
0.0193	1.75×10^{-5}	0.0687	0.0260
0.0320	2.16×10^{-5}	0.0719	0.0436
0.0697	1.02×10^{-5}	0.0824	0.0930
0.1008	1.18×10^{-5}	0.0943	0.1528
0.1363	7.18×10^{-5}	0.1117	0.2148
0.2107	5.00×10^{-4}	0.1404	0.2911
0.2439	9.64×10^{-4}	0.1533	0.3220
0.2708	1.76×10^{-3}	0.1656	0.3469
0.3095	2.72×10^{-3}	0.1806	0.3702
0.3326	3.70×10^{-3}	0.1876	0.3868
0.4180	1.04×10^{-2}	0.2279	0.4437
0.4423	1.45×10^{-2}	0.2494	0.4561

Table 4. Critical Point Composition for the Systems Water + Ethanol + Dialkyl Phthalate at 298.15 K Extrapolated by the Coolidge Method

system	x_1	x_2	x_3
water (1) + ethanol (2) + DMP (3)	0.6729	0.2479	0.0792
water (1) + ethanol (2) + DEP (3)	0.6038	0.3284	0.0678
water (1) + ethanol (2) + DBP (3)	0.4276	0.4815	0.0909

(i.e., diethyl phthalate + ethanol and dibutyl phthalate + ethanol) were not measured because of the high viscosity of the two phthalates. Detailed description of the instrument and its calibration are given elsewhere.[10]

Results and Discussion

Binodal curves and tie lines were determined for the ternary systems water + ethanol + dimethyl phthalate, water + ethanol + diethyl phthalate, and water + ethanol + dibutyl phthalate at 298.15 K and atmospheric pressure. Binodal curve data are summed in Table 2, and tie-line data are compiled in Table 3.

Experimental uncertainties evaluated from the acquired data are ±0.8% for the GC determination of ethanol, ±0.9% for dimethyl phthalate, ±1.7% for diethyl phthalate, and ±2.9% for dibutyl phthalate. The uncertainty of the deter-
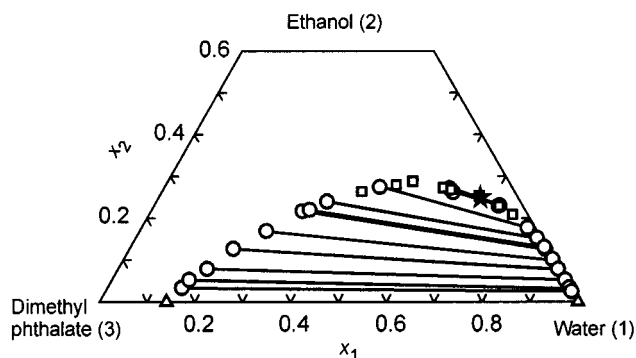
Figure 1. Liquid + liquid equilibrium data for the system water (1) + ethanol (2) + dimethyl phthalate (3) at 298.15 K: □, binodal curve data; ○, tie-line data; △, ref 1; s★, critical point.
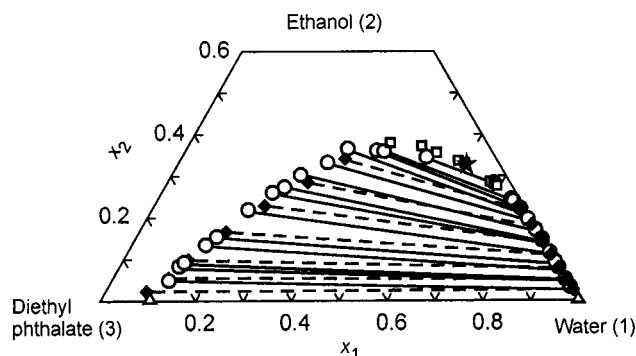

Figure 2. Liquid + liquid equilibrium data for the system water (1) + ethanol (2) + diethyl phthalate (3) at 298.15 K: □, binodal curve data; ○, tie-line data; △, ref 1; ◆, ref 2; ★, critical point.
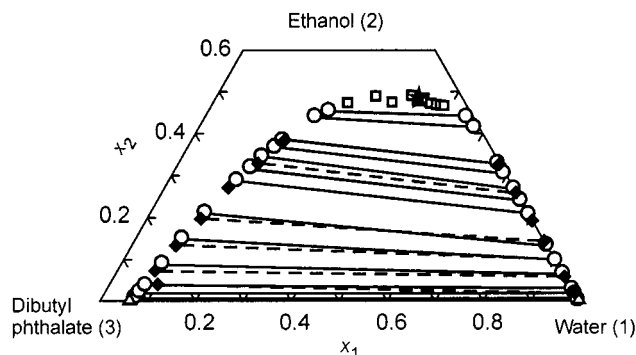

Figure 3.
Liquid + liquid equilibrium data for the system water (1) + ethanol (2) + dibutyl phthalate (3) at 298.15 K: □, binodal curve data; ○, tie-line data; △, ref 1; ◆, ref 2; ★, critical point.

mination of water content in samples of the organic phase by the Karl Fischer titration was evaluated to be ±0.6%.

Tie-line data were used to extrapolate the composition of the critical point of each studied ternary using a method proposed by Coolidge.[11] The method consists of constructing two triangles over each tie line, with sides parallel with the axes of the ternary diagram. A smooth curve connecting the apexes of the triangles intersects the binodal curve in the critical point. The calculated critical-point compositions for each ternary are in Table 4. Both experimental and calculated data are presented in Figures 1–3.

Obtained results were compared with those by Garcia et al.[2] Good agreement was observed for the system water + ethanol + dibutyl phthalate, but small differences

Table 5. Excess Enthalpy Data for the System Ethanol (1) + Dimethyl Phthalate (2) at 298.15 K

x_1	H_m^E/J mol^{-1}	x_1	H_m^E/J mol^{-1}	x_1	H_m^E/J mol^{-1}
0.1284	847	0.6506	1688	0.8667	922
0.2370	1330	0.7363	1487	0.9175	674
0.2372	1339	0.7364	1489	0.9404	521
0.3306	1607	0.7365	1489	0.9613	350
0.4114	1771	0.7367	1457	0.9615	356
0.4117	1730	0.7368	1463	0.9813	182
0.5450	1814	0.8072	1264		

between our data and the literature data could be observed in the system water + ethanol + diethyl phthalate. Our results correspond better to binary data published in a preceding paper[1] (see Figures 2 and 3). Moreover, Garcia et al.[2] rounded off their data to three decimal places only, and thus some of the values are given as equal to zero.

Excess enthalpies were determined at 298.15 K in the system dimethyl phthalate + ethanol. The results are compiled in Table 5 and shown in Figure 4. Relatively high viscosity of the phthalate and a higher difference in densities may have contributed to a rather imperfect mixing of the two compounds in the mixing cells and thus could have led to a higher measurement uncertainty. Excess enthalpies at various flow rates were measured. Uncertainty of ~10% was determined from these measurements.

Correlation of the Experimental Data

The experimental data were correlated (i.e., thermodynamically described) using the modified Wilson equation, which includes the original Wilson equation,[12] the Redlich–Kister[13] equation, and a ternary term[14] and describes the temperature and the composition dependence of the excess Gibbs energy in an N-component system:

$$Q = G^E/(RT) = Q_W + Q_{RK} + Q_T \tag{1}$$

$$Q_W = -\sum_{i=1}^{N} x_i \ln \sum_{j=1}^{N} x_j (V_j/V_i) \exp(-a_{ij}/T^*) \tag{2}$$

$$Q_{RK} = \sum_{i=1}^{N-1} \sum_{j>i}^{N} x_i x_j \sum_{k=1}^{n_{ij}} B_{ijk}(x_i - x_j)^{k-1} \tag{3}$$

$$Q_T = \sum_{i=1}^{N-2} \sum_{j>i}^{N-1} \sum_{k>j}^{N} x_i x_j x_k (C_{ijki} x_i + C_{ijkj} x_j + C_{ijkk} x_k) \tag{4}$$

$$\alpha_{ij} = \alpha_{ij} + \beta_{ij} T^* + \gamma_{ij}/T^* \tag{5}$$

$$B_{ijk} = \alpha_{ijk} + \beta_{ijk} T^* + \gamma_{ijk}/T^* \tag{6}$$

where Q is the dimensionless excess Gibbs energy, Q_W is the Wilson term, Q_{RK} is the Redlich–Kister term, Q_T is the ternary term, α_{ij}, β_{ij}, γ_{ij}, α_{ijk}, β_{ijk}, and γ_{ijk} are temperature-independent binary parameters, C_{ijki} are temperature-independent ternary parameters, and V_j and x_i are molar volumes and mole fractions of the individual components, respectively. The number of parameters n_{ij} of the Redlich–Kister term depends on the system to be correlated. A temperature transformation $T^* = T/T_{ref}$ was introduced to improve the numerical stability of the calculation. In this work $T_{ref} = 300$ K was used. Equations 5 and 6 express the general temperature dependence of the model parameters. Depending on the data to be correlated, either β_{ij} or γ_{ij} is put equal to zero.
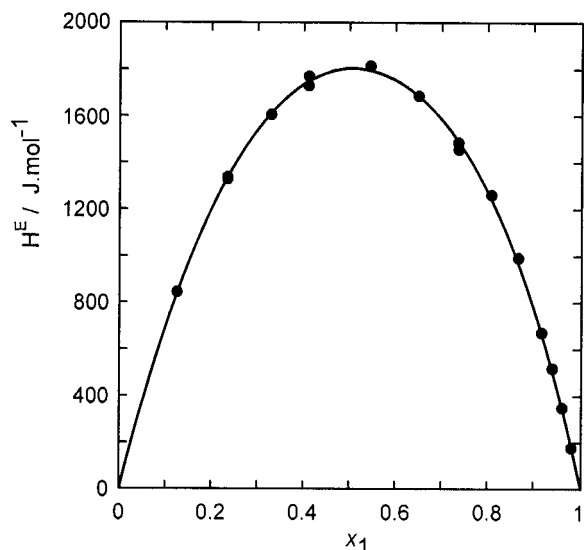
Figure 4. Experimental excess enthalpy data and correlation for the system ethanol (1) + dimethyl phthalate (2).
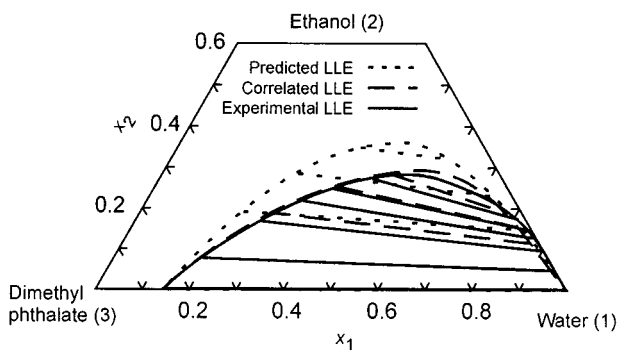

Figure 5. Experimental liquid + liquid equilibrium data, prediction, and correlation for the system water (1) + ethanol (2) + dimethyl phthalate (3).

Table 6. Parameters of the Modified Wilson Equation for the System Water (1) + Ethanol (2) + Dimethyl Phthalate (3)

Water (1) + Ethanol (2)	
$\beta_{12} = 1.1778^a$	
$\beta_{21} = -1.1778^a$	
$\alpha_{121} = 1.8177$	$\gamma_{121} = -0.62637$
$\alpha_{122} = 0.96752$	$\gamma_{122} = -0.64605$
$\alpha_{123} = 1.7117$	$\gamma_{123} = -1.7495$
$\alpha_{124} = 1.2780$	$\gamma_{124} = -1.3484$
Water (1) + Dimethyl Phthalate (3)[1]	
$\alpha_{13} = 2.3040$	$\gamma_{13} = 0.4000$
$\alpha_{31} = 10.308$	$\gamma_{31} = -5.5825$
$\alpha_{131} = 0.99718$	
Ethanol (2) + Dimethyl Phthalate (3)	
$\alpha_{23} = 2.7148$	$\beta_{23} = -1.2988$
$\alpha_{32} = 2.3961$	$\beta_{32} = -1.7192$
Water (1) + Ethanol (2) + Dimethyl Phthalate (3)	
$C_{1231} = -1.32$	$C_{1233} = 0.13$
$C_{1232} = -2.31$	

^{a} Constant values that eliminate the Wilson part Q_W.

the least-squares method. The maximum-likelihood method consists of minimizing the objective function F

$$F = \sum_i \sum_j \left(\frac{\nu_j^{\text{exptl}} - \nu_j^{\text{calcd}}}{\sigma_{\nu_j}} \right)_i^2 \qquad (7)$$

where ν_j^{exptl} and ν_j^{calcd} are the experimental and calculated values of the variable j, respectively, and σ_{ν_j} is the estimated standard deviation of the variable j. The summation comprises all of the available variables j (e.g., temperature, composition, pressure, and heat) and all of the experimental points i. Thus, the sum can include liquid + liquid equilibrium, vapor + liquid equilibrium, excess enthalpy, and activity coefficient data, which enables the best possible thermodynamic description of the studied system.

The calculated model parameters are compiled in Table 6. First, binary subsystems of the ternary system water + ethanol + dimethyl phthalate were correlated. Correlation of the binary system water + dimethyl phthalate has already been carried out in a previous work[1] using liquid + liquid equilibrium data. In the present paper correlation

The maximum-likelihood method[14] was employed to calculate the binary parameters α_{ij}, β_{ij}, γ_{ij}, α_{ijk}, β_{ijk}, and γ_{ijk}. The ternary parameters C_{ijki} were calculated by means of
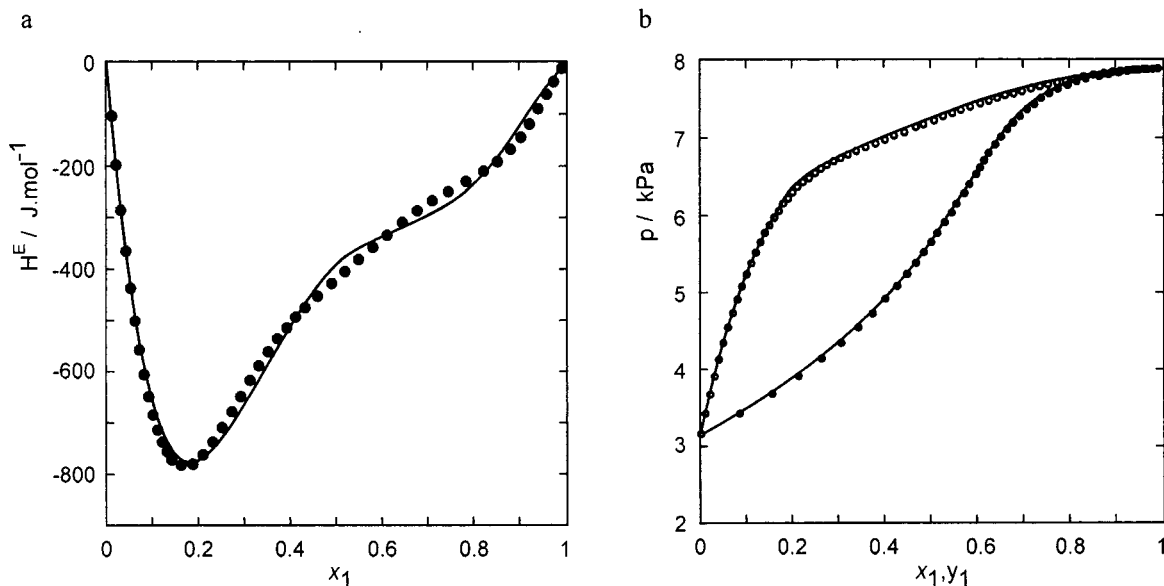
a

b

Figure 6. Correlation of excess enthalpy (a) and vapor + liquid equilibrium (b) data for the system ethanol (1) + water (2).

parameters for the binary subsystems water + ethanol and ethanol + dimethyl phthalate have been obtained. To correlate the binary system water + ethanol, literature VLE and H^E data[3] at 298.15 K were employed. The results of the correlation and the experimental results are shown in Figure 6. The binary system ethanol + dimethyl phthalate was correlated using the present excess enthalpy data (see Figure 4).

Before the correlation of the ternary system itself, liquid + liquid equilibrium for the ternary was predicted from the binary parameters only. This led to a little larger heterogeneous region and slightly different tie-line slopes compared with the experimental results. When the ternary term was involved in the correlation, very good agreement between the experimental and calculated data was obtained. Correlating ternary liquid + liquid equilibrium data with binary terms being maintained constant permitted obtaining ternary parameters of the model equation. The correlation parameters obtained are summarized in Table 6. Experimental, predicted, and correlated liquid + liquid equilibria are compared in Figure 5.

Conclusion

Liquid + liquid equilibrium data for the ternary systems water + ethanol + dimethyl (diethyl, dibutyl) phthalate have been acquired by two different methods: shapes of binodal curves were determined using the turbidimetry titration method, and direct analytical methods allowed the determination of tie lines. As is evident from Figures 1−3, the results obtained by the two methods are in good mutual agreement, and hence these methods are suitable for the determination of the liquid + liquid equilibrium.

Excess enthalpy data for the binary system dimethyl phthalate + ethanol at 298.15 K have been obtained. These data together with VLE data[3] (water + ethanol) and LLE data[1] (water + DMP) permitted the thermodynamic description of the ternary system water + ethanol + DMP to be undertaken. The modified Wilson equation appeared to correlate the binary subsystems very well and has therefore been employed. The subsequent use of the ternary parameters led to a very good thermodynamic description of the above-mentioned ternary system. Very few ternary systems containing both volatile (ethanol) and nonvolatile components for which all three binary subsystems have been thoroughly studied exist, and this system is one of them.

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