Separation of Water + Ethanol + (*o*-, *m*-, *p*-) Xylene Systems

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Separation of the ternary systems water + ethanol + (*o*-, *m*-, *p*-) xylene is discussed. Vapor−liquid equilibrium (VLE) data were measured in the homogeneous region of the ternary phase diagram for all three systems at two pressures (49.4 kPa and near atmospheric pressure). The measurements were made with a dynamic ebulliometer by sampling both the vapor and liquid phases. The parameters of UNIQUAC and NRTL thermodynamic local composition models were evaluated to describe the three-phase behavior of the systems and to simulate the appropriate distillation column. Residue curves for ternary mixtures were determined as were boundary lines which separate different separation fields for each system and cannot be crossed by simple distillation. Ternary azeotropic points were estimated from equilibrium data using the UNIQUAC and NRTL activity coefficient models and the objective function in terms of relative volatilities for the water + ethanol system with *m*-xylene and *p*-xylene. The system water + ethanol + *o*-xylene does not form a ternary azeotrope. This fact was confirmed by distillation on a NORMAG spinning band column. A strategy for solvent recovery from waste ternary mixtures generated in pathological laboratories was developed. It combines fractional distillation and carbon adsorption, where the latter method is suggested for xylene removal from the ternary azeotropic mixture.

Introduction

Medical laboratories use significant amounts of pure organic solvents in various tissue-preparation processes. To extract water and grease from the tissue cells, pure ethanol and xylene are usually used as solvents, sometimes with small addition of phenol, picric acid, and indicator dyes (all nonvolatile materials). Non-negligible amounts of solvents are used as well. Their commercial value and care for the environment have compelled the medical staff to search for a better solution toward the regeneration of pure components from mixtures. A proper collection procedure of spent solvents was introduced[1−3] in most of this country's hospitals to enable the separate treatment of ethanol-rich and xylene-rich mixtures. In Slovenia, a country of 2 million inhabitants, the amount of solvents used for this purpose is estimated to be about 10 000 L/year.

By far the most attractive separation method for volatile mixtures is distillation, due to its many advantages. However, the effective separation of the ternary system was found to be difficult because of the following reasons: (1) The system water + ethanol + xylene is not a ternary one in practice, since the xylene is present as three isomers (ortho-, meta-, para-). (2) No vapor−liquid equilibria data for these systems is available in the literature in order to help design the regeneration process. (3) Even when the system is considered as a ternary one, it is highly nonideal.

All three ternary systems were expected to show large deviations from the ideal solution phase behavior because they consist of components of very different polarity; namely, the dielectric constants for xylene, ethanol, and water are 2.3, 25.0, and 80 (dielectric constant in vacuum = 1), respectively. Thus, the energetic interactions between different species in the mixture are mainly responsible for nonidealities. The comparison with analogous ternary systems such as water + ethanol + benzene and water + ethanol + toluene implies the systems are highly nonideal, with a miscibility gap in the ternary phase diagram, and suggests the presence of a ternary azeotrope. Liquid−liquid equilibria of the three systems water + ethanol + (*o*-, *m*-, *p*-) xylene exhibit a phase diagram of type I, mainly because of the large difference in polarity between xylene and water. Looking at the binary pairs, the system water + ethanol forms a homogeneous pressure maximum azeotrope, the water + (*o*-, *m*-, *p*-) xylene systems exhibit heterogeneous pressure maximum azeotropes, and the mixture ethanol + xylene is zeotropic. All these data and the problems connected with the separation of the mentioned system supported the exsistence of the ternary azeotrope.

Since accurate knowledge of the vapor−liquid equilibrium of the system to be separated is required for the optimum design of rectification processes, vapor−liquid equilibria for the ternary mixtures water + ethanol + *o*-xylene, water + ethanol + *m*-xylene, and water + ethanol + *p*-xylene were studied[4] at two pressures by an ebulliometric technique. The data reduction procedure was performed simultaneously with the ASPEN PLUS data regression option, using the data available in the literature and measured ternary VLE data. With a knowledge of the real behavior, the residue curves were calculated for ternary mixtures, which characterize the trajectory of the liquid composition change in the still with time and represent a very effective tool for the design of separation processes. With the aid of the thermodynamic models, the boundary lines in ternary systems water + ethanol + (*o*-, *m*-, *p*-) xylene were determined, which divide the different separation fields for each system and cannot be crossed by simple distillation.[5] Furthermore, azeotropic points were calculated for the ternary systems water + ethanol + *m*-xylene and water + ethanol + *p*-xylene from UNIQUAC and NRTL models along with the objective function in terms of relative volatilities and the software package ASPEN PLUS, Release 10.0-1. The calculations were

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compared with experimental distillate data measured with the column.

The presence of a ternary pressure maximum azeotrope changed the whole regeneration strategy. Beside complex distillation processes, nondistillation or hybrid processes can be used to break the azeotrope. A separation strategy was developed and tested on a pilot scale apparatus. The separation of the solvent mixture can be achieved by a combination of differential distillation, rectification, and carbon adsorption. Adsorption of the minor component (xylene) from the ternary azeotropic mixture was chosen as a potential regeneration step toward required product specifications.

Experimental Section

Chemicals of high purity (GLC) were used. Ethanol was supplied by Riedel de Haen with a purity > 99.7% (wt); all three isomers of xylene were purchased from Fluka; *o*- and *p*-xylene contained <0.5% (wt) of the other two isomers. The water used was twice distilled. The chemicals were subsequently dried over molecular sieves. The purity was checked by gas chromatography, and the water content in the particulate component was determined by a coulometric Karl Fischer titration accurate to 0.002% (wt).

The vapor−liquid equilibrium measurements were performed on a Fischer Labodest 602 dynamic ebulliometer[6] with the recirculation of both phases and sampling of both the liquid and vapor phases. The apparatus can be used for equilibrium measurements from 0.25 kPa up to atmospheric pressure and a temperature range up to 250 °C. The amount of mixture loaded in the cell per experiment is about 85 cm^3. The temperature was measured with a digital precision platinum resistance thermometer (Hart Scientific, Model 1506), calibrated according to the MIL-STD-45662-A standard with a resolution of 0.0001 K and an accuracy of ±0.005 K. The pressure measurements were made with a pressure transducer (VKH 300), calibrated with an MKS Baratron type 170M system and maintained at its set point with an electric pressure controller within ±0.01 kPa. To achieve better pressure control, the nitrogen from a nitrogen reservoir was used as a balance against vacuum and a system of needle valves was introduced. To prevent loss of any components in the cell and to condense the circulating vapor phase, a refrigerating circulator (Haake F-3-K) was used.

The model mixtures were prepared on an analytical Mettler AT 261 balance with an accuracy of ±0.000 05 g The initial composition of the mixture loaded to the cell and the compositions of vapor and liquid samples were determined. Karl Fischer titration (Metrohm 684 KF Coulometer, cell without diaphragm) was used to determine the water content. Volatile components were analyzed by gas chromatography using a flame ionization detector (GC Carlo Erba Model 8130/FID, Spectra Physics Analytical Integrator) and a capillary column DB-WAX at 423.15 K. The calibration factors to determine the compositions from recorded peak areas were obtained from prepared mixtures with exactly known compositions.

Experiments were performed in the homogeneous ethanol-rich part of the ternary phase diagram along the lines with an approximate constant water composition (5, 7.5, 10, 20, 25 wt %) at two pressures, namely at 49.4 kPa and near atmospheric pressure. After each experiment, components from the cell were removed and the cell was rinsed several times with acetone and kept under vacuum. The uncertainty of the measured composition is 0.0002 mole fraction.

Table 1. Data Available from the Literature and Data Measured in This Work

system	source	type of data	*T* range/K
ethanol + water	5	azeotropic	298.15−623.13
water + *o*-xylene	7	azeotropic	367.65
water + *m*-xylene	7	azeotropic	365.15
water + *p*-xylene	7	azeotropic	365.15
water + ethanol + *o*-xylene	8	LLE	298.15
water + ethanol + *m*-xylene	8	LLE	298.15
water + ethanol + *p*-xylene	8	LLE	298.15
o-xylene + water	9	LLE	273.15−298.15
m-xylene + water	9	LLE	273.15−437.35
p-xylene + water	9	LLE	273.15−435.65
water + ethanol	10	VLE	298.14−421.65
ethanol + *p*-xylene	11	VLE	351.55−411.55
water + ethanol + *o*-xylene	this work	VLE	334.21−351.52
water + ethanol + *m*-xylene	this work	VLE	333.86−349.27
water + ethanol + *p*-xylene	this work	VLE	333.86−349.27

For distillation measurements, a commercially available spinning band column from NORMAG was used. The experiments were performed at the optimum speed 2000 rpm of the spinning band and at a total reflux ratio. Depending on the liquid load in the column, the column can have up to 55 theoretical stages at a low-pressure drop.

Results and Discussion

Table 1 summarizes the data available from the literature[5,7−11] and our measured data. Our work focused on measuring ternary VLE data of water + ethanol + (*o*-, *m*-, *p*-) xylene systems in order to reproduce the complex behavior over wide temperature and concentration ranges.

Vapor−liquid equilibrium *PTxy* data for water + ethanol + (*o*-, *m*-, *p*-) xylene systems were measured at two different pressures in the ethanol-rich part of the ternary phase diagram. Table 2 reports the experimental VLE results for the water + ethanol + *o*-xylene system at 49.4 and 98.4 kPa. The latter data are graphically presented in the three-component phase diagram in Figure 1. The results of VLE measurements for the other two systems water + ethanol + *m*-xylene and water + ethanol + *p*-xylene at 49.4 and 90.4 kPa are listed in Tables 3 and 4, respectively. A weak effect of pressure on the boiling temperature of the mixture as well as on the composition of the vapor phase is clearly visible.

All three-component systems appear to be highly nonideal, with positive deviations from Raoult's law and activity coefficients of all components $\gamma_i \geq 1$. This nonideality is most pronounced in the concentration region from 2.5 up to 7.5 mol % of (*o*-, *m*-, *p*-) xylene and from 12 up to 25 mol % of water. In this part of the triangular phase diagram, a change of (*o*-, *m*-, *p*-) xylene volatility occurs. By increasing the amount of water in the initial binary system water + ethanol, a significant increase of (*o*-, *m*-, *p*-) xylene volatility is noted in relation to that of water. A similar behavior was observed for this system at higher pressure as well as for the other two systems water + ethanol + *o*-xylene and water + ethanol + *p*-xylene at both measured pressures. The activity coefficients of ethanol calculated from the experimental *PTxy* data were approximately constant (about 1) in the whole measured region. The activity coefficients of water changed slightly in the range from 2 to 3. However, a distinct variation of (*o*-, *m*-, *p*-) xylene activity coefficients (from 4 to 16) was observed with respect to water content in the liquid phase. A slight temperature dependence of xylene activity coefficients was observed.

A data reduction procedure was performed, using binary data available from the literature (LLE of the system water + (*o*-, *m*-, *p*-) xylene, VLE of binary systems) and measured

Table 2. Measured VLE Isobars of the Water (1) + Ethanol (2) + *o*-Xylene (3) System

T/K	x_1	x_2	y_1	y_2	T/K	x_1	x_2	y_1	y_2	T/K	x_1	x_2	y_1	y_2
							$P = 49.4$ kPa							
334.21	0.1834	0.7964	0.1749	0.8026	334.29	0.2373	0.7115	0.2266	0.7210	334.41	0.2918	0.6179	0.2751	0.6435
334.23	0.1770	0.7811	0.1778	0.7795	334.35	0.2482	0.6871	0.2414	0.6916	334.54	0.3215	0.5758	0.3002	0.6119
334.31	0.1728	0.7592	0.1907	0.7554	334.36	0.2462	0.6506	0.2529	0.6699	334.67	0.3854	0.5968	0.2969	0.6664
334.38	0.1814	0.7222	0.2007	0.7315	334.45	0.2537	0.6163	0.2693	0.6471	334.65	0.4057	0.5598	0.3081	0.6310
334.45	0.1905	0.6885	0.2191	0.7030	334.46	0.2560	0.5869	0.2846	0.6235	334.65	0.4167	0.5313	0.3193	0.5988
334.49	0.1969	0.6564	0.2370	0.6785	334.45	0.3021	0.6777	0.2499	0.7192	335.14	0.4946	0.4903	0.3357	0.6174
334.55	0.2005	0.6134	0.2556	0.6542	334.30	0.3068	0.6559	0.2600	0.6903	334.95	0.5099	0.4622	0.3427	0.5776
334.38	0.2251	0.7669	0.2012	0.7883	334.34	0.3188	0.6203	0.2764	0.6539	335.38	0.5729	0.4157	0.3526	0.5939
334.26	0.2283	0.7416	0.2097	0.7598										
							$P = 98.4$ kPa							
350.64	0.1289	0.8504	0.1291	0.8565	350.81	0.1898	0.7607	0.1951	0.7617	350.83	0.2478	0.6671	0.2499	0.6832
350.70	0.1261	0.8314	0.1372	0.8292	350.89	0.1940	0.7347	0.2080	0.7366	350.75	0.2476	0.6448	0.2601	0.6649
350.80	0.1282	0.8047	0.1451	0.8083	350.96	0.2010	0.6988	0.2230	0.7113	350.86	0.3212	0.6617	0.2672	0.7074
350.93	0.1323	0.7741	0.1548	0.7884	351.11	0.2047	0.6724	0.2395	0.6881	350.86	0.3310	0.6305	0.2811	0.6703
351.07	0.1373	0.7412	0.1671	0.7664	351.20	0.2119	0.6344	0.2559	0.6664	350.97	0.3392	0.6053	0.2945	0.6428
351.18	0.1394	0.7105	0.1787	0.7472	350.74	0.2327	0.7490	0.2115	0.7677	351.38	0.4082	0.5768	0.3093	0.6606
351.29	0.1417	0.6787	0.1948	0.7258	350.73	0.2375	0.7232	0.2222	0.7384	351.19	0.4127	0.5552	0.3225	0.6232
350.72	0.1917	0.7979	0.1815	0.8072	350.73	0.2413	0.6973	0.2357	0.7111	351.52	0.4814	0.5050	0.3415	0.6212
350.71	0.1880	0.7835	0.1848	0.7887										

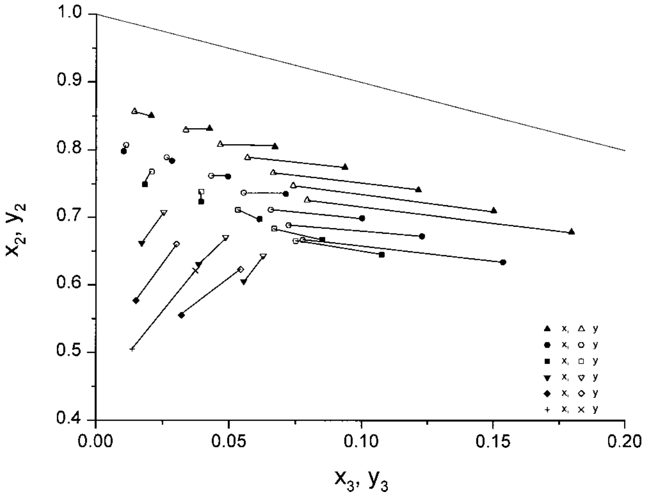

Figure 1. Three-component phase diagram of the water (1) + ethanol (2) + *o*-xylene (3) system near atmospheric pressure.

ternary vapor−liquid equilibrium data, to obtain binary interaction parameters of the UNIQUAC and NRTL G^E models. Vapor-phase corrections were calculated with the Redlich−Kwong equation of state. The ASPEN PLUS data regression option was used with a generalized least-squares method and objective function, based on the maximum likelihood principle, according to Prausnitz et al.[12] The Britt−Luecke algorithm was applied to obtain model parameters with the Deming initialization method.[13] The UNIQUAC and NRTL interaction parameters are defined as follows:

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

and

$$\text{NRTL} \qquad G_{ij} = \exp(-\alpha_{ij}\tau_{ij}), \quad \tau_{ij} = b_{ij}/T \qquad (2)$$

and are given in Tables 5 and 6, respectively.

The UNIQUAC G^E model satisfactorily describes the activity coefficients of components in the liquid phase and distribution coefficients of components between vapor and liquid phases in the temperature and concentration ranges of interest for water + ethanol + *o*-xylene and water + ethanol + *m*-xylene. A less satisfactory agreement was obtained for the water + ethanol + *p*-xylene system, particularly at a higher water content in the liquid phase in the vicinity of the miscibility gap. The NRTL activity coefficient model was more effective than the UNIQUAC model in describing the vapor−liquid equilibria of the latter system.

Calculations were performed on all binary and ternary data available, with the UNIQUAC and NRTL binary interaction parameters given above. The root-mean-square deviations of the measured variables presented in Tables 7 and 8 are defined as follows:

$$\sigma = (X^{\text{calc}} - X^{\text{exp}})^2/(N - 1) \qquad (3)$$

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

It can be noticed from Tables 7 and 8 that the NRTL model is better than UNIQUAC for calculating all the data available for the ternary system water (1) + ethanol (2) + *p*-xylene (3) as well as binary solubility data for the other two systems.

Discrepancies were very similar for both models in describing binary VLE data. The UNIQUAC model is better at describing ternary LLE data of systems with *o*-xylene and *m*-xylene as well as ternary VLE data of water (1) + ethanol (2) + *o*-xylene (3) and water (1) + ethanol (2) + *m*-xylene systems.

Our measurements on vapor−liquid equilibria and experiments on a real distillation column suggested a hypothetical exsistence of a ternary azeotropic mixture for all three systems water + ethanol + *o*-xylene, water + ethanol + *m*-xylene, and water + ethanol + *p*-xylene with a minimum boiling point. The azeotropic temperature and compositions of the systems water + ethanol + *m*-xylene and water + ethanol + *p*-xylene at different pressures were calculated using both UNIQUAC and NRTL G^E models with the objective function in terms of relative volatilities and with the ASPEN PLUS software package Release 10.0-1. The azeotropes of both systems are located in the homogeneous part of the triangular phase diagram with a maximum pressure. The third system water + ethanol + *o*-xylene does not exhibit azeotropic behavior. The predicted azeotropic information for these systems is listed in Table 9 with both UNIQUAC and NRTL G^E models.

Since Table 9 shows that the azeotropic composition is not affected very much by a temperature (or pressure) change, pressure swing distillation cannot be applied as an alternative separation process. The existence of a ternary azeotropic mixture often represents a huge problem

Table 3. Measured VLE Isobars of the Water (1) + Ethanol (2) + *m*-Xylene (3) System

T/K	x_1	x_2	y_1	y_2	T/K	x_1	x_2	y_1	y_2	T/K	x_1	x_2	y_1	y_2
							$P = 49.4$ kPa							
334.13	0.1229	0.8569	0.1227	0.8539	334.05	0.1900	0.7580	0.1924	0.7515	333.90	0.2463	0.6743	0.2417	0.6743
334.03	0.1295	0.8286	0.1355	0.8213	334.04	0.1917	0.7357	0.2055	0.7250	333.96	0.2691	0.6261	0.2667	0.6397
333.96	0.1312	0.8027	0.1443	0.7959	334.04	0.1979	0.7036	0.2150	0.7019	334.35	0.3560	0.6280	0.2881	0.6788
333.86	0.1363	0.7734	0.1554	0.7716	334.07	0.2062	0.6688	0.2310	0.6751	334.14	0.3486	0.6173	0.2868	0.6521
334.04	0.1378	0.7464	0.1668	0.7500	334.12	0.2105	0.6359	0.2461	0.6519	333.96	0.3590	0.5886	0.3033	0.6158
334.16	0.1496	0.7040	0.1868	0.7201	334.06	0.2315	0.7501	0.2060	0.7653	334.56	0.4079	0.5764	0.2996	0.6580
334.08	0.1468	0.6762	0.1959	0.7047	333.88	0.2346	0.7269	0.2141	0.7353	334.35	0.4066	0.5620	0.3039	0.6245
334.22	0.1811	0.8089	0.1694	0.8169	333.90	0.2418	0.6979	0.2297	0.7010	334.86	0.4751	0.5112	0.3238	0.6247
334.12	0.1861	0.7835	0.1803	0.7794										
							$P = 90.4$ kPa							
348.39	0.1273	0.8290	0.1353	0.8237	348.42	0.1932	0.7556	0.1949	0.7536	348.35	0.2447	0.6726	0.2463	0.6759
348.41	0.1303	0.8037	0.1446	0.7996	348.42	0.1970	0.7278	0.2070	0.7269	348.39	0.2517	0.6396	0.2821	0.6307
348.44	0.1358	0.7720	0.1571	0.7751	348.47	0.1987	0.7052	0.2125	0.7097	348.70	0.3513	0.6324	0.2919	0.6781
348.53	0.1381	0.7256	0.1683	0.7517	348.52	0.2026	0.6706	0.2322	0.6807	348.57	0.3409	0.6244	0.2880	0.6568
348.59	0.1423	0.7130	0.1825	0.7303	348.59	0.2017	0.6482	0.2427	0.6641	348.47	0.3550	0.5922	0.3050	0.6212
348.69	0.1427	0.6752	0.1947	0.7110	348.42	0.2244	0.7572	0.2061	0.7685	348.99	0.4067	0.5779	0.3077	0.6544
348.52	0.1843	0.8057	0.1743	0.8130	348.39	0.2370	0.7311	0.2219	0.7310	348.78	0.4161	0.5517	0.3217	0.6171
348.44	0.1889	0.7777	0.2011	0.7661	348.34	0.2394	0.7001	0.2270	0.7081	349.27	0.4699	0.5162	0.3344	0.6221

Table 4. Measured VLE Isobars of the Water (1) + Ethanol (2) + *p*-Xylene (3) System

T/K	x_1	x_2	y_1	y_2	T/K	x_1	x_2	y_1	y_2	T/K	x_1	x_2	y_1	y_2
							$P = 49.4$ kPa							
334.07	0.1267	0.8532	0.1266	0.8495	334.13	0.1862	0.7623	0.1863	0.7570	334.02	0.2449	0.6846	0.2366	0.6846
333.97	0.1280	0.8292	0.1361	0.8199	334.08	0.1903	0.7341	0.1983	0.7265	333.91	0.2475	0.6698	0.2438	0.6694
334.02	0.1315	0.8025	0.1446	0.7941	334.08	0.1943	0.7069	0.2103	0.7051	333.86	0.2531	0.6406	0.2565	0.6452
334.04	0.1340	0.7744	0.1532	0.7729	334.07	0.2007	0.6771	0.2274	0.6765	334.39	0.3229	0.6604	0.2656	0.6993
334.04	0.1380	0.7432	0.1659	0.7489	334.10	0.2057	0.6433	0.2428	0.6504	334.14	0.3306	0.6347	0.2718	0.6672
334.02	0.1403	0.7147	0.1793	0.7260	334.03	0.2242	0.6995	0.2229	0.6979	333.93	0.3373	0.6074	0.2774	0.6345
334.16	0.1430	0.6804	0.1935	0.7042	334.19	0.2326	0.7489	0.2059	0.7656	334.61	0.4078	0.5786	0.3069	0.6592
334.29	0.1805	0.8102	0.1792	0.8069	333.97	0.2353	0.7259	0.2140	0.7334	334.32	0.4137	0.5543	0.3156	0.6123
334.15	0.1847	0.7860	0.1767	0.7875	334.06	0.2424	0.6969	0.2308	0.6975	334.78	0.4786	0.5102	0.3275	0.6207
							$P = 90.4$ kPa							
348.38	0.1236	0.8557	0.1259	0.8521	348.40	0.1870	0.7618	0.1885	0.7592	348.34	0.2466	0.6687	0.2477	0.6708
348.36	0.1293	0.8283	0.1378	0.8214	348.38	0.1909	0.7329	0.2001	0.7310	348.37	0.2541	0.6389	0.2618	0.6456
348.40	0.1266	0.8067	0.1442	0.7992	348.44	0.1981	0.7003	0.2174	0.7020	348.71	0.3236	0.6601	0.2629	0.7034
348.44	0.1344	0.7734	0.1551	0.7759	348.47	0.2018	0.6728	0.2305	0.6807	348.55	0.3308	0.6338	0.2746	0.6691
348.51	0.1381	0.7429	0.1674	0.7527	348.50	0.2080	0.6385	0.2490	0.6530	348.47	0.3379	0.6069	0.2890	0.6332
348.59	0.1399	0.7122	0.1807	0.7288	348.48	0.2265	0.7553	0.2112	0.7632	348.99	0.4025	0.5815	0.3057	0.6540
348.64	0.1427	0.6771	0.1944	0.7065	348.38	0.2353	0.7264	0.2205	0.7331	348.79	0.4163	0.5540	0.3054	0.6258
348.53	0.1778	0.8118	0.1698	0.8165	348.36	0.2435	0.6957	0.2348	0.6995	349.27	0.4775	0.5091	0.3370	0.6174
348.44	0.1836	0.7852	0.1784	0.7868										

Table 5. UNIQUAC Parameters

binary system	a_{ij}	b_{ij}/K	a_{ji}	b_{ji}/K
Water (1) + Ethanol (2) + *o*-Xylene (3)				
water (1) + ethanol (2)	0.0135	−162.73	−0.0105	9.915
water (1) + *o*-xylene (3)	0.2333	−268.48	−0.5188	−426.29
ethanol (2) + *o*-xylene (3)	−0.0382	9.166	0.0786	−279.68
Water (1) + Ethanol (2) + *m*-Xylene (3)				
water (1) + ethanol (2)	0.7486	−410.53	−0.6186	211.94
water (1) + *m*-xylene (3)	0.5207	−333.03	0.8416	−962.47
ethanol (2) + *m*-xylene (3)	−0.5370	162.27	0.9268	−544.33
Water (1) + Ethanol (2) + *p*-Xylene (3)				
water (1) + ethanol (2)	0.0252	91.45	−0.1737	−201.44
water (1) + *p*-xylene (3)	−0.0150	59.97	0.0182	−1253.4
ethanol (2) + *p*-xylene (3)	0.1290	−100.21	−0.1424	−133.27

Table 6. NRTL Parameters $\alpha_{ij} = 0.25$

binary system	b_{ij}/K	b_{ji}/K
Water (1) + Ethanol (2) + *o*-Xylene (3)		
water (1) + ethanol (2)	768.005	−131.699
water (1) + *o*-xylene (3)	2592.411	1574.728
ethanol (2) + *o*-xylene (3)	616.141	82.091
Water (1) + Ethanol (2) + *m*-Xylene (3)		
water (1) + ethanol (2)	768.005	−131.699
water (1) + *m*-xylene (3)	2673.288	1510.358
ethanol (2) + *m*-xylene (3)	652.382	50.401
Water (1) + Ethanol (2) + *p*-Xylene (3)		
water (1) + ethanol (2)	768.005	−131.699
water (1) + *p*-xylene (3)	2641.080	1508.741
ethanol (2) + *p*-xylene (3)	648.810	50.239

in finding feasible rectification sequences and an optimum solution to reach desired product specifications. Most often special rectification or hybrid processes have to be used to overcome the azeotropic behavior of the mixture, and to do this, the type of azeotrope and pressure dependence have to be known. In ternary mixtures boundary residual curves represent phenomena of special importance, which cannot be crossed by distillation. Residue curve maps are a valuable tool[14−16] for designing feasible sequences for the distillation of nonideal azeotropic mixtures. They were determined with the aid of UNIQUAC and NRTL thermodynamic models and ASPEN PLUS software Release 10.0-1. Residue curves for all three systems (water + ethanol + *o*-xylene, water + ethanol + *m*-xylene, and water + ethanol + *p*-xylene) at 101.3 kPa are shown in Figure 2. The diagram convention is that used by Van Dongen et al.,[17] which presents the high-boiling pure component as the lower right corner and the low-boiling pure component as the upper left corner. According to the classification given by Matsuyama, discussed in the article of Fien and Liu,[14] the phase diagrams for water + ethanol + *m*-xylene and water + ethanol + *p*-xylene are of type 220-m. The system water + ethanol + *o*-xylene does not form a ternary azeotrope, and therefore it is of type 220. It is evident from Figure 2 that two different distillation fields arise, giving the ternary azeotrope, in the case of *m*-xylene and *p*-xylene,

Table 7. Root Mean Square Deviations Calculated for Water (1) + Ethanol (2) + (*o*-, *m*-, *p*-) Xylene Systems and the Binary Systems Available (UNIQUAC Temperature-Dependent Parameters)

data set[a]	comp	N	σT/K	σP/kPa	σx_1(L1)	σx_2(L1)	σx_3(L1)	σx_1(L2)	σx_2(L2)	σx_3(L2)	σy_1	σy_2	σy_3
Water (1) + Ethanol (2) + *o*-Xylene (3)													
AZ	1, 2, 3	1	0.141	0.035	0.0000	0.0000	0.0000				0.0040	0.0045	0.0052
BISOL	1, 3	2	4.865		0.0001		0.0001	0.0152		0.0152			
BIVLE1	1, 2	29	1.056	1.33	0.0050	0.0052							
BIVLE2	1, 2	29	1.597	1.11	0.0096	0.0099							
TRILLE	1, 2, 3	9	0.805		0.0285	0.0262	0.0064	0.0188	0.0731	0.0706			
TRIVLE1	1, 2, 3	25	0.012	0.13	0.0001	0.0026	0.0003				0.0061	0.0071	0.0025
TRIVLE2	1, 2, 3	25	0.016	0.10	0.0001	0.0027	0.0004				0.0029	0.0032	0.0016
Water (1) + Ethanol (2) + *m*-Xylene (3)													
AZ	1, 2, 3	1	0.408	0.10	0.0000	0.0000	0.0000				0.0032	0.0029	0.0030
BISOL	1, 3	5	5.779		0.0002		0.0002	0.0090		0.0090			
BIVLE1	1, 2	29	1.041	1.31	0.0049	0.0051							
BIVLE2	1, 2	29	1.584	1.14	0.0097	0.0100							
TRILLE	1, 2, 3	10	1.244		0.0394	0.0391	0.0020	0.0101	0.0439	0.0535			
TRIVLE1	1, 2, 3	25	0.015	0.171	0.0002	0.0003	0.0005				0.0042	0.0047	0.0019
TRIVLE2	1, 2, 3	25	0.024	0.165	0.0003	0.0006	0.0008				0.0068	0.0059	0.0022
Water (1) + Ethanol (2) + *p*-Xylene (3)													
AZ	1, 2, 3	1	0.614	0.153	0.0001	0.0001	0.0000				0.0201	0.0192	0.0086
BISOL	1, 3	1	0.7167		0.0028		0.0028	0.0000		0.0000			
BIVLE1	1, 2	29	1.333	1.66	0.0077	0.0080							
BIVLE2	1, 2	29	1.928	1.37	0.0137	0.0142							
TRILLE	1, 2, 3	9	1.835		0.1133	0.1121	0.0128	0.0146	0.0214	0.0151			
TRIVLE1	1, 2, 3	27	0.031	0.35	0.0007	0.0010	0.0016				0.0217	0.0242	0.0032
TRIVLE2	1, 2, 3	25	0.055	0.38	0.0006	0.0011	0.0017				0.0188	0.0193	0.0020

[a] AZ, azeotropic data; BISOL, solubility data; BIVLE1 and BIVLE2, binary VLE data; TRILLE, ternary LLE data; TRIVLE1 and TRIVLE2, measured ternary VLE data.

Table 8. Root Mean Square Deviations Calculated for Water (1) + Ethanol (2) + (*o*-, *m*-, *p*-) Xylene Systems and the Binary Systems Available (NRTL Parameters)

data set[a]	comp	N	σT/K	σP/kPa	σx_1(L1)	σx_2(L1)	σx_3(L1)	σx_1(L2)	σx_2(L2)	σx_3(L2)	σy_1	σy_2	σy_3
Water (1) + Ethanol (2) + *o*-Xylene (3)													
AZ	1, 2, 3	1	0.092	0.03	0.0000	0.0000	0.0000				0.0057	0.0054	0.0003
BISOL	1, 3	2	0.254		0.0000		0.0000	0.0005		0.0005			
BIVLE1	1, 2	29	1.034	1.31	0.0049	0.0051							
BIVLE2	1, 2	29	1.606	1.16	0.0099	0.0103							
TRILLE	1, 2, 3	9	0.337		0.0901	0.0817	0.0104	0.0223	0.0789	0.0990			
TRIVLE1	1, 2, 3	25	0.028	0.32	0.0278	0.0032	0.0004				0.0088	0.0097	0.0039
TRIVLE2	1, 2, 3	25	0.027	0.17	0.0001	0.0001	0.0002				0.0066	0.0055	0.0018
Water (1) + Ethanol (2) + *m*-Xylene (3)													
AZ1	1, 2, 3	1	0.514	0.13	0.0000	0.0000	0.0000				0.0073	0.0058	0.0014
BISOL	1, 3	5	0.477		0.0000		0.0000	0.0018		0.0018			
BIVLE1	1, 2	29	1.034	1.31	0.0049	0.0051							
BIVLE2	1, 2	29	1.606	1.16	0.0113	0.0103							
TRILLE	1, 2, 3	10	0.378		0.0708	0.0671	0.0054	0.0296	0.0919	0.1192			
TRIVLE1	1, 2, 3	25	0.029	0.34	0.0004	0.0006	0.0009				0.0088	0.0107	0.0027
TRIVLE2	1, 2, 3	25	0.044	0.3	0.0002	0.0004	0.0005				0.0098	0.0089	0.0024
Water (1) + Ethanol (2) + *p*-Xylene (3)													
AZ	1, 2, 3	1	0.687	0.17	0.0000	0.0000	0.0000				0.0071	0.0050	0.0021
BISOL	1, 3	1	0.000		0.0000		0.0000	0.0000		0.0000			
BIVLE1	1, 2	29	1.034	1.31	0.0049	0.0051							
BIVLE2	1, 2	29	1.606	1.16	0.0116	0.0099	0.0103						
TRILLE	1,2, 3	9	0.349		0.0756	0.0640	0.0164	0.0281	0.0839	0.1058			
TRIVLE1	1, 2, 3	27	0.019	0.22	0.0004	0.0004	0.0008				0.0085	0.0107	0.0035
TRIVLE2	1, 2, 3	25	0.027	0.19	0.0002	0.0003	0.0005				0.0075	0.0072	0.0020

[a] AZ, azeotropic data; BISOL, solubility data; BIVLE1 and BIVLE2, binary VLE data; TRILLE, ternary LLE data; TRIVLE1 and TRIVLE2, measured ternary VLE data.

as the top product at infinite reflux and with an infinite number of stages in the column.

The same trend was observed in distillation experiments on the NORMAG spinning band column at atmospheric pressure and total reflux, as shown in Table 10. The experimental distillate compositions were in good agreement with the calculated ones using the UNIQUAC model on a simulated column with approximately 55 theoretical stages for water + ethanol + *o*-xylene and water + ethanol + *m*-xylene systems, while the third system was better described by the NRTL model. Because of the nonideality of the systems, the azeotropic point was not reached in any of the systems. The distillate composition of the water + ethanol + *o*-xylene system approached the binary azeotropic point of the ethanol−water mixture, while the other two systems approached ternary azeotropic mixtures.

Conclusions

The VLE for water + ethanol + (*o*-, *m*-, *p*-) xylene systems was investigated over wide temperature and

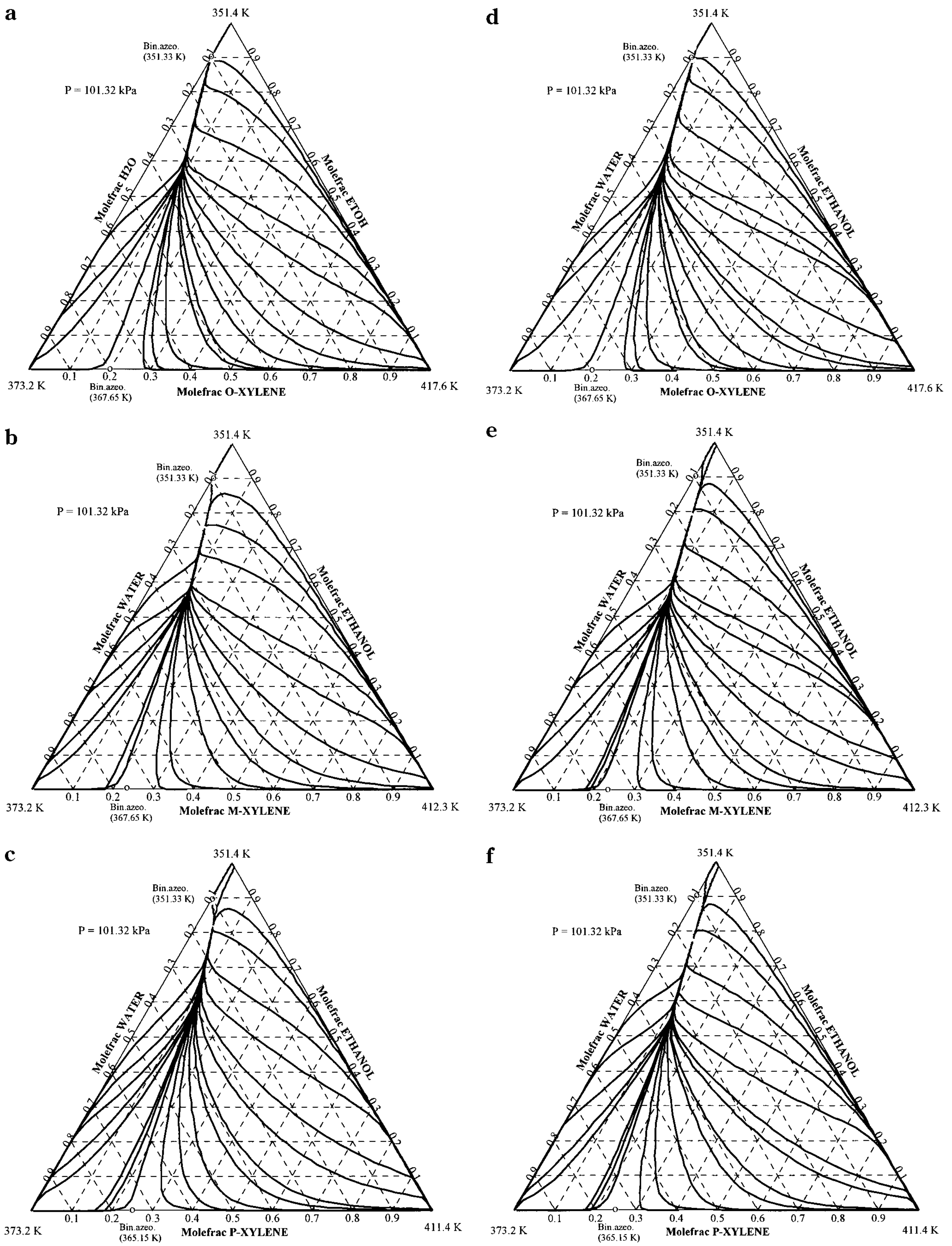

Figure 2. Residue curves and boundary lines for all three systems at 101.3 kPa: (a) UNIQUAC model, water (1) + ethanol (2) + *o*-xylene (3); (b) UNIQUAC model, water (1) + ethanol (2) + *m*-xylene (3); (c) UNIQUAC model, water (1) + ethanol (2) + *p*-xylene (3); (d) NRTL model, water (1) + ethanol (2) + *o*-xylene (3); (e) NRTL model, water (1) + ethanol (2) + *m*-xylene (3); (f) NRTL model, water (1) + ethanol (2) + *p*-xylene (3).

composition ranges. An ebulliometric technique was used to determine isobaric vapor−liquid equilibrium data in the ethanol-rich part of the triangular diagram at 49.4, 90.4, and 98.4 kPa, respectively. The thermodynamic behavior

Table 9. Predicted Azeotropic Information for Ternary Systems by ASPEN PLUS

	UNIQUAC model[a]			NRTL model			differences			
P/kPa	T/K	y_1	y_2	T/K	y_1	y_2	δy_1	δy_2	δy_3	type[b]
Water (1) + Ethanol (2) + *p*-Xylene (3)										
101.3	351.05	0.1373	0.8179	351.24	0.1731	0.7699	0.0358	−0.048	−0.0122	homPmax
100.0	350.72	0.1373	0.8179	350.91	0.175	0.767	0.0377	−0.0509	−0.0132	homPmax
90.4	348.19	0.1391	0.8163	348.37	0.170	0.772	0.0309	−0.0443	−0.0134	homPmax
49.4	333.87	0.132	0.815	334.03	0.160	0.777	−0.028	−0.038	−0.01	homPmax
Water (1) + Ethanol (2) + *m*-Xylene (3)										
101.3	351.18	0.1910	0.7560	351.27	0.157	0.795	−0.034	0.039	0.005	homPmax
100.0	350.85	0.1902	0.7568	350.94	0.158	0.792	−0.0322	0.0352	0.003	homPmax
90.4	348.32	0.1903	0.7546	348.41	0.156	0.794	−0.0343	0.0394	0.0051	homPmax
49.4	334.00	0.2052	0.7257	334.07	0.149	0.795	−0.0562	0.0693		homPmax
Water (1) + Ethanol (2) + *o*-Xylene (3)										
101.3										none
98.4										none
49.4										none

[a] Temperature-dependent parameters. [b] Abbreviations: homPmax, homogeneous pressure maximum azeotrope; none, zeotropic.

Table 10. Experimental Distillate Mole Fractions in Comparison to the Calculated Mole Fractions

	experiment			UNIQUAC model			NRTL model		
P/kPa	T/K	y_1	y_2	T/K	y_1	y_2	T/K	y_1	y_2
Water (1) + Ethanol (2) + *p*-Xylene (3)									
101.8	350.65	0.2219	0.7130	351.17	0.1396	0.8160	351.36	0.1719	0.77154
Water (1) + Ethanol (2) + *m*-Xylene (3)									
102.1	350.95	0.2178	0.7212	350.85	0.1907	0.7564	351.47	0.1614	0.7888
Water (1) + Ethanol (2) + *o*-Xylene (3)									
102.2	351.75	0.1473	0.8391	351.58	0.1220	0.8696	351.62	0.1127	0.8745

of the three-component systems was found to be highly nonideal with positive deviations from Raoult's law and activity coefficients of all components greater than or equal to 1. A small effect of pressure on the boiling temperature of the mixture as well as on the composition of the vapor phase was noticed.

UNIQUAC temperature dependent binary interaction parameters as well as NRTL parameters were evaluated from the literature data and from our measured ternary VLE data for each system. The UNIQUAC model satisfactorily describes water + ethanol + *o*-xylene and water + ethanol + *m*-xylene systems. A less satisfactory agreement was obtained for the water + ethanol + *p*-xylene system, particularly at a higher water content in the liquid phase in the vicinity of the miscibility gap. The NRTL activity coefficient model was more effective in comparison to the UNIQUAC model in describing the vapor−liquid equilibria of the latter system.

Azeotropic information was derived for each system from the measured ternary VLE data. It showed that water + ethanol + *m*-xylene and water + ethanol + *p*-xylene do form a homogeneous ternary azeotrope with minimum boiling point. The third system water + ethanol + *o*-xylene does not exhibit azeotropic behavior. UNIQUAC temperature dependent parameters reasonably predict the azeotropic temperature and composition of the water + ethanol + *m*-xylene system as well as the azeotropic temperature of the system water + ethanol + *p*-xylene. The azeotropic composition of the latter system is reliably described with the NRTL model, while the performance of the UNIQUAC prediction is less satisfactory for ternary VLE data of this system with higher water content.

The azeotropic behavior discussed above offers a reasonable explanation of the difficulties observed in the real separation process. Adsorption on active carbon was chosen as a potential method to remove the rest of the xylene from the ternary azeotropic mixture.

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