

EXTRACTIVE DISTILLATION OF ETHYLBENZENE AND STYRENE USING SULFOLANE AS SOLVENT: LOW PRESSURE ISOBARIC VLE DATA

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Abstract

The distillation of ethylbenzene (EB) from styrene (SM) is very energy intensive. By using extractive distillation instead, both capital and energy expenses are potentially reduced dramatically. Hereto we propose to use sulfolane (SF) as solvent. Currently there is no ternary vapor liquid equilibrium (VLE) data available of the system SM/EB/SF and the binary VLE data sets of EB/SM available in literature are found to be thermodynamically inconsistent. In this study thermodynamically consistent VLE data is obtained for the three binary systems and the ternary system in the pressure range of 50-200 mbar. Both the Wilson and NRTL model can adequately describe the experimental VLE data. The solvent SF increases the relative volatility significantly from 1.3-1.4 up to 2.3. Equilibrium process modeling suggests that an energy reduction of 50% compared to the traditional distillation process can be obtained with the extractive distillation process.

Keywords: Extractive distillation, VLE, styrene, ethylbenzene, sulfolane.

1. Introduction

Styrene (SM) production is among the ten biggest processes worldwide with a total production of 28 million metric tonnes a year, from which 85% is produced via the dehydrogenation of ethylbenzene (EB)¹. Distillation is used in this process to separate EB from SM. Due to the low relative volatility of 1.3-1.4², the distillation of EB from SM accounts for 75-80% of the total energy use in the distillation section of a typical SM production plant³.

A dramatic reduction in both capital and energy expenses may be obtained when the traditional distillation is replaced by extractive distillation^{2,4}. A reduction in energy consumption of 75% would reduce the worldwide CO₂ emission by 2.6 million metric tonnes CO₂ per year. However, no process evaluation is currently available in literature about the separation of EB/SM by extractive distillation. In this study the commonly applied solvent sulfolane (SF) was selected because it can increase the relative volatility to 2.2-2.6^{4,5}.

To evaluate the potential of extractive distillation for EB/SM separation, consistent vapor-liquid equilibrium (VLE) data are required to establish an equilibrium process model⁶. To establish an equilibrium process model, VLE data have to be known of the three binary systems EB/SM, EB/SF, and SM/SF as well as the ternary system EB/SM/SF. Currently no ternary VLE data is reported in literature. An overview of the binary VLE data is given in Table 1. Many binary data are already available for the EB/SM system⁷, but only the relevant low pressure data are given in Table 1. To prevent polymerization of SM, low temperatures are required and therefore the (extractive) distillation unit should operate at low pressure, typically between 50-200 mbar³. The consistency of the available binary data in the low pressure range is tested with the area method originally developed by Redlich et al.⁸ and Herington⁹, and later extended by Herington to make this test also applicable to isobaric data¹⁰. In this method, $\log(y_1/y_2)$ is plotted against x_1 and should the area above the horizontal axis be equal to the area below with a maximum area deviation of 10%. Moreover the point test method¹¹ was applied by a regression of the experimental data with the NRTL model. According to this test the experimental data are consistent if the average absolute deviation between calculated and measured vapour mole fractions of the lowest boiling component (AAD_v) is less than 0.01 and are scattered randomly about zero¹¹.

Table 1. Overview of reported binary VLE data in literature for the ethylbenzene(EB)/styrene(SM)/sulfolane(SF) system

Source	System	Isobaric/ isothermal	Pressure [kPa]	Area consistency [%]	AAD _y [-]	AAD _p [kPa]
Aucejo et al. ⁷	EB/SM	Isobaric	5	68.1	0.003	0.028
	EB/SM	Isobaric	15	21.3	0.001	0.066
Chaiyavech et al. ¹²	EB/SM	Isobaric	6.7	55.0	0.005	0.021
	EB/SM	Isobaric	13.3	51.7	0.004	0.049
	EB/SM	Isobaric	26.7	93.2	0.008	0.041
White et al. ¹³	EB/SM	Isobaric	13.3	51.9	0.01	0.05
Yu et al. ¹⁴	EB/SF	Isobaric	101.3	-	0.002	1.149
Chen et al. ¹⁵	SM/SF	Isothermal	0.04-5	-	-	-

It follows from the area consistency test, that the available low pressure VLE data of the binary system EB/SM is thermodynamically inconsistent, since the area deviation is larger than 10%. To determine the consistency of the VLE data, the experimental data of both the liquid and vapour phase have to be known¹². It was not possible to determine the consistency of the available EB/SF and SM/SF data. The vapour phase compositions in these VLE data were calculated due to the large boiling point difference between SF and EB/SM¹⁰. The binary VLE data of EB/SF and SM/SF are both not measured in the desired pressure range of 50-200 mbar. To obtain a good prediction of the ternary VLE data from the binary VLE data it is moreover advisable to measure the data in the same laboratory with the same experimental procedure⁶. Therefore it is required to measure the binary systems and the ternary system to obtain consistent data in the desired pressure range.

2. Experimental

2.1. Chemicals

Cyclohexane and acetone were respectively used as an internal standard and diluent. Acetone ($\geq 99.5\%$) was obtained from VWR, cyclohexane ($\geq 99\%$) and styrene ($\geq 99.5\%$) from Merck, ethylbenzene ($\geq 99\%$), sulfolane ($\geq 98\%$) and 4-tert-butylcatechol ($\geq 98\%$) from Fluka. All chemicals were used without further purification.

2.2. Apparatus and procedure

The VLE data of the pure components, binary and ternary systems were measured with an all glass ebulliometer (Fischer VLE 602/D), in which the equilibrium vessel is a dynamic recirculating still, equipped with a Cottrell circulation pump. The heating capacity and pressure are controlled using a control unit (Fisher VLE 2+). The pressure was maintained constant within a deviation of 0.5 mbar. The equilibrium temperature was measured with a Pt-100 measuring sensor with an uncertainty of 0.1 °C. Cooling of the vapor phase was done by means of a Julabo F12 cooling bath, operating at 15 °C. Equilibrium was reached after approximately 30-45 minutes, when the vapor temperature and the distillation rate were both constant. 4-tert-butylcatechol (0.005 wt%) was added as a polymerization inhibitor. In order to determine the equilibrium compositions, samples of 20 μL were taken from both the liquid and condensed gas phase using a 100 μL syringe. The samples were diluted with 120 μL of acetone and 10 μL of cyclohexane was added as internal standard. The equilibrium compositions were analyzed using a gas chromatograph (Varian CP-3800) equipped with a flame ionization detector and a Varian CP-SIL 5CB column (25m * 1.2 μm). The split ratio was 50 and the injection volume 0.5 μL .

2.3 Process modeling

ASPEN Plus software was used to perform the regression of the binary interaction parameters from the experimental VLE data and to simulate both the benchmark distillation process, and the extractive distillation process with SF. Both processes were compared for a typical production capacity of 500.000 mta³. The distillation feed contained 60 wt% SM and 40 wt% EB. The final impurity level of EB in SM was 10 ppm. In the current distillation process a reflux ratio of 7 is needed to meet the product requirements³.

3. Results and discussion

3.1. Pure component vapor pressure

The pure component vapor pressures of EB and SM were determined in the relevant temperature range. The Antoine equation was used to calculate the vapour pressures of EB and SM, shown in Equation 1. The vapor pressure of SF was calculated by using parameters determined by Riddick et al. for which the equation is shown in Equation 2.¹⁷ The obtained Antoine parameters are shown in Table 3.

$$\ln(P^{\text{sat}}(\text{Pa})) = A - \frac{B}{T(\text{K}) + C} \quad (1)$$

$${}^{10}\log(P^{\text{sat}}(\text{kPa})) = A - \frac{B}{T(\text{K})} - C({}^{10}\log(T(\text{K}))) \quad (2)$$

Table 3. Antoine coefficients of the pure components

Component	T [K]	A	B	C	Equation
Ethylbenzene	324-364	20.8051	3211.782	-63.045	1
Styrene	332-373	21.1275	3453.578	-58.499	1
Sulfolane	391.2-558.2	27.8073	4350.7	6.5633	2

3.2. Binary VLE data

The experimental VLE data of the three binary systems are shown in Figures 1 to 3. The binary system EB/SM almost forms an ideal solution and no azeotropes were found. The data was found to be consistent with area deviations of only 3.4, 1.1, and 0.4% for 50, 100 and 200mbar, respectively. The area deviations at the three measured pressures thus were all well below 10%.

Due to the large boiling point difference between SF and EB/SM, the concentration of SF in the vapour phase is very low and falls outside the detection limit of the gas chromatograph. However to perform a regression, the concentration of SF in the vapour phase is required. To get a starting value, Raoult's law was used to make an initial guess.

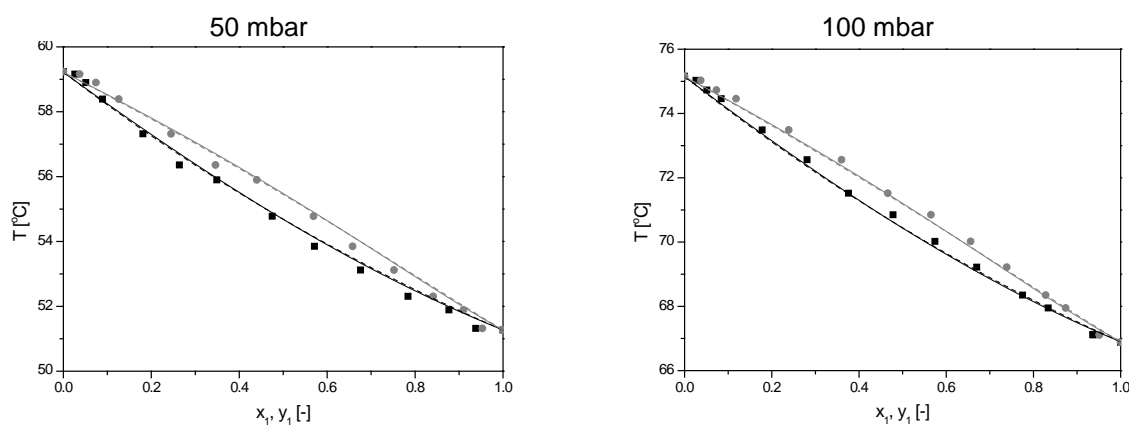


Figure 1. Txy diagram for the system ethylbenzene(1)/styrene(2) at 50, 100 and 200 mbar. ■, ●, experimental data, —, —, NRTL Model, ---, ---, Wilson Model.

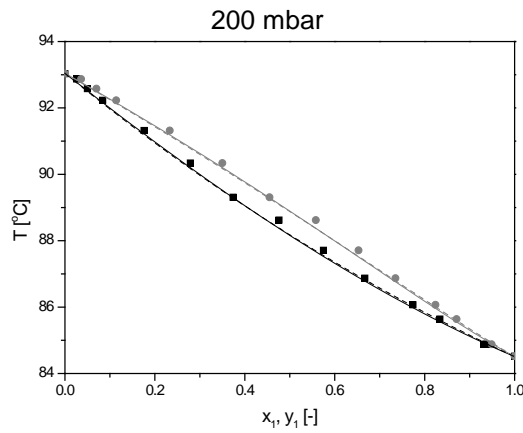


Figure 1. (Continued) Txy diagram for the system ethylbenzene(1)/styrene(2) at 50, 100 and 200 mbar. ■, ●, experimental data, —, —, NRTL Model, ---, ---, Wilson Model.

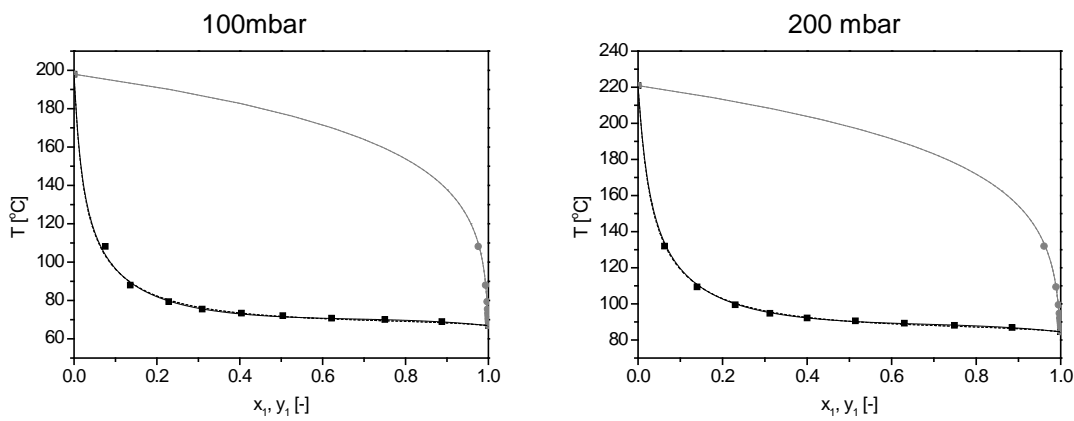


Figure 2. Txy diagram for the system ethylbenzene(1)/sulfolane(2) at 100 and 200 mbar. ■, ●, experimental data, —, —, NRTL Model, ---, ---, Wilson Model.

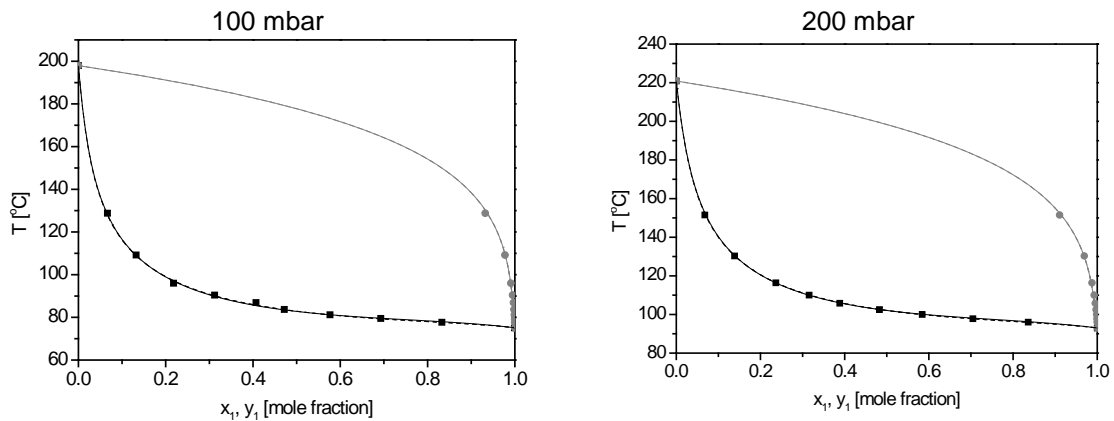


Figure 3. Txy diagram for the system styrene(1)/sulfolane(2) at 100 and 200 mbar. ■, ●, experimental data, —, —, NRTL Model, ---, ---, Wilson Model.

The VLE data were correlated in ASPEN Plus with the Wilson and NRTL activity coefficient models. Both models are able to calculate binary as well as ternary VLE data from binary interaction parameters¹⁸. The required parameters for the binary interactions for the Wilson and NRTL model are respectively shown in Equation 3 and 4.

$$\Lambda_{ij} = \frac{V_i}{V_j} \exp\left(-\frac{A_{ij}}{RT}\right) \quad (3)$$

$$\tau_{ij} = \frac{A_{ij}}{RT}, \quad G_{ij} = \exp(-\alpha_{ij}\tau_{ij}), \quad \alpha_{ij} = \alpha_{ji} \quad (4)$$

A_{ij} is in both the Wilson and NRTL model an energy parameter characterizing the interaction of molecule i with molecule j and this parameter is obtained by regression of the experimental VLE data. The parameter α_{ij} in the NRTL model is the non-randomness parameter and was kept constant at a value of 0.3. V_i/V_j in Equation 3 was also kept constant at a value of 1. ASPEN Plus normally uses the molar volume ratio also as a parameter which can be obtained by regression of the VLE data¹⁹. The molar volumes of EB and SM however are quite similar and by keeping the molar volume ratio one, the model becomes much simpler. The vapour phase was assumed to be ideal, since the working pressures were below atmospheric pressure¹⁸. The binary interaction parameters obtained from a regression of the experimental data are listed in Table 4. The absolute average deviations in vapour phase composition and pressure were correlated respectively with Equation 5 and 6.

$$AAD_y = 1/N \sum_{i=1}^N |y^{exp} - y^{cal}|_i \quad (5)$$

$$AAD_p = 1/N \sum_{i=1}^N |P^{exp} - P^{cal}|_i \quad (6)$$

Table 4. Thermodynamic interaction parameters obtained from binary VLE data.

	A_{12} [J/mole]	A_{21} [J/mole]	α_{12}	AAD_y	AAD_p
Ethylbenzene(1) + Styrene (2)					
Wilson	-1020.95	1391.35		0.0011	0.0005
NRTL	1177.59	-735.94	0.3 (fixed)	0.0012	0.0005
Ethylbenzene(1) + Sulfolane (2)					
Wilson	1728.73	5779.71		0.0006	0.0039
NRTL	5098.05	1104.49	0.3 (fixed)	0.0008	0.0028
Styrene (1) + Sulfolane (2)					
Wilson	324.29	5235.32		0.0010	0.00162
NRTL	5359.24	-416.19	0.3 (fixed)	0.0019	0.00162

From Figure 1 to 3 and Table 4 the conclusion can be drawn that both the Wilson and the NRTL model can adequately describe the binary experimental data and it is not necessary to take the molar volume ratio into account in the WILSON model.

3.3 Ternary VLE data

VLE measurements of the ternary system were carried out with solvent to feed ratios up to 5. Figure 5 displays the relative volatility in a ternary mixture as function of the mole fraction EB on solvent free bases.

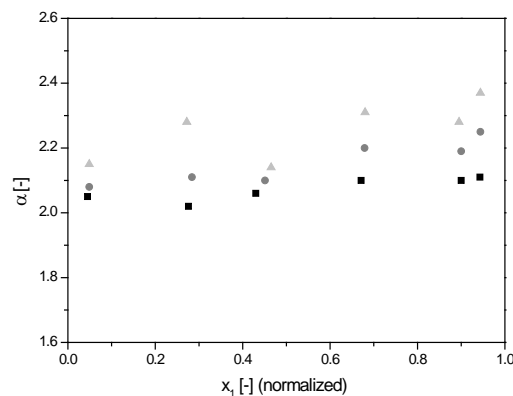


Figure 5. Relative volatility as function of the mole fraction of ethylbenzene on a solvent free basis (x_1) at a solvent to feed ratio of 2.5 (mass base). \blacktriangle = 50 mbar, \bullet = 100 mbar, \blacksquare = 200 mbar.

From Figure 5 the conclusion can be drawn that the addition of SF to the EB/SM mixture causes a large increase of the relative volatility from 1.3-1.5 without solvent to values up to 2.3. The relative volatility slightly increases if the mole fraction of EB on solvent free basis increases. The relative volatility moreover increases with decreasing pressure. This can be explained by the larger ratio of the pure component vapor pressures of EB and SM at lower temperatures.

3.4. Equilibrium process model

The extractive distillation process was modeled in ASPEN Plus to determine the savings in energy consumption and capital costs. From the equilibrium process model the conclusion can be drawn that the optimal solvent to feed ratio is 5 and the number of theoretical stages 60. An energy reduction of 50% was obtained, which is a result of the large decrease in reflux ratio from 7 to 1.7.

The required heat in the reboiler of the current EB/SM splitter equals 33 MW³ for a 500.000 mta plant. From the energy savings obtained with extractive distillation and the total worldwide annual SM production, the CO₂ emission reduction was calculated. The assumption was made that the steam required in the reboilers were generated by burning natural gas ($H_v = 32 \text{ MJ/m}^3$). The worldwide CO₂ release can be reduced by 1.8 million metric tonnes CO₂ per year by applying extractive distillation. The capital costs can be reduced with a factor 2.

4. Conclusions

Thermodynamically consistent vapor liquid equilibrium data were determined for the binary systems SM/EB, EB/SF and SM/SF and the ternary system EB/SM/SF in the pressure range of 50-200 mbar. All experimental data can be adequately described with both the Wilson and the NRTL model. The relative volatility increases largely from 1.3-1.4 without SF to values up to 2.3 at a solvent to feed ratio of 2.5. The relative volatility increases with increasing solvent to feed ratio, decreasing pressure and decreasing SM/EB ratio. Based on the equilibrium process model predictions, an energy reduction as much as 50% can be obtained when extractive distillation with SF as solvent is applied instead of the traditional distillation.

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