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Vapor–Liquid and Liquid–Liquid Equilibria for the Toluene + 1,2-Propanediol + Water System

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Vapor–liquid (VLE) and liquid–liquid (LLE) equilibria for the toluene + 1,2-propanediol + water system and the connected binaries have been measured, and the parameters of a thermodynamic model suitable for the description of the system and for the simulation of a multistage separation unit have been derived. The activity coefficients at infinite dilution were determined using GLC, exponential dilutor, and ebulliometry techniques. Comparison was made with previous literature results and from extrapolation of precise VLE results over the composition range determined using a computer-operated differential static apparatus at 303.81 and 343.73 K. In addition, some ternary LLE tie lines at 298.15 K were measured as well as a few ternary vapor–liquid–liquid equilibrium data at other temperatures. Regression analysis of the data was carried out to obtain UNIQUAC temperature-dependent binary interaction parameters. These parameters were used to model the three-phase distillation column with the help of a commercial process simulator.

Introduction

The removal of water from an esterification reactor is a crucial problem for obtaining a proper reaction product and a good conversion. Particularly, in the production of polyesters the removal of water is mostly performed by the addition of an aromatic solvent (toluene or xylene). The heterogeneous azeotrope is then directly removed from the stirred vessel using a distillation column situated on the top of the reactor. Optimization of the separation step represents optimization of the whole polycondensation process.

The thermodynamics of such systems is highly nonideal, with equilibrium constants K_x exhibiting a strong dependence on liquid compositions as well as on temperature. Because of the complexity of the system, thermodynamic information over a wide temperature and composition range was required. The distillation path was assumed to move from the homogeneous 1,2-propanediol-rich region in the bottom of the column toward higher concentrations of water and toluene at the top, where two partially miscible liquid phases are observed.

In order to reproduce this complex behavior over a wide temperature (357.15–433.15 K) and concentration range, including the description of vapor and two liquid phases, good thermodynamic model parameters are needed. To ensure the internal consistency of the experimental information, a large set of data (binary and ternary) was measured using a variety of experimental techniques.

Experimental Section

Toluene and 1,2-propanediol (both GLC purity) were fractionated through a 40 theoretical plate column, and the middle fraction was collected, boiled over a ±0.02 K range, and subsequently dried over molecular sieves. The water used was bidistilled. The water content in the 1,2-propanediol was determined by a Karl Fisher titration accurate to 0.002% (w).

A number of techniques were used to measure the binary and ternary equilibrium in the temperature and concentration range studied.

Ternary liquid–liquid equilibria (LLE) at 298.15 K exhibit a phase diagram of type II with a narrow homogeneous region on the 1,2-propanediol side of the triangle. On the assumption that the liquid phase at two points in the column (top and bottom) consists only of one component with small amounts of the others, a decision was made to measure activity coefficients at infinite dilution at different temperatures. Various methods (GLC, dilutor, ebulliometry) were used according to the applicability of the methods to a particular binary system at the chosen temperature.

The activity coefficient is not a directly measured quantity. In all cases, direct quantities were measured and the error propagation law has been applied for estimating the uncertainty in γ^∞.

Gas/Liquid Chromatographic Method. Activity coefficients at infinite dilution were measured using the GLC method for the binary system toluene (solute) + 1,2-propanediol (solvent) at temperatures lower than 298.15 K where the vapor pressure of the solvent still did not exceed 0.027 kPa.

The GC column (2 m length, inner diameter 4 mm) containing the solid support (Chromosorb R WHP) coated with 1,2-propanediol was held in a constant-temperature (±0.1 K) water bath at four different temperatures: 283.15, 288.15, 293.15, and 298.15 K. Temperature was measured by a digital precision platinum resistance thermometer (Systemteknik, model S-1220), calibrated against a platinum resistance thermometer Pt25 (Rosemount, model 163 CE) with an accuracy of ±0.02 K. The retention time of the solute, injected into the column by means of a syringe, was determined. The measured parameters (*1*) were column temperature, ambient temperature, the inlet column pressure, the outlet column pressure, carrier gas flow rate, the amount of stationary phase without the solid support, and the retention time of the inert gas (dead time). The vapor-phase corrections were applied to the GLC data measured. The uncertainty of the results obtained with this method is estimated to be less than 3%.

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Dilutor Technique. The infinite dilution activity coefficients for toluene in 1,2-propanediol at different temperatures (298.15, 313.15, and 333.15 K) were measured with the dilutor technique. About 23 cm^3 of solvent was introduced into the equilibrium still, and the liquid solute was injected (10 μL syringe) through the septum. The carrier gas passed through a capillary system in order to be dispersed into small bubbles. The carrier gas was introduced into the thermostated equilibrium cell at a chosen flow rate, controlled by a needle valve. The pressure drop between the needle valve and the still was measured by a pressure gauge. The flow rate was kept within the range of 45–85 $cm^3\ min^{-1}$. The still was thermostated to ±0.1 K; the gas outlet and gas-sampling valve were wrapped with heating tape and held at a higher temperature in order to avoid condensation of vapors from the carrier gas sample stream. The valve was connected to a gas chromatograph, Carlo Erba GC 6000 Vega Series, equipped with a HWD detector and a Shimadzu integrator. The equilibrium temperature was measured by a digital precision platinum resistance thermometer (Systemteknik, model S-1220); see above.

The variation of the solute peak area with time, the initial amount of solvent introduced into the cell, the carrier gas flow rate, the temperature of the solvent in the still, and the volume of the vapor phase in the still had to be known for the calculation of the activity coefficient (*2*). The uncertainty of the results obtained with this method is estimated to be less than 3%.

Differential Ebulliometry. An ebulliometer allowing sampling of both the liquid and gas phases was used, using the technique of Malanowski and Rogalski (*3*). Temperature was measured by a digital precision platinum resistance thermometer (Systemteknik, model S-1220); see above. Pressure was measured by a quartz Bourdon tube pressure gauge (Battara, model 100) with an accuracy of ±0.02 kPa and maintained at its set point by an electric pressure controller (Battara, model 101).

Measurements were made for water (solvent) + 1,2-propanediol (solute) at two pressures (40.0 and 80.0 kPa). Because of the small effect of 1,2-propanediol on the total pressure above the mixture, relatively high concentrations of 1,2-propandiol in water were used. The results were treated as described in ref 4 to obtain γ^∞. The uncertainty of the results obtained with this method is estimated to be less than 2%.

Ternary LLE Measurements. The ternary mixtures were equilibrated in a water bath at 298.15 ± 0.1 K by agitation with a magnetic stirrer for at least 2 h, followed by a settling period of 20 h. The glass equilibrium cells used are described elsewhere (Kikic et al. (*5*)). For each phase, a minimum of three samples were withdrawn for GLC analysis by means of a syringe. The mixtures were analyzed by a gas chromatographic thermal conductivity detector (Carlo Erba GC 6000 Vega Series, ICU 600, and Shimadzu Chromatopac E-1A integrator). A Porapac Q column at 453.15 K was used. The helium gas flow rate was set to 50 $cm^3\ min^{-1}$. The chromatographic factors were determined for mixtures of known composition. All chemicals used were GLC quality and were preliminarily treated. No detectable impurities were revealed by GLC analysis. The determination of the conjugate phases was carried out at 298.15 K.

Ternary VLLE Measurements. The vapor–liquid–liquid equilibrium (VLLE) for toluene + 1,2-propanediol + water was investigated using a semistatic glass cell (Figure 1) placed in the thermostated chamber, allowing direct GLC analysis of the vapor and of two liquid phases. The components were not degassed, and the equilibrium total pressure was calculated. The vapor phase was sampled by a very small flow of nitrogen, directed through the vapor space of the cell. The cell was connected to a GC by a short capillary and sampling valve, both wrapped with a heating tape in order to prevent any condensation of the components in the vapor phase.

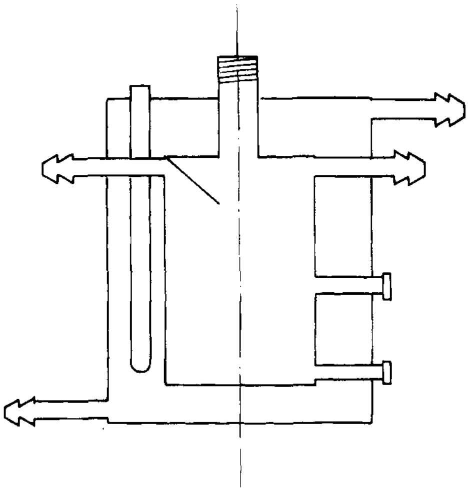

Figure 1. Scheme of the semistatic glass cell.

The constructed cell was first tested on acetonitrile + heptane + benzene at 318.15 K, for already known compositions of two liquid phases and one vapor phase. The results were in good agreement with those from the literature (*6*).

Toluene + 1,2-propanediol + water was investigated at 313.15, 333.15, and 343.15 K (±0.1 K) for two different total compositions.

Ternary VLE Measurements. A set of experiments with the ternary system was carried out on a computer-operated differential static apparatus, designed and constructed by Rarey (*7*). The apparatus can be used to obtain very precise measurements of binary and ternary vapor–liquid equilibrium (VLE) up to 100 kPa differential pressure. Additionally, activity coefficients at infinite dilution, gas solubilities, pure component vapor pressure data, and isothermal compressibilities of liquids can be determined.

Experiments were performed for three different initial compositions of the binary mixture 1,2-propanediol + water, loaded into the equilibrium cell of volume 68.0 cm^3 and immersed into a thermostated oil bath, at two temperatures, 303.15 and 343.15 K.

For these measurements the pure components were further purified by distillation with simultaneous degassing. The degassing procedure described by Kolbe and Gmehling (*8*) was used. The degassed 1,2-propanediol and water were transferred to the equilibrium cell by using a common manifold, previously evacuated in order to prevent contamination. The initial composition of the binary mixture was determined by mass, and a small sample was taken for water determination (Karl Fischer). The mixture was loaded into the piston injector and was first compressed to 1 MPa to prevent contamination with air. Then it was compressed several times to 1.8 MPa to obtain the rough compressibility of the mixture. The injection procedure described by Rarey (*7*) was used. The piston in the pump was moved by a high-resolution stepping motor, with an accuracy of injected volumes of $\pm 1 \times 10^{-6}$ dm^3. The injected volume was calculated from the difference in motor steps.

The pump was carefully cleaned and evacuated. The third degassed component (toluene) was injected several

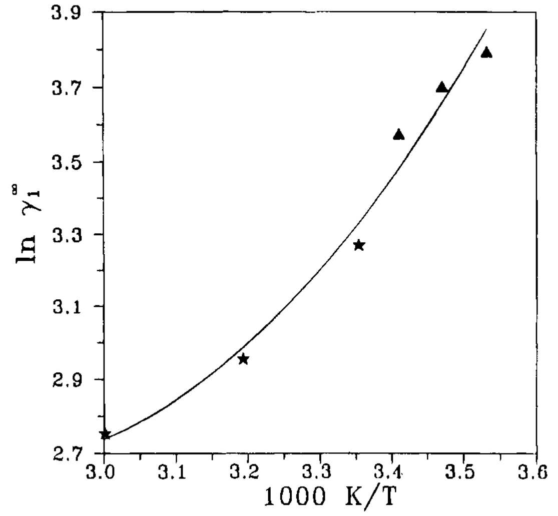

Figure 2. Activity coefficients of toluene (1) in 1,2-propanediol (2) at infinite dilution by (△) GLC and (*) dilutor techniques.

Table 1. Data Available from the Literature

system	source	type of data	*T* range/K
toluene + 1,2-propanediol	12	LLE	305.15–380.15
	1	activity coefficients	316.15–324.15
toluene + water	13	LLE (water-rich phase)	273.15–473.55
		LLE (toluene-rich phase)	264.15–473.55
water + 1,2-propanediol	14	VLE	291.15–414.15

Table 2. Data Measured in This Work

type of data	technique	*T* range/K
γ^∞ (toluene in 1,2-propanediol)	GLC, dilutor	283.15–333.15
γ^∞ (1,2-propanediol in water)	ebulliometry	349.15–366.15
γ^∞ (1,2-propanediol in toluene)	ebulliometry	351.15–375.15
ternary LLE		298.15
ternary VLLE	semistatic method	313.15–343.15
ternary VLE	diff. static method	303.15–343.15

times, using the second feed capillary to the cell. Very small increments of toluene were injected in order to reach the onset of the miscibility gap, observed by a computer plot of the total *P* against the approximate liquid composition in the cell.

After each experiment, components from the cell were removed by means of a water pump and the whole apparatus was rinsed first with water and then with acetone and kept under vacuum. The uncertainties of the method are ±0.005 K, ±2 Pa, and 0.0001 mole fraction.

Results and Discussion

The binary data available from the literature are given in Table 1. The data measured in this work are summarized in Table 2.

Activity coefficients of toluene (1) in 1,2-propanediol (2) at infinite dilution were measured using the GLC and dilutor technique. Strong temperature dependence was observed (Figure 2 and Table 3). The only measurements reported in the literature are those of Leitman et al. (*9*), using the gas liquid chromatographic method at 316.15 and 324.15 K. They did not make vapor-phase corrections. The measured values of γ_1^∞ in 1,2-propanediol are lower than those given by Leitman et al. One reason could be the purity of the 1,2-propanediol, since the presence of water considerably affects the value of γ_1^∞. The second reason may be the method used for measuring γ_1^∞ at higher temperatures. Table 9 clearly demonstrates the temperature dependence of γ_1^∞ in 1,2-propanediol + water for three different initial binary compositions. Increasing the amount of water in the binary 1,2-propanediol + water mixture causes a significant increase of the activity coefficient of toluene in the binary mixture at infinite dilution. Activity coefficients of toluene at infinite dilution in 1,2-propanediol, measured in this work (Table 3), are in good agreement with those calculated from the experimental ternary VLE results.

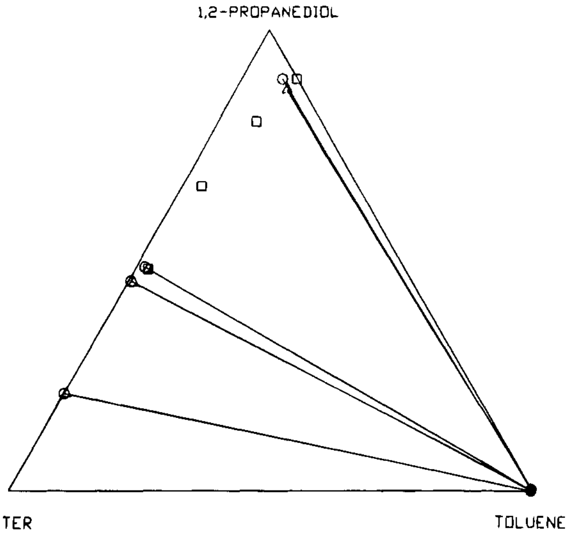

Figure 3. Toluene (1) + 1,2-propanediol (2) + water (3) LLE at 298.15 K: (○) LLE results at 298.15 K; (△) UNIQUAC model at 298.15 K; (□) solubility data from ternary VLE data measurements at 303.15 K.

Table 3. Activity Coefficient at Infinite Dilution of Toluene (1) in 1,2-Propanediol (2)

T/K	γ_1^∞	V_g/(cm^3·g^{-1})	*P*/kPa	method
283.15	44.4	403.97	101.25	GLC
288.15	40.5	331.69	101.25	GLC
293.15	35.7	270.60	101.25	GLC
298.15	26.3			dilutor
313.15	19.2			dilutor
333.15	15.7			dilutor

Table 4. Activity Coefficient at Infinite Dilution of 1,2-Propanediol (2) in Water (3) and in Toluene (1) Obtained by the Ebulliometric Method

solvent	*T*/K	*P*/kPa	γ_2^∞
water	366.45	80.0	2.97
	349.91	40.0	2.63
toluene	351.15	20.0	30.00
	375.15	40.0	34.50

The activity coefficients at infinite dilution of 1,2-propanediol in water and in toluene were measured at two temperatures (Table 4), using differential ebulliometry. Activity coefficients of 1,2-propanediol in water are small and do not show a strong temperature dependence, while activity coefficients of 1,2-propanediol in toluene are much larger.

Good agreement was observed between the solubility data of toluene in 1,2-propanediol + water determined from the ternary VLE data measurements at 293.15 K and the directly measured LLE (Figure 3).

G^E model parameters for the description of the behavior of toluene + 1,2-propanediol + water, based on the binary results such as activity coefficients at infinite dilution, solubility data of toluene + water and toluene + 1,2-propanediol and VLE for water + 1,2-propanediol, did not give satisfactory results. It was necessary to include some

Table 5. Experimental LLE Tie Lines for the System Toluene (1) + 1,2-Propanediol (2) + Water (3) at 298.15 K

x_2		x_3	
phase 1	phase 2	phase 1	phase 2
0.8934	0.0046	0.0285	0.0000
0.4602	0.0020	0.5354	0.0015
0.4903	0.0030	0.4934	0.0010
0.2133	0.0010	0.7862	0.0020

Table 6. Experimental VLLE Data for the System Toluene (1) + 1,2-Propanediol (2) + Water (3)

	x_1		x_2	x_3		
T/K	L_2 phase	V phase	L_1 phase	L_1 phase	L_2 phase	V phase
313.45	0.9958	0.7148	0.2919	0.7071	0.0042	0.2851
333.55	0.9930	0.6391	0.2922	0.7054	0.0070	0.3608
343.35	0.9895	0.5235	0.2851	0.7096	0.0104	0.4764
313.45	0.9965	0.3928	0.5846	0.3994	0.0035	0.3927
333.55	0.9863	0.3792	0.5940	0.3835	0.0060	0.3791
343.35	0.9779	0.6253	0.5858	0.3880	0.0067	0.3746

Table 7. UNIQUAC Parameters

binary system	a_{ij}	b_{ij}	a_{ji}	b_{ji}
1,2-propanediol (2) + toluene (1)	−0.7183	228.92	4.7438	−2056.10
water (3) + toluene (1)	−1.9925	254.44	6.7935	−3039.50
1,2-propanediol (2) + water (3)	−0.2505	−235.87	0.5092	126.59

ternary data in the data reduction procedure (*10*). Additional ternary data such as LLE, VLLE, and VLE were therefore measured. Activity coefficients at infinite dilution were used as a quality check of the chosen G^E model.

Measurements of LLE on the conjugate phases were made at 298.15 K and are reported in Table 5. Figure 3 gives a graphical comparison between experimental binodal curves and binodal curves predicted by the UNIQUAC method with temperature-dependent interaction parameters, obtained from the data reduction procedure. The UNIQUAC interaction parameters are defined as follows:

$$\tau_{ij} = \exp(a_{ij} + b_{ij}/T) = \exp(\Delta u_{ij}/RT) \qquad (1)$$

The main reason for using UNIQUAC temperature-dependent interaction parameters was the very strong temperature dependence of solubilities (1,2-propanediol in toluene, toluene in 1,2-propanediol). These parameters allow a better description of the liquid phase. VLLE results for the toluene + 1,2-propanediol + water system are given in Table 6. Table 8 reports the experimental VLE results for toluene (1) + 1,2-propanediol (2) + water (3).

Total vapor pressure measurements on the system toluene (1) + 1,2-propanediol (2) + water (3) at two different temperatures (293.15 and 343.15 K) and different initial compositions of the binary system 1,2-propanediol + water, with respect to the toluene added to the system, are presented in Figure 4. This figure shows the effect of temperature and composition on the miscibility gap. These results are in good agreement with the measured ternary LLE results. The results were fitted using a Legendre polynominal as described by Kolbe and Gmehling (*8*). Calculated activity coefficients at infinite dilution of toluene in the binary mixture 1,2-propanediol (1) + water (2) are given in Table 9.

The Redlich–Kwong method was used to describe the nonidealities of the vapor phase, and the UNIQUAC method with temperature-dependent interaction parameters was employed to account for nonidealities in the liquid phase. The regression was performed using the ASPEN PLUS data regression package.

The binary interaction parameters for water + toluene and 1,2-propanediol + toluene were derived from the solubility data (*13*). The calculated UNIQUAC binary parameter are given in Table 7.

With fixed binary parameters for toluene + water and toluene + 1,2-propanediol, the regression procedure was performed on the large set of measured ternary VLE data (144 points) to derive the binary parameters of the pair 1,2-propanediol + water (Table 7).

The regression method used was the generalized least-squares method, based on the maximum-likelihood principle. The Britt-Luecke algorithm was used to obtain the model parameters with the Deming initialization method (*11*). The software used was Aspen$^+$ DRS version 8.5−3, the pure component properties were taken from the data bank included in the package (*15*), and the model used is that described in ref 16.

Calculations were performed on all binary and ternary results available for the system toluene + 1,2-propanediol + water, with the binary interaction parameters given above. The root mean square deviations of all the measured variables listed in Table 10 are defined as follows:

$$\sigma = \sum (X^{\text{exp}} - X^{\text{calc}})^2/(N-1) \qquad (2)$$

where X is T, P, x, and y.

A higher discrepancy was obtained for the TRI-VLLE data set in the composition of the vapor phase. This can be attributed to the small amount of the sampled vapor phase and inaccuracy of the chosen analytical method.

Separation of the Ternary System

On the basis of the above phase equilibrium data, the separation of the mixture toluene + 1,2-propanediol + water was studied. The ASPEN PLUS process simulator was adopted, using the Redlich–Kwong method to describe the nonidealities of the vapor phase and UNIQUAC activity coefficient model with temperature-dependent parameters for the description of the behavior of the liquid phase.

The detailed description of the separation process is outside the scope of this work. The results of a steady-state simulation of the process are reported here to demonstrate the applicability of the parameters obtained above. The separation is simulated with a column in which the vapor feed in the bottom stage is set to the composition of the vapor phase leaving the reactor. The purpose of the distillation is to remove as much water as possible from the system without losses of 1,2-propanediol. Design specifications are less than 0.02 mol % 1,2-propanediol in the top product and a negligible amount of toluene in the bottom product. Three-phase calculation was performed in each stage, and two liquid phases were found only in the first stage. The effect of the reflux ratio and number of theoretical stages on the liquid composition at the top and bottom of the column is shown in Table 11. The optimal condition is set to 5−6 theoretical stages and a reflux ratio of 1.0.

Conclusions

VLE, LLE, and VLLE for toluene + 1,2-propanediol + water over a wide temperature and composition range were investigated. Because of the complexity of the system, different methods were used to determine the equilibrium data of interest (activity coefficients at infinite dilution, ternary LLE, VLE, and VLLE).

Activity coefficients at infinite dilution of toluene in 1,2-propanediol were measured using GLC and dilutor tech-

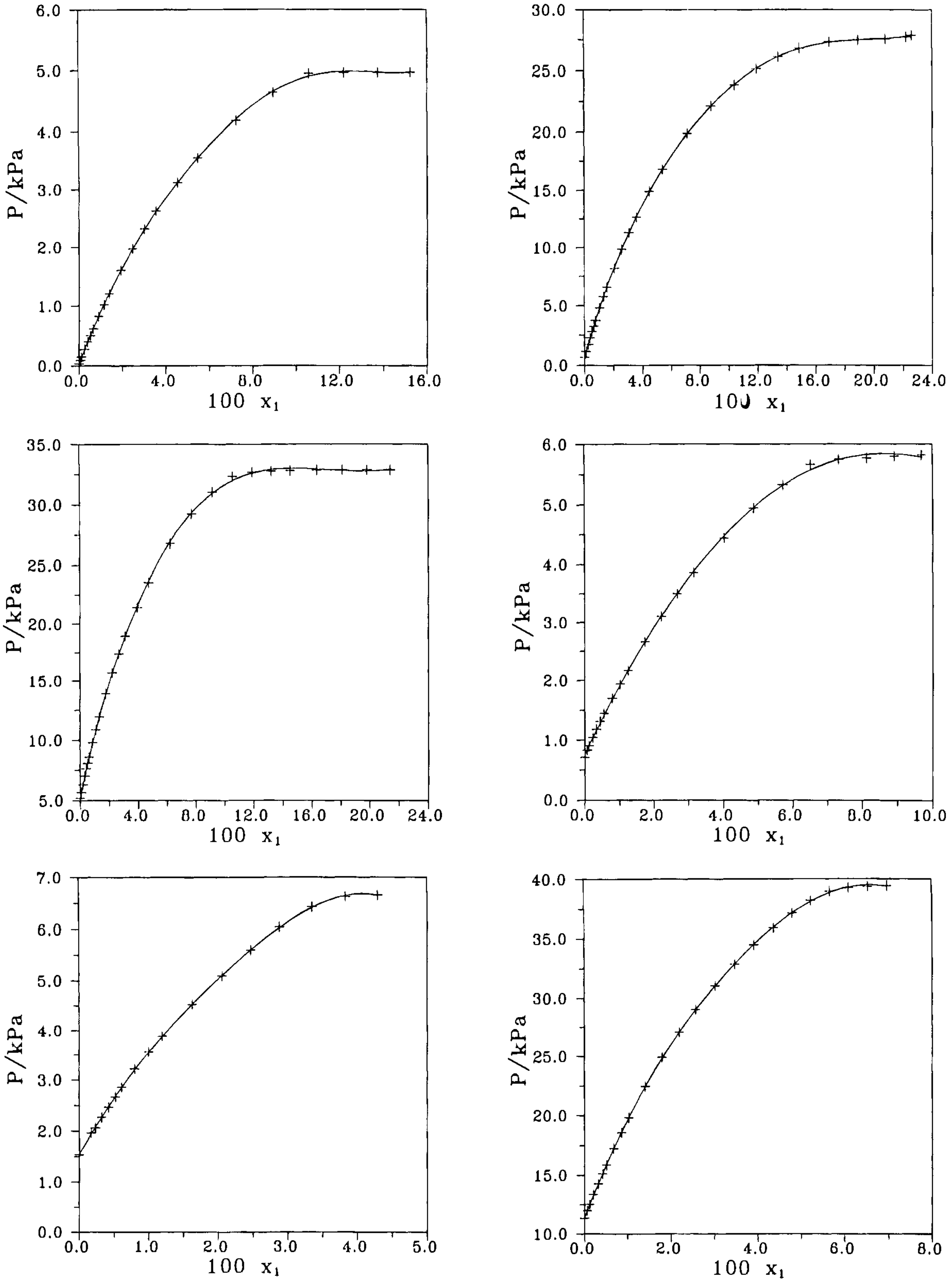

Figure 4. Total vapor pressure for the system toluene (1) + 1,2-propanediol (2) + water (3): addition of toluene (1) to the binary mixture 1,2-propanediol (2) + water (3) of initial composition (a, top left) x_2 = 0.9991, x_3 = 0.0009 at 303.23 K, (b, top right) x_2 = 0.9991, x_3 = 0.0009 at 343.61 K, (c, middle left) x_2 = 0.8654, x_3 = 0.1346 at 343.59 K, (d, middle right) x_2 = 0.8654, x_3 = 0.1346 at 303.38 K, (e, bottom left) x_2 = 0.6908, x_3 = 0.3092 at 303.81 K, and (f, bottom right) x_2 = 0.6951, x_3 = 0.3049 at 343.75 K. The values of y_1 have been calculated from the Gibbs–Duhem equation.

niques in the temperature range from 283.15 to 333.15 K. These results showed a strong temperature dependence. The results agree fairly well with those calculated from the measured VLE data of the ternary system.

Tie lines for the system toluene + 1,2-propanediol + water at 298.15 K were determined in addition to some VLLE data at 313.15, 333.15, and 343.15 K and VLE data at 303.15 and 343.15 K for three different binary initial compositions.

UNIQUAC parameters were calculated from binary solubilities available from the literature and from measured ternary VLE data for the system toluene + 1,2-

Table 8. Measured VLE Isotherms of the Toluene (1) + 1,2-Propanediol (2) + Water (3) System

P/kPa	x_1	x_2	y_1	P/kPa	x_1	x_2	y_1	P/kPa	x_1	x_2	y_1
					T = 303.23 K						
0.032	0.0000	0.9991	0.0000	1.022	0.0116	0.9875	0.9689	4.185	0.0724	0.9267	0.9928
0.090	0.0006	0.9985	0.6349	1.212	0.0140	0.9851	0.9738	4.639	0.0896	0.9096	0.9935
0.149	0.0012	0.9978	0.7802	1.612	0.0194	0.9797	0.9804	4.946	0.1061	0.8931	0.9939
0.273	0.0026	0.9965	0.8812	1.979	0.0248	0.9743	0.9841	4.959	0.1221	0.8771	0.9940
0.396	0.0040	0.9951	0.9179	2.317	0.0302	0.9689	0.9865	4.961	0.1375	0.8617	0.9940
0.499	0.0052	0.9939	0.9353	2.625	0.0355	0.9636	0.9881	4.962	0.1524	0.8469	0.9939
0.614	0.0065	0.9926	0.9474	3.122	0.0452	0.9539	0.9901				
0.824	0.0091	0.9900	0.9614	3.548	0.0546	0.9445	0.9914				
					T = 303.38 K						
0.710	0.0000	0.8654	0.0000	1.939	0.0101	0.8567	0.6373	5.333	0.0571	0.8160	0.8720
0.829	0.0007	0.8649	0.1112	2.171	0.0125	0.8546	0.6801	5.667	0.0653	0.8089	0.8788
0.903	0.0012	0.8644	0.1854	2.663	0.0174	0.8504	0.7395	5.751	0.0734	0.8019	0.8828
1.044	0.0023	0.8635	0.2998	3.104	0.0221	0.8463	0.7768	5.768	0.0814	0.7950	0.8847
1.180	0.0033	0.8625	0.3820	3.500	0.0268	0.8422	0.8027	5.802	0.0892	0.7882	0.8847
1.313	0.0044	0.8616	0.4472	3.859	0.0315	0.8381	0.8218	5.823	0.0969	0.7816	0.8829
1.443	0.0055	0.8606	0.5006	4.444	0.0402	0.8307	0.8461				
1.697	0.0079	0.8586	0.5826	4.948	0.0487	0.8233	0.8618				
					T = 343.59 K						
5.193	0.0000	0.8654	0.0000	15.706	0.0221	0.8463	0.6756	32.807	0.1451	0.7399	0.8535
5.673	0.0008	0.8647	0.0851	17.376	0.0266	0.8424	0.7082	32.853	0.1635	0.7240	0.8529
6.306	0.0020	0.8637	0.1776	18.905	0.0310	0.8386	0.7326	32.875	0.1810	0.7088	0.8521
7.011	0.0032	0.8627	0.2600	21.407	0.0391	0.8316	0.7655	32.874	0.1979	0.6942	0.8519
7.623	0.0043	0.8617	0.3176	23.546	0.0471	0.8247	0.7883	32.894	0.2140	0.6802	0.8531
8.071	0.0052	0.8610	0.3566	26.820	0.0622	0.8116	0.8162	32.893	0.2140	0.6802	0.8531
8.603	0.0062	0.8601	0.3983	29.247	0.0770	0.7988	0.8325	32.895	0.2140	0.6802	0.8531
9.802	0.0086	0.8580	0.4744	31.042	0.0913	0.7864	0.8424	32.893	0.2140	0.6802	0.8531
10.864	0.0108	0.8561	0.5261	32.303	0.1053	0.7743	0.8483	32.855	0.2140	0.6802	0.8531
11.941	0.0132	0.8540	0.5708	32.666	0.1190	0.7625	0.8516				
13.919	0.0177	0.8501	0.6327	32.745	0.1322	0.7510	0.8531				
					T = 343.61 K						
0.654	0.0000	0.9991	0.0000	8.176	0.0206	0.9785	0.9223	26.111	0.1341	0.8951	0.9770
1.144	0.0013	0.9978	0.4592	9.835	0.0257	0.9734	0.9349	26.779	0.1487	0.8506	0.9776
1.721	0.0028	0.9963	0.6402	11.310	0.0307	0.9684	0.9435	27.303	0.1694	0.8298	0.9781
2.286	0.0040	0.9951	0.7158	12.654	0.0359	0.9632	0.9500	27.454	0.1892	0.8101	0.9784
2.808	0.0052	0.9939	0.7678	14.895	0.0449	0.9543	0.9576	27.541	0.2080	0.7913	0.9786
3.272	0.0064	0.9927	0.8009	16.817	0.0539	0.9453	0.9627	27.845	0.2259	0.7734	0.9787
3.740	0.0077	0.9914	0.8280	19.848	0.0710	0.9282	0.9689	27.833	0.2259	0.7734	0.9787
4.783	0.0104	0.9887	0.8644	22.122	0.0875	0.9117	0.9724	27.701	0.2259	0.7733	0.9787
5.746	0.0131	0.9860	0.8876	23.845	0.1036	0.8956	0.9746				
6.566	0.0155	0.9836	0.9019	25.144	0.1191	0.8801	0.9760				
					T = 303.81 K						
1.535	0.0000	0.6908	0.0000	2.857	0.0061	0.6866	0.4661	5.599	0.0247	0.6737	0.7317
1.964	0.0017	0.6896	0.2107	3.218	0.0080	0.6853	0.5261	6.044	0.0288	0.6709	0.7514
2.064	0.0023	0.6892	0.2560	3.558	0.0100	0.6839	0.5727	6.431	0.0335	0.6676	0.7667
2.271	0.0032	0.6885	0.3265	3.879	0.0119	0.6826	0.6072	6.627	0.0383	0.6643	0.7745
2.469	0.0042	0.6879	0.3826	4.519	0.0163	0.6795	0.6645	6.655	0.0429	0.6611	0.7752
2.665	0.0052	0.6872	0.4291	5.093	0.0206	0.6766	0.7040				
					T = 343.75 K						
11.334	0.0000	0.6951	0.0000	18.565	0.0086	0.6891	0.3961	34.509	0.0391	0.6679	0.6818
11.989	0.0006	0.6947	0.0503	19.827	0.0103	0.6880	0.4345	35.920	0.0436	0.6648	0.6951
12.525	0.0012	0.6943	0.0905	22.459	0.0141	0.6853	0.5025	37.150	0.0480	0.6618	0.7056
13.365	0.0021	0.6936	0.1493	24.914	0.0180	0.6826	0.5518	38.199	0.0523	0.6588	0.7136
14.283	0.0032	0.6929	0.2077	27.090	0.0219	0.6799	0.5886	38.961	0.0567	0.6557	0.7194
15.118	0.0042	0.6922	0.2541	29.016	0.0257	0.6773	0.6173	39.269	0.0610	0.6527	0.7230
15.870	0.0051	0.6916	0.2901	31.065	0.0302	0.6742	0.6439	39.378	0.0654	0.6496	0.7243
17.245	0.0068	0.6904	0.3469	32.889	0.0346	0.6710	0.6650	39.428	0.0698	0.6466	0.7233

Table 9. Calculated Activity Coefficient at Infinite Dilution of Toluene (1) in the Binary mixture 1,2-Propanediol (2) + Water (3) from the Legendre Polynomial

T/K	x_2	γ_1^∞	T/K	x_2	γ_1^∞
303.23	0.9991	18.66	343.59	0.8654	20.89
343.61	0.9991	15.34	303.81	0.6908	49.11
303.38	0.8654	27.12	343.76	0.6951	34.36

propanediol + water. Those parameters predict reasonably well the ternary LLE as well as the VLLE.

Simulation of the three-phase distillation column was performed in order to highlight the proper use of the aromatic solvent in the polycondensation process. The column was found optimal having 5−6 theoretical stages

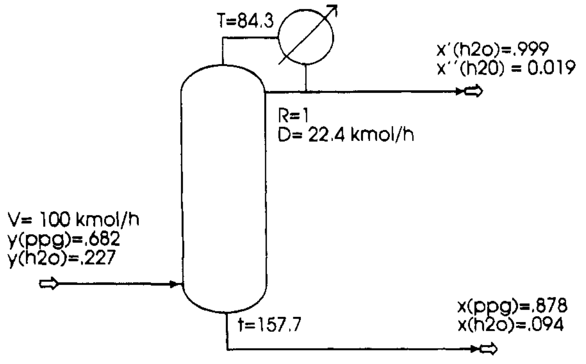

Figure 5. Distillation scheme used in the simulation procedure.

Table 10. Root Mean Square Deviations Calculated for Toluene (1) + 1,2-Propanediol (2) + Water (3) and the Connected Binaries[a]

data set	comp	N	σT/K	σP/kPa	$\sigma x_1(L_1)$	$\sigma x_2(L_1)$	$\sigma x_3(L_1)$	$\sigma x_1(L_2)$	$\sigma x_2(L_2)$	$\sigma x_3(L_2)$	σy_1	σy_2	σy_3
BI-SOL2	1, 2	21	0.000		0.0032	0.0032		0.0050	0.0050				
BI-SOL3	1, 3	12			0.0000		0.0000	0.0016		0.0016			
BI-SOL4	1, 3	2			0.0009		0.0009	0.0000		0.0000			
BI-VLE	2, 3	10	0.254	0.78		0.0022	0.0022						0.0042
TRI-LLE	1, 2, 3	4	0.008		0.0117	0.0119	0.0036	0.0016	0.0014	0.0000			
TRI-VLLE	1, 2, 3	6	0.009	24.9	0.0108	0.0120	0.0038	0.0029	0.0040	0.0015		0.0029	0.0836
VLEA	1, 2, 3	22	0.076	0.42	0.0006	0.0006	0.0001				0.0124		
VLED	1, 2, 3	22	0.123	0.55	0.0016	0.0017	0.0002				0.0077		
VLEE	1, 2, 3	17	0.153	0.53	0.0048	0.0048	0.0002				0.0232		
VLEB	1, 2, 3	28	0.083	2.17	0.0008	0.0011	0.0003				0.0103		
VLEC	1, 2, 3	31	0.195	3.74	0.0017	0.0019	0.0003				0.0131		
VLEF	1, 2, 3	24	0.148	2.36	0.0038	0.0040	0.0003				0.0207		

[a] N, number of data; σ, root mean square deviation.

Table 11. Operating Conditions of the Distillation Scheme for Toluene (1) + 1,2-Propanediol (2) + Water (3)[a]

		bottom			L_1 top			L_2 top			bottom	top
R	NST	x_1	x_2	x_3	x_1	x_2	x_3	x_1	x_2	x_3	T/K	T/K
0.7	5	0.0300	0.8752	0.0948	0.0002	0.0144	0.9854	0.9791	0.0017	0.0192	430.00	357.70
0.7	6	0.0300	0.8755	0.0944	0.0002	0.0128	0.9871	0.9793	0.0015	0.0192	430.07	357.68
1.0	4	0.0235	0.8773	0.0954	0.0001	0.0046	0.9953	0.9804	0.0006	0.0191	430.71	357.55
1.0	5	0.0276	0.8781	0.0943	0.0001	0.0004	0.9994	0.9809	0.0001	0.0190	430.91	357.49
1.0	6	0.0276	0.8782	0.0942	0.0001	0.0000	0.9998	0.9810	0.0000	0.0190	430.93	357.48

[a] Mole fractions y_i are feed compositions. R, reflux ratio; NST, number of theoretical stages; $y_1 = 0.0909$; $y_2 = 0.6818$; $y_3 = 0.2273$.

at a mixed reflux ratio of 1.0 to assure the required product purities at the top and bottom of the column.

The different experimental techniques used for measuring binary results and their internal consistency are remarkable proof of the reliability of the binary data. Furthermore, the consistency between the binary results and the extrapolation of the ternary VLE and LLE allow us to conclude that the data measured in this work are reliable enough for the estimation of binary interaction parameters of the UNIQUAC model. A further check of the performance of the UNIQUAC prediction has been made on some selected ternary VLLE, thus assuring that the simulation of the column is thermodynamically consistent and reliable.

Literature Cited

(1) Tiegs, D.; Gmehling, J.; Medina, A.; Soares, M.; Bastos, J.; Alessi, P.; Kikic, I. *Activity Coefficients at Infinite Dilution*; Chemistry Data Series; DECHEMA: Frankfurt, 1986; Vol. IV, Part 1.
(2) Richon, D.; Antoine, P.; Renon, H. *Ind. Eng. Chem. Process Des. Dev.* **1980**, *19*, 144.
(3) Rogalski, M.; Rybakiewicz, K.; Malanowski, S. *Ber. Bunsen-Ges. Phys. Chem.* **1977**, *81*, 1070.
(4) Dohanl, V.; Novotna, M. *Fluid Phase Equilib.* **1985**, *23*, 303.
(5) Kikic, I.; Alessi, P.; Lapasin, R. *Chem. Eng. J.* **1979**, *18*, 39.
(6) Palmer, D. A.; Smith, R. D. *J. Chem. Eng. Data* **1972**, *17*, 71.
(7) Rarey, J. R.; Gmehling, J. *Fluid Phase Equilib.* **1993**, *83*, 279.
(8) Kolbe, B.; Gmehling, J. *Fluid Phase Equilib.* **1985**, *23*, 213.
(9) Leitman, Y. I.; Gaile, A. A. *Zh. Fiz. Khim.* **1971**, *45*, 76.
(10) Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hsieh, R.; O'Connell, J. P. *Computer calculations for multicomponent vapor-liquid and liquid-liquid equilibria*; Prentice-Hall: New York, 1980; pp 63–69.
(11) Aspen DRS User Manual, Aspen Technology Inc., Cambridge, MA, 1990.
(12) Macedo, M. E. A.; Rasmussen, P. *LLE Data Collection*; DECHEMA: Frankfurt, 1987; Supplement 1, Vol. V, Part 4, pp 61–62.
(13) Sorensen, J. M.; Arlt, W. *LLE Data Collection, Binary Systems*; 1979; Vol. V, Part 1, p 450.
(14) Gmehling, J.; Onken, J. U. *VLE Data Collection, Aqueous Systems*; 1977; Vol. I, Part 1, p 337.
(15) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1988; Appendix A.
(16) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1988; pp 256–257.

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