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Vapor−Liquid Equilibrium and Density of the Binary System 1-Phenylethylamine + Toluene

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Isobaric (p = 98.71 kPa) and isothermal (T = 363.15 K, 383.15 K) vapor−liquid equilibria, as well as densities at 298.15 K, have been measured for the system 1-phenylethylamine + toluene. Good predictions of the vapor−liquid equilibrium data by the UNIFAC model were confirmed.

Introduction

For the design and optimization of distillation processes, a knowledge of the vapor−liquid equilibrium is necessary. For systems in which experimental data are not available, the group contribution method can be used for the prediction of the required vapor−liquid equilibria. There are no experimental VLE data in the literature for the binary system 1-phenylethylamine + toluene. The purification of this amine by distillation is an important fragment of the pantolactone production technology, designed in the Laboratory of Technological Processes. The aim of this work is to determine if the UNIFAC method can predict VLE for this system and to provide additional information about the thermodynamics of this system.

Experimental Section

Materials. (±)-1-Phenylethylamine (PhEA) (Merck, >98%) and toluene (Chempur, Poland, p.a.) were fractionally distilled using a 10-plate laboratory column. Final purities (GC) were 99.5% (FEA) and 99.8% (toluene). All experiments were conducted in an atmosphere of purified argon. (PhEA forms carbonate solid deposits during contact with air.) The physical constants of pure compounds are collected in Table 1.

Vapor−Liquid Equilibrium. The vapor pressure of PhEA and the vapor−liquid equlibria for the system PhEA/toluene were determined by the dynamic method as described by Domańska et al.[3] For the binary system, the compositions of both the liquid and the vapor phases were analyzed. The overall pressure was measured using a mercury manometer equipped with a cathetometer with an accuracy of ±0.005 kPa. Readings were corrected according to standard methods.[4] Temperature was measured using a calibrated platinum resistant thermometer (Frontec S1223) with an accuracy of ±0.01 K. In an equilibrium state, pressure was constant within ±0.04 kPa for isobaric measurements, and temperature was constant within ±0.02 K for isothermal measurements.

Table 1. Properties of Pure Components[a]

	$n_D^{298.15}$		$\rho^{298.15}$/g·cm^{-3}	
compound	exptl	lit	exptl	lit
PhEA	1.52437	1.5260[1]	0.94958	
toluene	1.49419	1.49413[2]	0.86239	0.86231[2]

[a] $n_D^{298.15}$: refractive index; $\rho^{298.15}$: standard liquid density.

Table 2. Vapor Pressure of PhEA as a Function of Temperature

T/K	p/kPa	T/K	p/kPa
363.78	3.762	396.84	14.638
367.95	4.487	397.71*	15.122*
372.30	5.443	399.45	16.102
375.40	6.236	400.49	16.694
379.58	7.429	402.81	18.200
379.54*	7.477*	405.53	20.048
383.04	8.528	407.62*	21.539*
387.04	10.029	410.22	23.641
387.53*	10.283*	414.91	27.665
390.62	11.561	419.25	31.857
394.20	13.286		

The composition of the liquid and vapor was determined by a precision refractometer (Carl Zeiss, Jena). The refractive index (n_D) was measured with an accuracy of ±0.00001 at 298.15 K. The calibration curve was made, and the mole fractions of PhEA (x) were determined from the equation

$$x = 133.88204(n_D^{298.15})^2 - 371.46226n_D^{298.15} + 256.12613 \quad (1)$$

which approximates the mole fraction with an rmsd equal to 0.003.

Calculations by the UNIFAC method were done using the modified Dortmund model, described by Gmehling et al.[5] The PhEA molecule was assumed to consist of five ACH groups and the following single groups: AC, CH_3, and $CHNH_2$.

Density. Density was determined using an Anton Paar DMA 02C densimeter at (298.15 ± 0.05) K, calibrated with air and water according to the standard procedure. Its accuracy is estimated to be $\pm 1 \times 10^{-5}$ g·cm^3, which gives the error of the reported excess volumes not to exceed 0.003 cm^3·mol^{-1}.

Results and Discussion

Vapor−Liquid Equilibrium. The vapor pressure data of PhEA are collected in Table 2. These data were obtained in two series: the first one, in which pressure was

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Table 3. VLE Data[a] at $p = 98.71$ kPa for the System PhEA/Toluene

x	y	T/K
0.0122	0.0001	383.4
0.0409	0.0005	384.4
0.0859	0.0050	385.8
0.1331	0.0113	387.5
0.1862	0.0256	389.4
0.2572	0.0211	391.9
0.2841	0.0292	392.7
0.3280	0.0382	394.5
0.3721	0.0418	396.3
0.4716	0.0643	401.2
0.5214	0.0670	404.5
0.5870	0.0778	408.8
0.6726	0.1168	414.1
0.6667	0.1432	414.7
0.7148	0.1560	417.6
0.7572	0.2073	422.1

[a] x, y: mole fractions of PhEA in the liquid and vapor, respectively; T: boiling point.

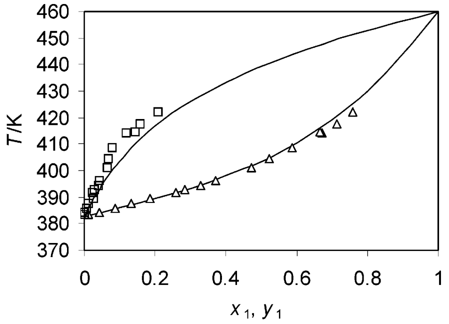

Figure 1. VLE diagram at $p = 98.71$ kPa of the system PhEA (1) + toluene: □, vapor; Δ, liquid (experimental points); −, calculated by the UNIFAC model.

increased up to the highest value of temperature (ca. 423 K), and the second one (data marked by *), in which pressure was decreased. An analysis of these data shows no trends and allows us to exclude the amine decomposition during this experiment. The data can be approximated by the Antoine equation

$$\ln(p/\mathrm{kPa}) = 14.084 - \frac{3509.4}{T - 89.00} \qquad (2)$$

with the rmsd equal to 0.04 kPa. This gives the normal boiling point temperature of 459.76 K and the entropy of vaporization at the normal boiling point of $\Delta S^{\mathrm{vap}} = 97.6$ $\mathrm{J{\cdot}K^{-1}\,mol^{-1}}$.

The isobaric VLE equilibrium data for $p = 98.71$ kPa are collected in Table 3 and compared with the results of calculations by the UNIFAC method (Figure 1).

Isobaric data at the pressure close to atmospheric were needed to design the distillation process. It was possible to obtain only the points for which the equilibrium temperature did not exceed the value of ca. 420 K because of the characteristics of the still used and to prevent the possible decomposition of PhEA. Hence, only a part of the VLE diagram for the system investigated was obtained (Figure 1). To test the prediction of the VLE for the whole composition range, isothermal equilibrium measurements were carried out at two temperatures. Equilibrium data for 363.15 K and 383.15 K are collected in Tables 4 and 5 and compared with the results of calculations by the UNIFAC method (Figures 2 and 3, Table 6).

The results of the prediction concerning the three data sets are shown in Table 6. The observed accuracy is fairly good but is slightly worse for the isobaric data.

Table 4. VLE Data[a] at $T = 363.15$ K for the System PhEA/Toluene

x	y	p
0.0000	0.0000	54.25
0.0253	0.0050	53.89
0.0770	0.0050	51.14
0.1731	0.0086	45.04
0.2897	0.0165	39.76
0.5495	0.0768	28.34
0.6206	0.1047	25.07
0.6500	0.1105	22.93
0.7070	0.1348	19.58
0.7889	0.1993	14.33
0.8462	0.2565	11.29
0.8591	0.2773	11.73
0.9254	0.4817	7.88

[a] x, y: mole fractions of PhEA in the liquid and vapor, respectively; p: pressure in kPa.

Table 5. VLE Data[a] at $T = 383.15$ K for the System PhEA/Toluene

x	y	p
0.0262	0.0094	98.29
0.0458	0.0086	96.06
0.0580	0.0103	93.85
0.1841	0.0156	81.77
0.2710	0.0262	74.36
0.3500	0.0387	69.18
0.5393	0.0695	54.35
0.6836	0.1475	40.64
0.7770	0.1786	33.35
0.8047	0.2403	27.17
0.8086	0.2366	28.53
0.8541	0.3141	22.40
0.8937	0.4155	18.24

[a] x, y: mole fractions of PhEA in the liquid and vapor, respectively; p: pressure in kPa.

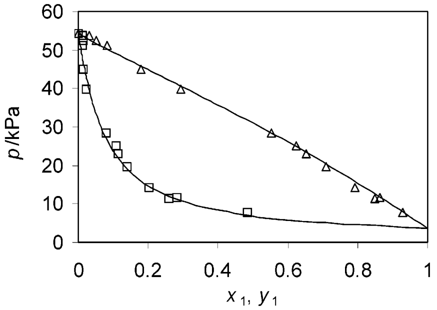

Figure 2. VLE diagram at $T = 363.15$ K of the system PhEA (1) + toluene: □, vapor; Δ, liquid (experimental points); −, calculated by the UNIFAC model.

All of the data sets were correlated using the Redlich−Kister equation to represent the excess Gibbs energy

$$G^{\mathrm{E}} = x_1x_2\sum_{i=0}^{n}a_i(x_1 - x_2)^i \qquad (3)$$

where 1 and 2 are the components (1 − PhEA, 2 − toluene) and a_i represents the parameters that are independent of temperature.

The values of the parameters and standard deviations (rmsd) are given in Table 7. Their number, which is justified statistically, varies from one for the isobaric data to up to three for the isothermal data. It may be concluded from the results that the system exhibits a low deviation from ideality with the maximum value of the excess Gibbs energy of about 100 $\mathrm{J{\cdot}mol^{-1}}$. This function is mainly

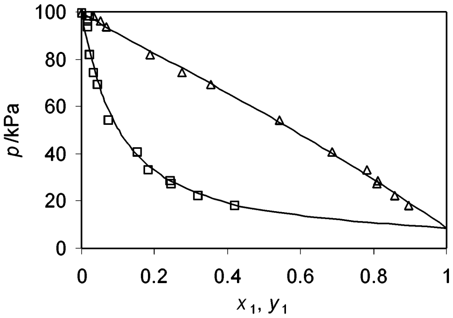

Figure 3. VLE diagram at T = 383.15 K of the system PhEA (1) + toluene: □, vapor; Δ, liquid (experimental points); −, calculated by the UNIFAC model.

Table 6. Results of the Prediction of the UNIFAC Model

system	rmsd^a of	
p or T const	a^b	b^b
98.71 kPa	1.3 K	0.043
363.15 K	0.90 kPa	0.024
383.15 K	1.32 kPa	0.014

[a] rmsd = $[\sum_{i=1}^{n}(x_i - x_i^{\text{calcd}})^2\}/n]^{1/2}$, where x_i and x_i^{calcd} are the experimental and calculated values of the pressure and temperature and n is the number of experimental points. [b] Total pressure (a) or boiling temperature (b) mole fraction of the PhEA in the vapor phase.

Table 7. Parameters of the Redlich−Kister Equation and the Standard Deviations

	p or T	a_0	a_1	a_2	rmsd
G^E	98.71 kPa	622.3			0.32K
G^E	363.15 K	339.3	−319.0	−452.2	0.58 kPa
G^E	383.15 K	502.7	−304.3	−896.0	0.82 kPa
V^E	298.15 K	0.1107	−0.2977	−0.1048	0.0024 cm^3·mol^{-1}

positive but slightly S shaped with a small negative region at higher concentrations of PhEA, although the number and the quality of the data do not allow us to draw definite conclusions. Such shape is not predicted by the UNIFAC model.

The isothermal data positively passed the test of consistency proposed by Van Ness et al.[6] It was not applied to the isobaric data because of the lack of data at higher temperatures.

Density. The density data of the system PhEA/toluene at 298.15 K as a function of the mole fraction of PhEA are collected in Table 8, together with the values of the V^E function. The latter were correlated by the Redlich−Kister equation (Figure 4). The values of the parameters are given in Table 7.

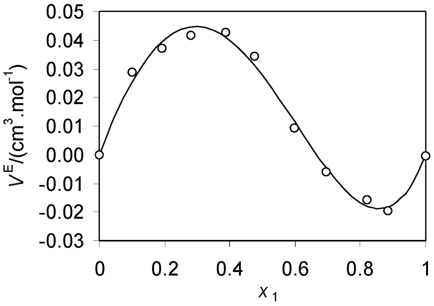

Figure 4. V^E at 298.15 K of the system PhEA (1) + toluene: ○, experimental points; −, calculated by the Redlich−Kister equation.

Table 8. Density (ρ), Molar Volume (V_M), and Excess Volume (V^E) for the System PhEA/Toluene at 298.15 K as a Function of the Molar Fraction of PhEA

x	ρ/g·cm^{-3}	V_M/ cm^3·mol^{-1}	V^E/ cm^3·mol^{-1}	V^E_{calcd}/ cm^3·mol^{-1}
0	0.86239	106.844	0.000	0.000
0.10199	0.87257	108.992	0.029	0.0256
0.19156	0.88133	110.860	0.037	0.0394
0.28166	0.88987	112.737	0.042	0.0447
0.38860	0.89968	114.959	0.043	0.0409
0.47672	0.90756	116.781	0.034	0.0310
0.59835	0.91814	119.283	0.009	0.0114
0.69531	0.92622	121.282	−0.006	−0.0047
0.82064	0.93621	123.875	−0.016	−0.0181
0.88315	0.94103	125.170	−0.019	−0.0183
1	0.94958	127.617	0.000	0.000

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