m_T. The calculated values of the activity coefficient of thorium nitrate in the ternary system are strongly dependent on the fitting function, but, within the error limits of the data, are the same at 50 °C as those found at 25 °C (*1*).

Acknowledgment

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Isobaric Vapor–Liquid Equilibria of the Ethylbenzene–*p*-Xylene System

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Boiling temperatures were measured for the close boiling ethylbenzene–*p*-xylene binary system at 500, 760, 1250, and 1500 mmHg. The data were correlated by the NRTL equation, and the relative volatility of ethylbenzene to *p*-xylene was calculated.

Introduction

In the recovery of aromatics from oil fractions a mixture of C_8 is obtained which contains ethylbenzene and the isomers of xylene.

The demand for individual pure C_8 has grown very rapidly, recently, since ethylbenzene is the main raw material employed for the manufacture of styrene, and xylene isomers are used to obtain phthalic anhydride and phthalic acids. For example, much of the *p*-xylene is converted to dimethyl terephthalate which is employed to produce polyester fibers.

The purity required for these products in the subsequent processing is usually very high. For example, dehydrogenation of ethylbenzene to styrene requires a product with a purity greater than 99.5%.

The production of individual components of very high purity from C_8 aromatic isomers is difficult because of the low relative volatility. The separation of ethylbenzene (ETB) from *p*-xylene (*p*-X) by conventional rectification requires the use of columns containing more than 200 plates and high reflux ratio since their normal boiling points are very close to each other ($T_{b,ETB}$ = 135.9 °C; $T_{b,p\text{-}X}$ = 138.1 °C).

Several papers have appeared in the literature (*1*–*3*) concerning the effect of adding agents in order to increase the relative volatility. However only few authors (*4*, *5*) report data on the vapor–liquid equilibrium of the ETB–*p*-X binary system.

Because of the closeness of the vapor and liquid compositions, experimental work is difficult, but the effort is justified since relative volatilities must be known with great accuracy in order to design reliable distillation columns.

Values of relative volatility ranging from 1.035 to 1.06 are reported in the literature (*1*, *2*). However, the experimental source of these data is not clear or seems too rough (*1*) for the accurate evaluation of this thermodynamic property.

In any case, the assumption of ideal solution may give unacceptable results because of the criticality of the separation. Furthermore, measurements of excess enthalpies for this system (*6*) show nonzero values which exclude the hypothesis of ideality. The assumption of symmetrical deviation from ideality should be more acceptable.

Therefore, in order to obtain a wider range of information about the thermodynamic behavior of this system, we carried out measurements of boiling temperatures. The deviations from ideality were studied by evaluating the activity coefficients and correlating their values by a suitable model of the liquid phase.

Previous measurements of vapor pressures for pure components were carried out by means of the same apparatus as used for mixtures.

Experimental Section

A pair of Swietoslawski ebulliometers (*7*) was used for the measurements of the boiling points of pure substances or mixtures. The condensers of the ebulliometers were connected together, through a dead volume, to an ejector or to a nitrogen cylinder to ensure the required pressure. An U mercury manometer allowed a rough determination of the pressure.

The pressure is regulated by a valve at the required constant value which is then exactly determined via the boiling point of high-purity water used as reference substance in one of the ebulliometers. The temperature of water and that of the mixture (or pure component) were detected simultaneously by two LAUDA platinum resistance thermometers and a digital display with a ±0.01 °C resolution.

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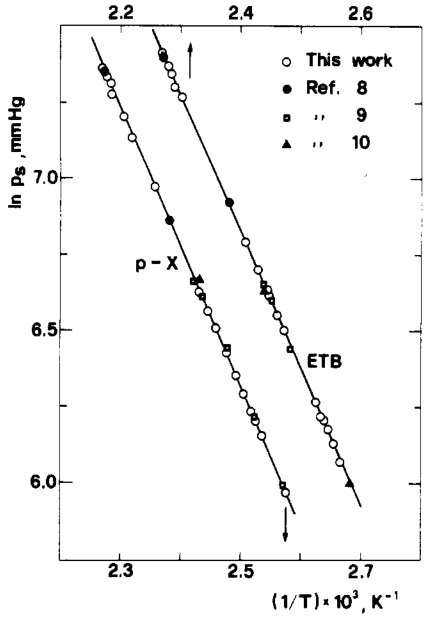

Figure 1. Vapor pressure of ethylbenzene and *p*-xylene.

Table I. Parameters of Antoine's Equation[a]

	A	B	C
ethylbenzene	7.085 87	1510.819	223.36
p-xylene	7.124 75	1551.287	227.22

[a] $\log p_s = A - B/(t + C)$; p_s in mmHg, t in °C.

Before the measurements were carried out, the thermometers were calibrated by the ice point and the normal boiling point of pure water.

For mixtures, determination of the boiling curve alone (P, T, x) was carried out. Mixtures of known composition were prepared gravimetrically and introduced into the ebulliometer. Since the relative volatility of the components is very close to unity, the equilibrium composition of the liquid phase was assumed equal to the initial value. When the steady state was reached, the temperature was read.

ETB and *p*-X used were pure-grade products from Carlo Erba (RPE quality) with a claimed purity of 99% for *p*-X and 99.5% for ETB. The reference substance was redistilled water. Its vapor pressure was taken from Steam Tables (*8*).

The estimated precision of the equilibrium mixture composition was assumed to be ±0.001 mole fraction. The estimated uncertainties in equilibrium temperature and pressure were ±0.03 °C and ±1 mmHg, respectively.

Results and Discussion

The first stage of the experimental work was the measurement of vapor pressures of pure ETB and *p*-X over the temperature range 120–170 °C.

The results are reported in Figure 1 and are compared with the data from the literature (*9–11*). A very good agreement can be observed. The saturated vapor pressure data were correlated with temperature by means of the Antoine equation in the whole range of temperatures (120–170 °C). The values of the obtained constants are reported in Table I. Standard deviations are 0.13 for ETB and 0.27 for *p*-X with maximum errors of 1.04 and 1.05 mmHg, respectively.

For the binary system, boiling point curves were determined at 500, 760, 1250, and 1500 mmHg. The experimental data are reported in Tables II and III.

Table II. Boiling Temperatures of Ethylbenzene (1)-*p*-Xylene (2) Mixtures at 500 and 760 mmHg

500 mmHg		760 mmHg	
x_1	T, °C	x_1	T, °C
0.048	123.12	0.048	138.06
0.085	122.97	0.085	137.92
0.221	122.66	0.124	137.86
0.276	122.54	0.221	137.60
0.341	122.42	0.276	137.45
0.408	122.26	0.341	137.34
0.500	122.07	0.408	137.17
0.548	121.85	0.500	136.98
0.633	121.77	0.548	136.78
0.661	121.69	0.633	136.68
0.783	121.46	0.661	136.63
0.883	121.37	0.783	136.34
0.894	121.15	0.883	136.18
0.945	121.10	0.894	136.14
		0.945	136.02

Table III. Boiling Temperatures of Ethylbenzene (1)-*p*-Xylene (2) Mixtures at 1250 and 1500 mmHg

1250 mmHg		1500 mmHg	
x_1	T, °C	x_1	T, °C
0.048	157.61	0.048	165.30
0.085	157.47	0.085	165.28
0.124	157.44	0.124	165.17
0.221	157.07	0.221	164.77
0.276	156.88	0.276	164.60
0.341	156.82	0.341	164.51
0.408	156.60	0.408	164.33
0.500	156.43	0.500	164.07
0.548	156.18	0.548	163.91
0.633	156.03	0.633	163.67
0.783	155.71	0.783	163.44
0.894	155.63	0.883	163.27
0.945	155.52	0.945	163.23

The reduction of these data and the calculation of vapor-phase composition can be performed if a model is assumed for calculating the Gibbs energy excess in the liquid phase. The empirical parameters of the model can then be calculated from the experimental data and the following constraining equation which gives the total boiling pressure:

$$P = \frac{\gamma_1(x_1,T)x_1 p_{s1}(T)\phi_{s1}(T)\nu_{L1}(P,T)}{\hat{\phi}(y_1,P,T)} + \frac{\gamma_2(x_1,T)x_2 p_{s2}(T)\phi_{s2}(T)\nu_{L2}(P,T)}{\hat{\phi}_2(y_1,P,T)} \quad (1)$$

In eq 1, γ_1 and γ_2 are the activity coefficients whose expression is given by the liquid-phase model chosen; ν_{L1} and ν_{L2} represent the Poynting effect, and $\hat{\phi}_i$ and ϕ_{si} are the fugacity coefficients in the vapor mixture and that of the pure component at saturation condition, respectively. Since $\hat{\phi}_i$ depends on the vapor-phase composition, an iterative procedure is required to find the parameters of the model. A correction for the imperfection of the vapor is important even at low pressure in this type of system with closely boiling components. Therefore, following the suggestions of Redlich and Kister (*5*), the usual approximation $\hat{\phi}_i = 1$, $\phi_{si} = 1$ was not adopted in the reduction of the experimental data.

The model chosen to describe the activity coefficients in the liquid phase is the NRTL model (*12*)

$$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + G_{21}x_2}\right)^2 + \tau_{12}\frac{G_{12}}{(x_2 + G_{12}x_1)^2}\right] \quad (2)$$

$$\ln \gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + G_{12}x_1}\right)^2 + \tau_{21}\frac{G_{21}}{(x_1 + G_{21}x_2)^2}\right]$$

where

$$\tau_{12} = \Delta g_{12}/RT \qquad \tau_{21} = \Delta g_{21}/RT$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \qquad G_{21} = \exp(-\alpha_{12}\tau_{21})$$

Table IV. Thermodynamic Data[a] Used for Evaluating Second Virial Coefficients

	T_c, K	p_c, atm	v_c, cm^3/mol	ω	μ, D
ethylbenzene	617.1	35.6	374	0.3011	0
p-xylene	616.2	34.7	379	0.324	0

[a] T_c, p_c, v_c: critical parameters; ω: acentric factor; μ: dipole moment.

and the parameters are α_{12}, $\Delta g_{12} = g_{12} - g_{22}$, and $\Delta g_{21} = g_{21} - g_{11}$ with $g_{12} = g_{21}$.

The three-parameter model can be reduced to a one-parameter model (*12*) by fixing the value of α_{12} and by assuming $g_{ii} = -k(\Delta H_{v,i} - RT)$, where k is a proportionality factor which can be set at $^1/_5$, and $\Delta H_{v,i}$ is the enthalpy of vaporization of pure component i at the temperature T.

The parameter estimation was carried out by minimizing the following objective function

$$F = \sum_{i=1}^{n_{\mathrm{exptl}}} \frac{(T_{\mathrm{exptl}} - T_{\mathrm{calcd}})_i^2}{n_{\mathrm{exptl}}} \tag{3}$$

where T_{exptl} and T_{calcd} are the experimental and calculated values of the boiling temperatures at the ith run for a mixture at composition x and pressure P, and n_{exptl} is the number of experimental data. The calculation of the boiling temperature at each point was made by solving eq 1.

The Poynting effect was calculated by means of the usual expression

$$\nu_L = \exp\left[\frac{v_L(P - p_s)}{RT}\right] \tag{4}$$

where v_L is the molar volume of liquid component. In the range of the examined temperatures, v_L can be expressed by the following relationships

$$\text{ETB} \qquad v_{L1} = 80.17 + 0.139T + 2.08 \times 10^{-5}T^2 \tag{5}$$

$$p\text{-X} \qquad v_{L2} = 105.58 - 1.25 \times 10^{-3}T + 20.83 \times 10^{-5}T^2$$

with T in K and v_L in cm^3/mol.

The fugacity coefficients $\hat{\phi}_i$ and ϕ_{si} were evaluated by means of the virial equation of state

$$\ln \phi_{si} = B_i p_{si}/RT \tag{6}$$

$$\ln \hat{\phi}_i = (P/RT)[B_i + (1 - y_i)^2\delta_{12}]$$

with $\delta_{12} = 2B_{12} - B_1 - B_2$.

The second virial coefficients were calculated by the O'Connell correlation (*13*). The thermodynamic data required are reported in Table IV.

The results of the correlation indicate that temperature-independent parameters represent the experimental data quite well. However, a better correlation quality over the entire range of pressure was obtained with temperature-dependent parameters.

From the three-parameter model, with $\alpha_{12} = 0.2$, the following temperature dependence was found

$$\Delta g_{12} = -99.8 + 0.0326t \tag{7}$$

$$\Delta g_{21} = 93.1 + 0.156t$$

where t is in °C and Δg_{12}, Δg_{21} are in cal/(g mol).

In Figures 2 and 3 the boiling temperatures calculated by these parameters are plotted vs. the liquid-phase mole fraction of ethylbenzene.

Accounting for this temperature dependence of the parameters we calculated the excess enthalpy of liquid solutions at 25 °C. In Figure 4 our results are compared with the experimental data reported in the literature (*6*). The quality of the prediction can be considered very good if one remembers that the evaluation of ΔH^E from vapor-liquid equilibrium data is usually unsatisfactory.

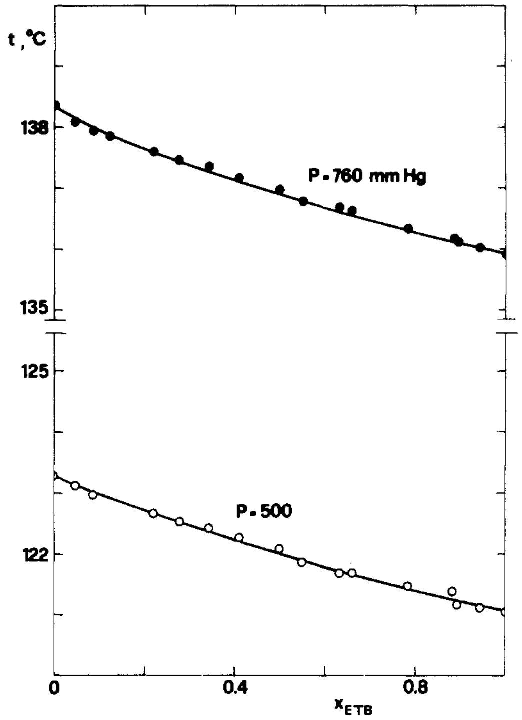

Figure 2. Boiling curves at 500 and 760 mmHg.

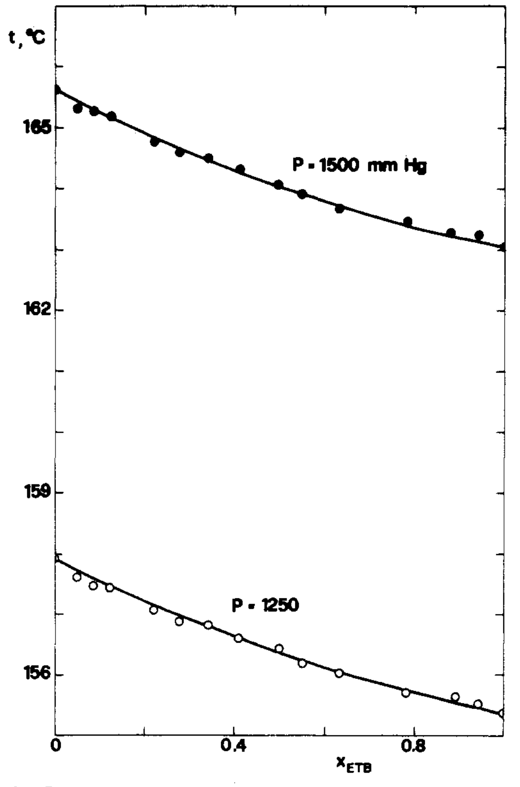

Figure 3. Boiling curves at 1250 and 1500 mmHg.

Once the parameters of the NRTL equation are obtained, the relative volatility β_{12} of ethylbenzene to *p*-xylene can be calculated. Table V shows the values of β_{12} at infinite dilution of *p*-xylene calculated as

$$\lim_{x_2 \to 0} \beta_{12} = \nu_{L1} p_{s1} \hat{\phi}_2^{\infty} / (\gamma_2^{\infty} p_{s2} \phi_2 \nu_{L2}) \tag{8}$$

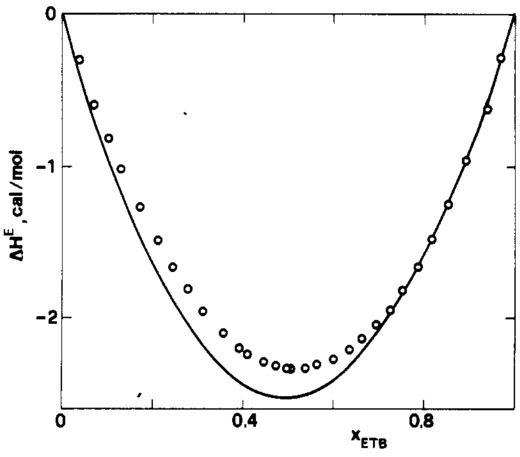

Figure 4. Heat of mixing at 25 °C.

Table V. Activity Coefficients at Infinite Dilution and Relative Volatility of ETB to *p*-X at $x_2 = 0$

t, °C	p, mmHg	γ_1^∞	γ_2^∞	β_{12}^∞	P_{s1}/P_{s2}
121.03	500		1.0167	1.048	1.068
123.29	500	1.0182			
135.93	760		1.0196	1.043	1.066
138.31	760	1.0212			
155.39	1250		1.0231	1.035	1.063
157.92	1250	1.0248			
163.06	1500		1.0244	1.032	1.062
165.64	1500	1.0261			

together with the ideal values of β_{12} ($=p_{s1}/p_{s2}$). In the same table the activity coefficients at infinite dilution are reported at the boiling temperature for each pressure.

The relative volatility, which is a critical parameter in the distillation, appears to be very low and largely influenced by pressure, ranging from 1.048 at 500 mmHg to 1.032 at 1500 mmHg. These values are in quite good agreement with the values reported in the literature (*1*, *2*).

An attempt was made to correlate the experimental data by means of the one-parameter NRTL equation. Calculations were carried out with $\alpha_{12} = 0.2$ and $\Delta H_{v,i}$ deduced from vapor pressures by the Clausius-Clapeyron equation.

The values of g_{12}, obtained by minimizing the objective function of eq 3, depend on the temperature according to the expression

$$g_{12} = -1860.2 + 1.702t \qquad (9)$$

with t in °C and g_{12} in cal/(g mol).

The accuracy of vapor-liquid correlation is comparable with that obtained by the two-parameter NRTL equation, but at 25 °C the calculation of the excess enthalpies gives unacceptable results.

Finally, the activity coefficients were evaluated by using the first-order conformal solution theory

$$RT \ln \gamma_1 = (\tilde{U} - U^*)^0 d_{12} x_2^2 \qquad (10)$$

$$RT \ln \gamma_2 = (\tilde{U} - U^*)^0 d_{12} x_1^2$$

where d_{12} is an empirical binary constant and $(\tilde{U} - U^*)^0$ is the difference of the configurational energy between the real fluid and an ideal gas.

Ellis and Chao (*14*) suggest the use of eq 10 for the purpose of describing nearly ideal systems and report a value of $d_{12} = -0.000\,79$ obtained from data by Redlich and Kister (*5*).

The calculation gives values of activity coefficients at infinite dilution which are smaller than those obtained by the NRTL equation. Furthermore, they decrease when temperature increases, thus giving a positive value of the excess enthalpy. A more accurate value of d_{12} could now be obtained from the measurements reported in this work.

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Registry No. ETB, 100-41-4; *p*-X, 106-42-3.

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