

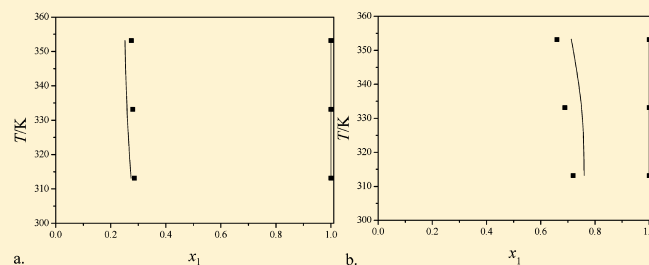
Binary and Ternary Vapor–Liquid Equilibrium Data of the System (Ethylbenzene + Styrene + 4-Methyl-*N*-butylpyridinium Tetrafluoroborate) at Vacuum Conditions and Liquid–Liquid Equilibrium Data of Their Binary Systems

Mark T. G. Jongmans,^{*,†} Mark Raijmakers,[†] Boelo Schuur,[‡] and André B. de Haan[†]

[†]Process Systems Engineering Group (SPS), Chemical Engineering and Chemistry Department, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

[‡]Faculty of Science and Technology, Thermo-Chemical Conversion of Biomass Group, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

ABSTRACT: Ethylbenzene and styrene are currently separated by ordinary fractional distillation, which is challenging due to the low relative volatility of this mixture of 1.3 to 1.4. Extractive distillation is a promising alternative to save capital and operational expenditures. Recently, ionic liquids (ILs) have been reported as a promising option to replace commonly used organic solvents like sulfolane. The IL 4-methyl-*N*-butylpyridinium tetrafluoroborate ([4-mebupy][BF₄]) is an IL with a strong effect on the relative volatility of the ethylbenzene/styrene mixture. In this work, binary VLE data in the range of (3 to 30) kPa, ternary VLE data at (5, 10, and 15) kPa, and binary LLE data at (313.2, 333.2, and 353.2) K have been determined for the system (ethylbenzene + styrene + [4-mebupy][BF₄]). The ternary VLE experiments show that [4-mebupy][BF₄] can enhance the relative volatility up to 2.7 to 2.8, and thereby [4-mebupy][BF₄] has a stronger effect on the relative volatility than the benchmark solvent sulfolane, which can increase the relative volatility up to 2.3. Therefore, [4-mebupy][BF₄] is a promising solvent for use in extractive distillation to separate ethylbenzene from styrene. The binary and ternary VLE data were correlated separately with the NRTL model and were regressed both together with the binary LLE data. The NRTL model could describe both data sets properly. The ternary VLE data could not be properly calculated by the binary NRTL parameters determined solely from the binary systems.



INTRODUCTION

Styrene is most commonly produced from ethylbenzene by a dehydrogenation process.¹ Since the conversion of ethylbenzene in this process is typically (50 to 70) %, ² styrene has to be separated from ethylbenzene after the dehydrogenation reactor. This separation is currently performed by distillation and requires about 85 % of the total energy demand in the distillation section,² due to the low relative volatility of 1.3 to 1.4.³ Extractive distillation can decrease the energy requirements of close boiling mixtures by the addition of a solvent to the distillation column.⁴ The solvent enhances the relative volatility of the mixture, and thereby, it simplifies the distillative separation. As a consequence, the operation and capital expenditures will decrease. Sulfolane is a commonly applied organic solvent, which can increase the relative volatility of the (ethylbenzene + styrene) mixture up to 2.3.⁵

Lately, ionic liquids (ILs) have been often reported as promising candidates to replace common organic solvents in extraction and extractive distillation processes.^{6,7} An IL is a salt, that is liquid at room temperature (< 100 °C), and commonly consists of a bulky asymmetric organic cation and an organic/inorganic anion.⁸ An IL combines the advantages of a liquid

solvent and a solid salt.⁹ ILs have a negligible vapor pressure^{10,11} and are therefore often reported as green solvents. Many ILs also possess high chemical and thermal stability, and they exhibit a broad liquid range.^{12,13} Moreover, because of the large variety of cations and anions available, ILs are often called designer solvents.¹⁴

Recently, we performed an IL screening study to separate ethylbenzene from styrene by extractive distillation.¹⁵ This study showed that several ILs have a larger selectivity to styrene over ethylbenzene compared to the benchmark solvent sulfolane. Nevertheless, there was a clear trade-off between the selectivity and the solvent capacity. ILs with a high capacity usually have a low selectivity, whereas ILs with high selectivity exhibit low capacity.¹⁵ A conceptual design study should demonstrate which property has the largest influence on the energy efficiency of an IL extractive distillation process: the selectivity or the solvent capacity. The IL 4-methyl-*N*-butylpyridinium tetrafluoroborate ([4-mebupy][BF₄]) is an

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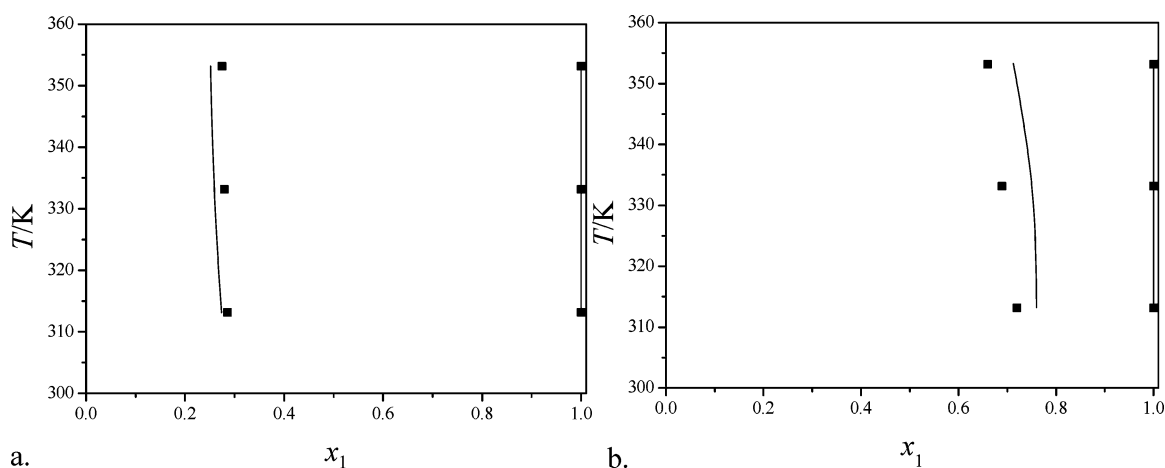


Figure 1. Pure component solubilities (x_1) of ethylbenzene and styrene in [4-mebupy][BF₄] at (313.2, 333.2, and 353.2) K. a, Ethylbenzene (1) + [4-mebupy][BF₄] (2). b, styrene (1) + [4-mebupy][BF₄] (2). ■, Experimental values; lines refer to NRTL correlations with parameters from only binary LLE and binary VLE data (Table 5).

example of an IL, which can enhance the relative volatility to 2.6, thus higher than the benchmark solvent sulfolane ($\alpha = 2.3$), and still has a reasonable solvent capacity ($x_{\max} = 0.234$ for ethylbenzene and $x_{\max} = 0.414$ for styrene, on mass base at 348.2 K).¹⁵ The IL [4-mebupy][BF₄] can thus decrease the reflux ratio of an extractive distillation column more than sulfolane for the ethylbenzene/styrene separation and thereby possibly save energy in the reboiler.

Commonly, vapor–liquid equilibrium (VLE) data are required for the ternary system and the constituent binary systems to setup a conceptual design for systems that contain ILs.^{16–19} This VLE data is currently not available for the system (ethylbenzene + styrene + [4-mebupy][BF₄]) in the open literature. Therefore, the aim of this study is to determine VLE data for this system in the pressure range of (3 to 30) kPa. These vacuum conditions are required to keep temperatures low because styrene polymerizes at elevated temperatures.²⁰ Next to the VLE experiments, also liquid–liquid equilibrium (LLE) experiments were performed for the binary systems to be able to describe liquid–liquid phase splitting. These experiments were required because ethylbenzene and styrene are not fully miscible with [4-mebupy][BF₄]. The NRTL model was used to describe the experimental LLE and VLE data.

EXPERIMENTAL SECTION

Materials. Acetone (100 $w = 99.5$) was obtained from VWR, cyclohexane (100 $w = 99$), styrene (100 $w = 99.5$), and 4-methyl-*N*-butylpyridinium tetrafluoroborate (100 $w = 98$) from Merck, and ethylbenzene (100 $w = 99$) and 4-*tert*-butylcatechol (100 $w = 98$) from Fluka. [4-mebupy][BF₄] was stored under deep vacuum in a desiccator filled with molecular sieves. The water content in [4-mebupy][BF₄] was determined with Karl Fischer titration and was for all experiments less than 100 $w = 0.2$. All chemicals were used without further purification.

Apparatus and Procedure. The LLE experiments of the binary systems (ethylbenzene + [4-mebupy][BF₄]) and (styrene + [4-mebupy][BF₄]) were performed to determine the pure component solubilities of styrene and ethylbenzene in [4-mebupy][BF₄], using the same experimental setup and approach as specified by Hansmeier et al.²¹ The organic feed (ethylbenzene/styrene) (25 mL) and [4-mebupy][BF₄] (15 mL) were added to 70 mL thermostatted vessels. The vessels

were closed by a PVC-cover through which a stainless steel axis passed with two impellers, which were powered by an electronic stirrer (IKA Eurostar powercontrol-visc P1). To ensure good mixing, the impellers were situated at the interface between the IL and the organic feed. The experiments were carried out at (313.2, 333.2, and 353.2) K \pm 0.1 K. The inhibitor 4-*tert*-butylcatechol was added (100 $w = 0.005$) to the styrene mixtures to prevent polymerization. The mixtures were stirred at 1300 rpm. Although equilibrium was obtained typically after 5 min,²² the mixtures were stirred for approximately 20 min to guarantee equilibrium. After stirring, the mixtures were settled for 2 h. From the IL phase, samples were taken of 0.2 mL with a 2 mL syringe.

All VLE experiments were performed with an all glass ebulliometer (Fischer VLE 602/D). The VLE equilibrium chamber is a dynamic recirculating still, equipped with a Cottrell circulation pump. The pressure and immersion heater were both kept constant using a control unit (Fischer VLE 2+). The vapor condensation rate was kept constant at one drop per second. Water of 288.15 K, provided by a cooling bath (Julabo F12), was used to condense the vapor phase. The equilibrium temperature was determined with an accuracy of 0.1 K. Equilibrium was reached when the equilibrium temperature and condensation rate were both constant, which was typically after (30 to 45) min.

For the binary mixtures (ethylbenzene + [4-mebupy][BF₄]) and (styrene + [4-mebupy][BF₄]) the pressure was changed respectively from (5 to 30) kPa and (3 to 22.5) kPa \pm 0.01 kPa. Mixtures of 100 mL were prepared for both binary systems. The binary mixtures with ethylbenzene comprised (10, 15, and 20) mL of ethylbenzene. The binary systems with styrene contained (10, 14.5, 19, 25, 37.5, and 50) mL of styrene. To the styrene binaries, the polymerization inhibitor 4-*tert*-butylcatechol (100 $w = 0.005$) was added. A small amount was added to not disturb the equilibrium. Although inhibitor was added, no VLE could be obtained above 100 °C for the mixtures containing styrene. Styrene started to polymerize above this temperature, and therefore, the composition of the liquid mixture was changing in time. As a result, the temperature could not be kept constant and no VLE could be obtained. The IL regeneration was performed in a rotary evaporator (Büchi rotavapor R-200). Methanol was added to the regenerated IL to precipitate possibly formed styrene polymer. Methanol is a

commonly used antisolvent to separate (styrene) polymers from organic solutions.^{23–25} Indeed styrene polymer precipitation was observed with the addition of methanol to the IL [4-mebupy][BF₄], and thereby, this method was verified.

Samples of 20 μL were taken from the liquid phase using a 100 μL syringe. No samples were taken from the vapor phase because it consisted only of either ethylbenzene or styrene due to the negligible vapor pressure of the IL.

The VLE experiments for the ternary system were conducted at (5, 10, and 15) kPa. Mixtures of 100 mL were prepared with a solvent-to-feed (S/F) ratio of 4 on volume base. It was not possible to measure VLE of mixtures with lower S/F ratios due to liquid–liquid phase splitting, nor with higher S/F ratios due to the higher equilibrium temperature at higher IL content (polymerization > 100 °C). Samples of 20 μL were taken from the liquid as well as the vapor phase using a 100 μL syringe.

Analysis. The samples from the binary LLE experiments were diluted with 1.2 mL of acetone, and 0.1 mL of cyclohexane was added as the internal standard. Acetone (120 μL) and cyclohexane (10 μL) were added to the samples from the VLE experiments. The equilibrium mass fractions were measured by a gas chromatograph (Varian CP-3800) equipped with a flame ionization detector (FID) and a Varian CP-SIL 5CB column (50 m \times 1.2 μm). Samples of 0.5 μL were injected into the gas chromatograph with a split ratio of 50. All samples were injected three times to avoid analytical mistakes. The concentration of [4-mebupy][BF₄] was calculated by a mass balance since ILs do not have a vapor pressure and therefore cannot be detected. The IL was gathered in a cup linear to avoid pollution of the analytical column and was replaced after (80 to 100) injections. The mole fractions of the aromatics could be determined with a deviation of 0.002.

RESULTS AND DISCUSSION

Binary LLE Data. The results for the binary LLE experiments for the systems (ethylbenzene + [4-mebupy]-[BF₄]) and (styrene + [4-mebupy][BF₄]) at (313.2, 333.2, and 353.2) K are depicted correspondingly in Figure 1a,b. The experimental data are provided in Table 1. The pure

Table 1. Binary LLE Data of the Systems (Ethylbenzene + [4-mebupy][BF₄]) and (Styrene + [4-mebupy][BF₄])^a

T/K	x_1^{I}	x_1^{II}
Ethylbenzene (1) + [4-mebupy][BF ₄] (2)		
313.2	0.9999	0.286
333.2	0.9999	0.280
353.2	0.9999	0.275
Styrene (1) + [4-mebupy][BF ₄] (2)		
313.2	0.9999	0.720
333.2	0.9999	0.689
353.2	0.9999	0.660

^a $\sigma(T) = 0.1$ K; $\sigma(x) = 0.002$.

component solubility of styrene in [4-mebupy][BF₄] is a factor of 2.4 to 2.5 larger than the ethylbenzene solubility. The interaction of an IL with an aromatic molecule is above all dominated by the interaction between the π -system of the aromatic molecule with the IL cation alkyl groups and the IL π -system.^{26,27} This behavior is called liquid clathrate formation,²⁷ and this ordered crystalline type of structure is formed for many aromatic-IL systems.^{27,28} Styrene is a flat molecule due to its unsaturated side chain and has a larger delocalized π -system

compared to ethylbenzene. The flat structure facilitates liquid clathrate formation,²⁹ and the larger π -system in styrene creates a stronger interaction with the IL compared to that in ethylbenzene.^{21,30} Therefore, styrene dissolves better in [4-mebupy][BF₄]. Figure 1 also illustrates that the styrene as well as the ethylbenzene solubility decrease with increasing temperature. This is a common behavior for aromatic-IL systems.²¹ The higher kinetic energy of the molecules at high temperatures breaks down the ordered liquid clathrate structure²⁷ and thereby reduces the specific aromatic-IL interaction. This temperature effect is weaker for the ethylbenzene-IL system compared to the styrene-IL system. This behavior together with the lower ethylbenzene solubility in [4-mebupy][BF₄] implicates that for ethylbenzene, it is more difficult to form a liquid clathrate structure with [4-mebupy]-[BF₄].

Binary VLE Data. The results for the binary VLE experiments of the systems (ethylbenzene + [4-mebupy][BF₄]) and (styrene + [4-mebupy][BF₄]) are depicted, respectively, in Figures 2 and 3. The experimental data are listed in Tables 2 and 3. To calculate the activity coefficient of the aromatic components in [4-mebupy][BF₄], Raoult's law was used and is defined as

$$\gamma_i P = \gamma_i x_i P_i^0 \quad (1)$$

where the subscript i refers to component i , y and x are correspondingly the vapor and liquid mole fractions, P is the total pressure, γ is the activity coefficient, x is the liquid mole fraction, and P^0 is the pure component vapor pressure. The pure component vapor pressures of ethylbenzene and styrene were calculated by the Antoine equation. The parameters for the Antoine equation were taken from our earlier work.⁵ The equilibrium temperatures in the experiments for the binary mixtures are increasing with increasing IL mole fraction and increasing pressure, which can be seen in Figures 2a and 3a. The boiling points of the binary mixtures increase with increasing IL concentration because [4-mebupy][BF₄] has a negligible vapor pressure. The increasing temperature with increasing pressure can be explained by the Antoine equation.

Figures 2b and 3b show that the ethylbenzene activity coefficient in [4-mebupy][BF₄] is larger than the styrene activity coefficient. This trend matches with the results from the binary LLE experiments. From Figure 2b, it can be seen that the ethylbenzene activity coefficient decreases with decreasing ethylbenzene mole fraction in the measured ethylbenzene concentration range (0.12 < x < 0.224). The activity coefficient of styrene also decreases with decreasing styrene concentration in the low styrene mole fraction range (x < 0.28). The activity coefficients of ethylbenzene and styrene are plotted as function of their liquid mole fraction at (333.2 and 353.2) K in Figure 4. The activity coefficients in Figure 4 were determined from the NRTL parameters obtained from the fitting of the binary LLE and VLE data. The NRTL model and the parameter fitting are explained in more detail further on in this paragraph. The activity coefficient of styrene exhibits a maximum at a styrene mole fraction of 0.28. For ethylbenzene also, a maximum exists because the ethylbenzene activity coefficient is one at an ethylbenzene mole fraction of one. However, liquid–liquid phase splitting occurs at an ethylbenzene mole fraction around 0.28. The maximum in activity coefficient has not been reached yet at this ethylbenzene mole fraction. The maximum in activity coefficient of the aromatic components as a function of their

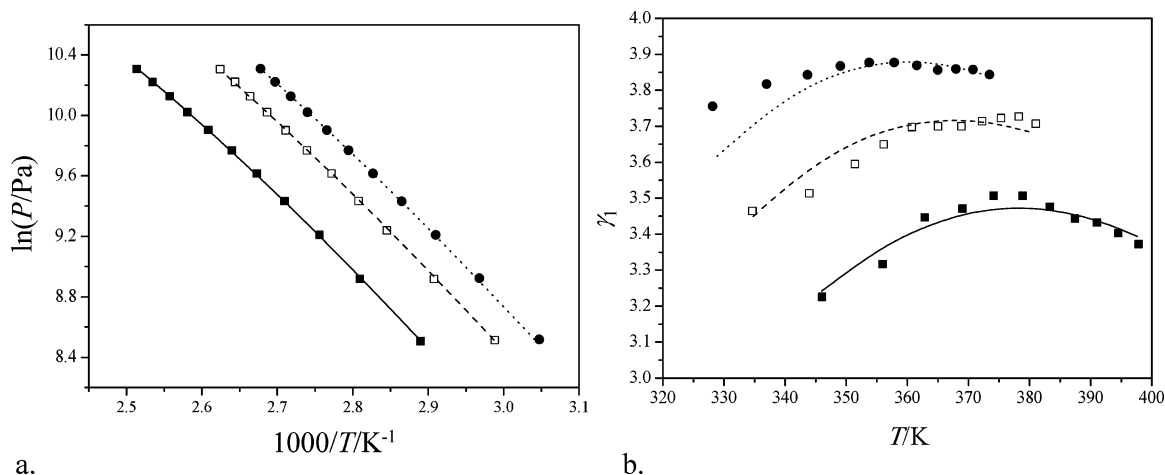


Figure 2. a, Vapor pressures for the binary mixture ethylbenzene (1) + [4-mebupy][BF₄] (2) at different ethylbenzene mole fractions x_1 . b, Activity coefficient of ethylbenzene γ_1 in the binary mixture ethylbenzene (1) + [4-mebupy][BF₄] (2) at different ethylbenzene mole fractions x_1 and temperatures. ■, $x_1 = 0.120$; □, $x_1 = 0.181$; ●, $x_1 = 0.224$. Lines refer to NRTL correlations with parameters from only binary LLE and binary VLE data (Table 5).

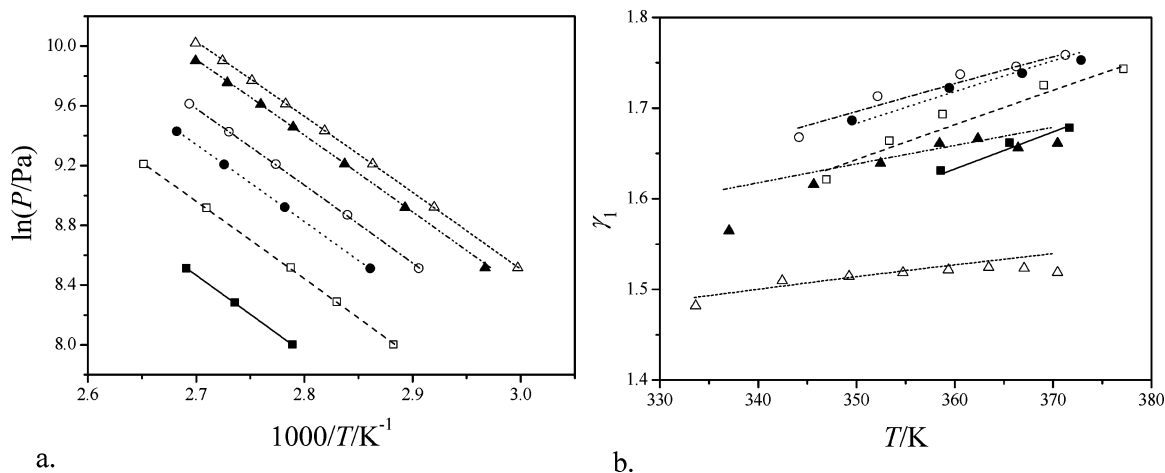


Figure 3. a, Vapor pressures for the binary mixture styrene (1) + [4-mebupy][BF₄] (2) at different styrene mole fractions x_1 . b, Activity coefficient of styrene γ_1 in the binary mixture styrene (1) + [4-mebupy][BF₄] (2) at different styrene mole fractions x_1 and temperatures. ■, $x_1 = 0.122$; □, $x_1 = 0.195$; ●, $x_1 = 0.280$; ○, $x_1 = 0.355$; ▲, $x_1 = 0.516$; △, $x_1 = 0.635$. Lines refer to NRTL correlations with parameters from only binary LLE and binary VLE data (Table 5).

Table 2. Vapor Pressure Data of the Binary System Ethylbenzene (1) + [4-mebupy][BF₄] (2)^a

P	T	P	T	P	T
kPa	K	kPa	K	kPa	K
$x_1 = 0.120$		$x_1 = 0.181$		$x_1 = 0.224$	
4.95	346.1	4.98	334.7	5.00	328.2
7.47	356.0	7.47	344.0	7.50	337.0
9.99	362.9	10.29	351.5	9.99	343.7
12.50	369.1	12.49	356.2	12.48	349.1
15.00	374.2	14.99	360.8	15.00	353.8
17.49	378.9	17.49	365.1	17.49	357.9
20.00	383.4	19.96	368.9	19.98	361.6
22.49	387.5	22.49	372.3	22.48	365.0
24.99	391.1	24.99	375.4	24.98	368.0
27.47	394.6	27.50	378.3	27.48	370.8
29.95	397.9	29.92	381.1	29.98	373.5

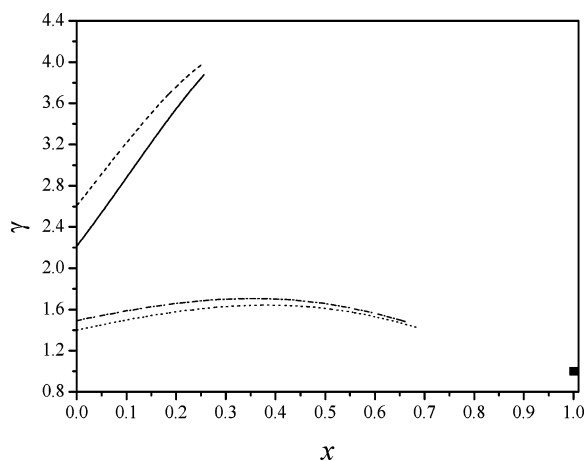
^a $\sigma(P) = 0.01$ kPa; $\sigma(T) = 0.1$ K; $\sigma(x) = 0.002$.

mole fractions originates from the difference in molecular interaction between aromatics and ILs at different compositions. At low aromatic mole fractions for aromatic-IL systems, a very ordered liquid clathrate structure can be formed.^{27,31} With increasing aromatic mole fraction, however, the aromatics disturb more the regular structure of the IL, and it is energetically less favorable to form a liquid clathrate than at low aromatics content. Therefore, the aromatic-IL interaction reduces with increasing aromatic mole fraction. Previously, we have measured this trend also for the behavior of ethylbenzene and styrene in the IL 3-methyl-*N*-butylpyridinium tetracyanoborate,³² and this trend is typical for aromatic-IL systems.^{33,34}

From Figures 2b and 3b also, the conclusion can be drawn that the activity coefficients of the aromatic components increase with increasing temperature. This behavior was also seen in the binary LLE experiments and can be explained by the same mechanism. Nevertheless, for high temperatures ((350 to 360) K), the ethylbenzene activity coefficient slightly reduces with increasing temperature. The styrene activity coefficient decreases also at high temperatures, however, only for high

Table 3. Vapor Pressure Data of the Binary System Styrene (1) + [4-mebupy][BF₄] (2)^a

P	T	P	T	P	T
kPa	K	kPa	K	kPa	K
$x_1 = 0.146$		$x_1 = 0.211$		$x_1 = 0.280$	
2.99	358.6	2.99	347.0	4.97	349.6
3.96	365.6	3.98	353.4	7.50	359.5
4.98	371.7	5.00	358.8	9.97	366.9
		7.46	369.1	12.45	372.9
		10.00	377.2		
$x_1 = 0.349$		$x_1 = 0.516$		$x_1 = 0.635$	
4.98	344.2	4.99	337.1	4.99	333.7
7.11	352.2	7.47	345.7	7.50	342.5
10.00	360.6	10.01	352.5	10.00	349.3
12.42	366.3	12.83	358.5	12.50	354.8
14.97	371.3	14.92	362.4	14.97	359.4
		17.25	366.5	17.50	363.5
		19.98	370.5	19.96	367.1
				22.48	370.5

^a $\sigma(P) = 0.01$ kPa; $\sigma(T) = 0.1$ K; $\sigma(x) = 0.002$.**Figure 4.** Activity coefficient γ of ethylbenzene (EB) and styrene (SM) in [4-mebupy][BF₄] as function of mole fraction x at (333.2 and 353.2) K. Lines are calculated with the NRTL parameters obtained from binary LLE and VLE data. —, EB, 333.2 K; - -, EB, 353.2 K; ···, SM, 333.2 K; - · -, SM, 353.2 K.

styrene mole fractions. This behavior arises from the fact that at higher temperatures, the thermal expansion of the IL becomes the more dominant effect, in contrast to the specific aromatic-IL interactions at lower temperatures. Because of the thermal expansion of the IL, the aromatics gain more freedom to arrange themselves between the ions, and their activity coefficient drops.

The binary experimental data have been correlated with the NRTL model. The binary LLE and VLE have been regressed together to obtain only one set of binary interaction parameters to describe both equilibria. The NRTL model is often used to describe multicomponent LLE as well as VLE data³⁵ and is used often for IL-organic systems.^{21,36} The required binary interaction parameters (eq 2) need to be determined by a regression of the experimental data.

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}, \quad G_{ij} = \exp(-\alpha_{ij}\tau_{ij}), \quad \alpha_{ij} = \alpha_{ji}$$

for $i \neq j$ where $i, j = 1, 2$

(2)

The parameters a_{ij} and b_{ij} describe the interaction between the two molecules i and j . The parameter α_{ij} is the nonrandomness parameter. All parameters were kept variable when regressing the experimental data by the Aspen Plus Data Regression tool, which is common for IL systems.^{17,21,37} The vapor phase was assumed as ideal because the experiments were performed under vacuum conditions.³⁵ As an objective function, the maximum likelihood principle was used. A weight factor of 1 was dedicated to the binary LLE data and 100 to the binary VLE data. This difference in weight factor was necessary to obtain a proper correlation of the binary VLE data. The rmsd (relative root-mean-square deviation) was calculated for the temperature, pressure, and liquid mole fraction to determine if the NRTL model could correlate the experimental data well. The rmsd is defined as

$$\text{rmsd} = 100 \sqrt{\frac{\sum_i^N \left(\frac{\theta^{\text{exp}} - \theta^{\text{cal}}}{\theta^{\text{exp}}} \right)^2}{n}} \quad (3)$$

where n represents the number of data points, and θ represents the pressure, temperature, or liquid mole fraction. Tables 5 and

Table 4. Ternary VLE Data for the System Ethylbenzene (1) + Styrene (2) + [4-mebupy][BF₄] (3) at (5, 10, and 15) kPa and a Solvent-to-Feed (S/F) Ratio of 4 on Volume Base^a

T/K	x_1	x_2	y_1	y_2
5 kPa				
348.0	0.023	0.230	0.194	0.806
346.2	0.028	0.238	0.220	0.781
341.4	0.070	0.200	0.460	0.540
339.1	0.106	0.137	0.666	0.334
334.1	0.160	0.093	0.820	0.180
330.3	0.209	0.039	0.936	0.064
328.7	0.233	0.028	0.958	0.042
10 kPa				
364.2	0.023	0.230	0.192	0.808
361.3	0.028	0.237	0.219	0.781
357.0	0.070	0.206	0.449	0.551
355.4	0.106	0.138	0.654	0.346
348.8	0.162	0.100	0.808	0.193
345.8	0.210	0.040	0.934	0.066
344.3	0.231	0.030	0.954	0.046
15 kPa				
375.1	0.023	0.229	0.190	0.810
371.8	0.028	0.238	0.211	0.789
367.4	0.068	0.203	0.436	0.564
366.0	0.105	0.140	0.638	0.362
358.4	0.163	0.098	0.806	0.194
356.1	0.209	0.041	0.928	0.072
354.2	0.231	0.029	0.954	0.047

^a $\sigma(P) = 0.01$ kPa; $\sigma(T) = 0.1$ K; $\sigma(x) = 0.002$; $\sigma(y) = 0.002$.

6 show, respectively, the obtained binary interaction parameters and the correlation statistics. The rmsd values in Table 6 and Figures 1 to 3 demonstrate that the NRTL model can properly calculate the binary LLE and VLE data. The binary LLE data is

Table 5. Binary NRTL Interaction Parameters for the Binary LLE and VLE Data and Ternary VLE Data of the System Ethylbenzene + Styrene + [4-mebupy][BF₄]

system	a_{12}	a_{21}	b_{12}/K	b_{21}/K	α
From Solely Binary LLE and VLE Data					
ethylbenzene (1) + [4-mebupy][BF ₄] (2)	-11.76	-1.99	8956.6	-639.9	0.077
styrene (1) + [4-mebupy][BF ₄] (2)	5.144	0.126	-193.5	-389.6	0.262
From Solely Binary LLE and Ternary VLE Data					
ethylbenzene (1) + styrene (2) ^a			304.61	-226.71	0.3
ethylbenzene (1) + [4-mebupy][BF ₄] (2)	9.10	0.83	-205.36	-107.46	0.254
styrene (1) + [4-mebupy][BF ₄] (2)	7.08	1.30	352.84	-340.85	0.340

^aNRTL binary interaction parameters for the system ethylbenzene + styrene were taken from ref 5.

Table 6. Relative Root-Mean-Square Deviations (*r*RMSD) in Liquid and Vapor Mole Fraction, Pressure and Temperature for the Correlation of the VLE and LLE Data by the NRTL Model for the System Ethylbenzene (1) + Styrene (2) + [4-mebupy][BF₄] (3)

data set	rrmsd/% ^a				
	P	T	x_1	x_2	y_1
Binary LLE + Binary VLE Data					
binary LLE data (1) + (3)		0.004	7.1		
binary LLE data (2) + (3)		0.29		8	
binary VLE data (1) + (3)	0.05	0.06	0.07		
binary VLE data (2) + (3)	0.04	0.05		0.03	
Binary LLE + Ternary VLE Data					
binary LLE data (1) + (3)		0.003	21		
binary LLE data (2) + (3)		0.008		7.2	
ternary VLE data (1) + (2) + (3)	0.23	0.25	0.28	0.26	1.78

^aSee eq 3.

correlated less accurately than the binary VLE data, which originates from the difference in weight factor given to these data sets.

Ternary VLE Data. The results for the ternary VLE data are illustrated in Figure 5, in which the relative volatility is shown as function of the ethylbenzene solvent free concentration in the liquid phase for an S/F ratio of 4 on volume base. The experimental results are depicted in Table 4. The relative volatility is defined as

$$\alpha = \frac{y_i/x_i}{y_j/x_j} = \frac{\gamma_i P_i^0}{\gamma_j P_j^0} \quad (4)$$

where y and x are, respectively, the vapor and liquid mole fraction, γ is the activity coefficient, P^0 is the pure component vapor pressure, and the subscripts represent the molecules i and j . From Figure 5, it can be seen that the IL [4-mebupy][BF₄] can increase the relative volatility of the system (ethylbenzene + styrene) up to 2.7 to 2.8, meaning that [4-mebupy][BF₄] has a stronger effect on the relative volatility than the benchmark solvent sulfolane, which can increase the relative volatility up to 2.3.⁵ It may therefore be concluded that it can be an interesting option to replace sulfolane by this IL. The here presented results are in accordance with the findings in our previously reported solvent screening study.¹⁵ It also follows from Figure 5

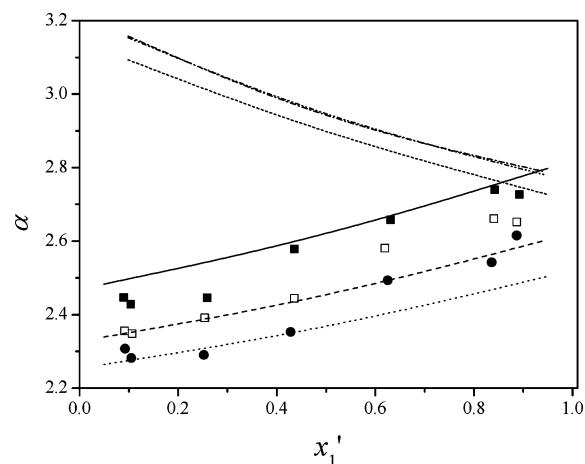


Figure 5. Relative volatility α as a function of the solvent free ethylbenzene mole fraction in the liquid phase x_1' and different pressures for the ternary system ethylbenzene (1) + styrene (2) + [4-mebupy][BF₄] (3) for a solvent-to-feed ratio of 4 on volume base. Experimental: ■, $P = 5$ kPa; □, $P = 10$ kPa; ●, $P = 15$ kPa. Relative volatility calculated with NRTL parameters from only binary LLE and ternary VLE data (Table 5): —, $P = 5$ kPa; - - -, $P = 10$ kPa; ···, $P = 15$ kPa. Relative volatility calculated with NRTL parameters determined solely from binary LLE and binary VLE data (Table 5): ····, $P = 5$ kPa; ·····, $P = 10$ kPa; ·····, $P = 15$ kPa.

that the relative volatility increases with decreasing pressure. This behavior originates from the higher pure component vapor pressure ratio at lower temperatures. The ethylbenzene/styrene ratio influences the relative volatility only slightly since the interaction between styrene and ethylbenzene is almost ideal.⁵

The NRTL model was also used to correlate the ternary VLE data. The regression of the NRTL model to the ternary VLE data was done with binary LLE data included in the objective function (using the maximum likelihood method) because the ability to describe liquid–liquid phase splitting when modeling an extractive distillation column is essential. The parameters for the interaction between (ethylbenzene + styrene) were taken from earlier work.⁵ The parameters between (ethylbenzene + [4-mebupy][BF₄]) and (styrene + [4-mebupy][BF₄]) were kept variable to regress the ternary VLE data. The ternary VLE data were correlated separately from the binary VLE data because it is difficult to describe binary and ternary VLE data with just one set of binary NRTL parameters.^{16,17,38,39} This is also illustrated in Figure 5 by the lines for the correlation of the relative volatility from only the binary systems. It can be seen that these lines do not fit the experimental data, whereas the parameter regression with floating binary parameter sets for (ethylbenzene + [4-mebupy][BF₄]) and (styrene + [4-mebupy][BF₄]) yielded a much better fit. The NRTL parameters obtained from the ternary VLE data are listed in Table 5, and the rrmsd values are reported in Table 6. From these values and the graphs in Figure 5, it may be concluded that the NRTL model can adequately describe the ternary VLE data.

CONCLUSIONS

In this study, binary VLE data in the pressure range of (3 to 30) kPa, ternary VLE data at (5, 10, and 15) kPa, and binary LLE data at (313.2, 333.2, and 353.2) K have been measured for the system (ethylbenzene + styrene + [4-mebupy][BF₄]). The

binary VLE data for the systems (ethylbenzene + [4-mebupy][BF₄]) and (styrene + [4-mebupy][BF₄]) showed that the activity coefficient of both aromatics decrease with decreasing aromatic mole fraction at low aromatic mole fractions ($x < 0.28$). The styrene activity coefficient shows a maximum as a function of its mole fraction in the binary system (styrene + [4-mebupy][BF₄]) at a styrene mole fraction of 0.28. Ethylbenzene also exhibits a maximum; however, liquid–liquid phase splitting occurs before reaching this maximum. The ternary VLE experiments show that [4-mebupy][BF₄] can enhance the relative volatility of the ethylbenzene/styrene system up to ~2.7 to 2.8 and thus has a stronger effect on the relative volatility than the benchmark solvent sulfolane, which can increase the relative volatility up to 2.3. Therefore, it may be concluded that it may be beneficial to use [4-mebupy][BF₄] in an extractive distillation process to separate ethylbenzene from styrene. The binary and ternary VLE data were correlated separately with the NRTL model. Both data sets were regressed together with the binary LLE data. The NRTL model was able to describe both data sets adequately. The ternary VLE data could not be properly described by the binary NRTL parameters determined solely from the binary systems.

AUTHOR INFORMATION

Corresponding Author

*Tel: +31 40 247 2424. Fax: +31 40 246 3966. E-mail: m.t.g.jongmans@tue.nl.

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