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Isothermal Vapor−Liquid Equilibria of *o*-, *m*-, and *p*-Xylene with *N*-Methylpyrrolidone at 373.15 K and 393.15 K

S. K. Gupta[†]

Indian Institute of Petroleum, Mohkampur, Dehradun-248 005, India

Isothermal vapor−liquid equilibria for *o*-, *m*-, and *p*-xylenes with *N*-methylpyrrolidone (NMP) at 373.15 K and 393.15 K have been measured. The results have been correlated using the NRTL, Wilson, and three-constant Redlich−Kister models. The root-mean-square deviation (RMSD) between experimental and calculated *y*-values show that the data for all the three xylenes with NMP are well represented by the Wilson, NRTL, and three-constant Redlich−Kister models.

Introduction:

Xylenes are important petrochemicals and are present in catalytic reformed naphthas as well as in a straight run naphtha feeds in the boiling range of 125 °C−140 °C. Owing to their close boiling points, separation has always been a problem. Various methods have been used for their separation, which include crystallization, isomerization, and selective adsorption such as the UOP Parex Process. In the present paper vapor−liquid equilibrium (VLE) studies have been made on *o*-, *m*-, and *p*-xylenes with *N*-methylpyrrolidone at 373.15 K and 393.15 K under isothermal conditions.

This study is an extension of our previous work carried out on model hydrocarbons for the production of food grade hexane with NMP to process feedstocks of higher boiling range such as 55 °C to 140 °C for dearomatization of special boiling point (SBP) solvents.

The data on these systems have not been reported in the literature and will be useful in the design of extractive distillation/stripper columns for the removal of xylenes from naphtha feedstocks.

Experimental Section

Chemicals. *o*-, *m*-, and *p*-Xylenes (E. Merck, Germany, 99+% GC) were used as such without further purification. The NMP (BDH Chemicals Ltd. Poole, England, 99.5+% GC) was redistilled and a heart cut was used. The water content of NMP (Karl Fischer Method, UOP-20659) was found to be less than 0.2 mass %.

Procedure. The VLE studies were carried out in a still (Smith and Bonner, 1949) provided with a magnetic stirrer with a charge capacity of about 400 cm^3. The details of the procedure have been outlined by Gupta and Rawat (1991). The present studies were carried out at temperatures (373.15 ± 0.2) K and (393.15 ± 0.2) K. These temperatures were maintained by controlling the system pressures with the help of a Cartesian manostat attached to a vacuum pump and a mercury manometer.

Trial runs on the systems established the time of equilibration to be 2−3 h. Accordingly, the phases were equilibrated for 4 h before a sample was taken for analysis. As a very little condensed vapor sample (∼1 cm^3) was withdrawn for analysis, the liquid-phase composition was assumed to be uneffected.

Analysis. The vapor samples of all the three xylene + NMP systems were analyzed by refractive index−composition charts prepared at 20 °C in the entire composition range. The accuracy of the results obtained was checked by gas−liquid chromatographic technique by cross-checking about four samples for each system and was found to be within ±0.05 mass %.

Results and Discussion

The experimental VLE data (P, t, x, y) for the three xylenes with NMP at 373.15 K and 393.15 K are reported in Table 1. The liquid-phase activity coefficients for all these systems were calculated by using the relation (Van Ness, 1964)

$$\gamma_i = \frac{y_i P}{x_i P_i^s}\exp\left[\frac{(B_{ii} - V_i^L)(P - P_i^S)}{101.325RT} + \frac{P\delta_{ij}(1 - y_i)^2}{101.325RT}\right] \qquad (1)$$

and

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \qquad (2)$$

where x_i and y_i are the liquid- and vapor-phase mole fractions of component i, P and P_i^s are total pressure and pure component vapor pressures, V_i^L is the liquid molar volume of component i, B_{ii}, B_{jj}, and B_{ij} are the pure component second virial and cross-coefficients, respectively, R is the universal gas constant, and T is the temperature in K.

The pure component vapor pressures for all the three xylene isomers were calculated from the Antoine constants (Dreisbach, 1955). The vapor pressure values for NMP were, however, calculated from Antoine constants reported by Gierycz et al. (1985). The second virial coefficients for all the four components required in eq 1 for the computation of activity coefficients were calculated by Pitzer and Curl's correlation (1957) as modified by Tsonopoulos (1974). The critical constants and acentric factors for all the four constituents were taken from the literature (Reid et al., 1987; Daubert and Danner, 1985). The values of the molar volumes for the three xylenes were calculated using density values at three different temperatures as reported by Dreisbach (1955). For NMP the values were calculated

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[†] FAX: 0091-135-671986. E-mail: iipddn @ del2.vsnl.net.in.

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Table 1. Experimental VLE Results

system pressure/kPa	liquid comp. x_1	vapor comp. y_1	γ_1	γ_2	GE/RT
		$t = 373.15$ K			
		o-Xylene (1) + NMP (2)			
7.47	0.0940	0.5650	1.7096	1.0187	0.0672
10.33	0.1910	0.7115	1.4644	1.0474	0.1103
12.91	0.2854	0.7884	1.3548	1.0866	0.1460
17.33	0.4819	0.8784	1.1981	1.1572	0.1627
21.40	0.6824	0.9350	1.1099	1.2464	0.1411
25.34	0.8941	0.9789	1.0485	1.4380	0.0808
		m-Xylene (1) + NMP (2)			
8.59	0.0983	0.6231	1.7678	1.0208	0.0746
11.57	0.1865	0.7456	1.4995	1.0290	0.0988
14.96	0.2860	0.8143	1.3790	1.1072	0.1646
20.23	0.4757	0.8942	1.2280	1.1622	0.1765
24.57	0.6865	0.9397	1.0834	1.3455	0.1480
29.34	0.8942	0.9805	1.0348	1.5418	0.0764
		p-Xylene (1) + NMP (2)			
8.93	0.0957	0.6370	1.8739	1.0192	0.0773
12.16	0.1903	0.7534	1.5150	1.0530	0.1209
15.21	0.2878	0.8216	1.3646	1.0838	0.1468
21.30	0.4769	0.9027	1.2641	1.1283	0.1749
25.76	0.6863	0.9477	1.1128	1.2235	0.1366
30.45	0.9005	0.9840	1.0389	1.3962	0.0676
		$t = 393.15$ K			
		o-Xylene (1) + NMP (2)			
14.64	0.0940	0.5028	1.5684	1.0113	0.0524
20.50	0.1910	0.6819	1.4624	1.0150	0.0846
25.53	0.2854	0.7702	1.3740	1.0343	0.1148
33.74	0.4819	0.8641	1.2027	1.1157	0.1457
41.61	0.6824	0.9296	1.1231	1.1634	0.1273
40.05	0.8941	0.9755	1.0361	1.4031	0.0676
		m-Xylene (1) + NMP (2)			
16.50	0.0983	0.5581	1.6154	1.0180	0.0632
22.44	0.1865	0.7140	1.4780	0.9937	0.0677
29.63	0.2860	0.8039	1.4290	1.0258	0.1203
39.63	0.4757	0.8895	1.2665	1.0538	0.1399
48.24	0.6865	0.9407	1.1260	1.1523	0.1259
55.62	0.8942	0.9786	1.0341	1.4220	0.0672
		p-Xylene (1) + NMP (2)			
16.56	0.0957	0.5702	1.6609	0.9912	0.0403
23.33	0.1903	0.7164	1.4756	1.0295	0.0975
30.93	0.2878	0.8102	1.4586	1.0391	0.1360
40.26	0.4769	0.8832	1.2446	1.1344	0.1703
49.42	0.6863	0.9412	1.1274	1.1701	0.1316
56.95	0.9005	0.9805	1.0286	1.4112	0.0597

from density values as reported earlier by Gupta and Rawat (1991).

The experimental VLE data have been correlated by NRTL (Renon and Prausnitz, 1968) and Wilson (1964) models using Nelder and Mead's simplex optimization (Nelder and Mead, 1964) technique as mentioned by Gupta and Rawat (1991) by minimizing the following objective function

$$\mathrm{O.F.} = \sum_{i=1}^{N} (\gamma_{i,\mathrm{exptl}} - \gamma_{i,\mathrm{calcd}})^2 \tag{3}$$

where, N is the number of components.

The data were further correlated by the three-constant Redlich−Kister (1948) model using the least-squares technique (Smith, 1963). The estimated binary parameters along with the root-mean-square deviation (RMSD) calculated for n data points as

$$\mathrm{RMSD} = \sqrt{\sum_{i=1}^{N} \frac{(y_{i,\mathrm{exptl}} - y_{i,\mathrm{calcd}})^2}{n}} \tag{4}$$

Table 2. Correlation Parameters for the Three Binaries at 373.15 K and 393.15 K

	system		
	o-xylene (1)−NMP (2)	m-xylene (1)−NMP (2)	p-xylene (1)−NMP (2)
	t = 373.15 K		
	1. NRTL (three-parameter)		
$\Delta g_{12}/R$	−32.028 K	−10.708 K	−17.268 K
$\Delta g_{21}/R$	273.627 K	273.586 K	273.598 K
$\alpha_{12}{}^{a}$	0.30	0.30	0.30
RMSD, y_1	0.0044	0.0038	0.0093
	2. Wilson		
λ_{12}/R	431.068 K	174.090 K	434.296 K
λ_{21}/R	−62.963 K	100.027 K	−42.758 K
RMSD, y_1	0.0096	0.0040	0.0098
	3. Redlich−Kister (three-constant)		
B12	0.2199	0.2542	0.2345
C12	−0.0305	−0.0312	−0.0374
D12	0.0370	0.0188	0.0475
RMSD, y_1	0.0060	0.0035	0.0112
	t = 393.15 K		
	1. NRTL (three-parameter)		
$\Delta g_{12}/R$	−45.147 K	−33.6677 K	−28.748 K
$\Delta g_{21}/R$	273.653 K	273.630 K	273.621 K
$\alpha_{12}{}^{a}$	0.30	0.30	0.30
RMSD, y_1	0.0092	0.0125	0.0094
	2. Wilson		
λ_{12}/R	174.163 K	174.144 K	174.129 K
λ_{21}/R	62.308 K	72.148 K	80.348 K
RMSD, y_1	0.0101	0.0134	0.0102
	3. Redlich−Kister (three-constant)		
B12	0.2107	0.2275	0.2294
C12	0.0147	0.0471	0.0062
D12	0.0053	−0.0098	0.0033
RMSD, y_1	0.0092	0.0121	0.0115

[a] The α_{12} values were chosen a priori as 0.3.

between experimental ($y_{i,\mathrm{exptl}}$) and calculated ($y_{i,\mathrm{calcd}}$) vapor-phase compositions for all the three binaries at 373.15 K and 393.15 K are given in Table 2. The vapor-phase compositions from the different models using calculated γ-values were computed.

Conclusions

From Table 2 it is concluded that the VLE data for all the three binaries at two temperatures are well represented by the Wilson model, the three-parameter NRTL equation, and the three-constant Redlich−Kister model.

The values of the activity coefficients (Table 1) for the three xylene isomers under identical conditions are in the increasing order of their decreasing polarity from ortho to para isomers ($\mu = 0.62$ D > 0.36 D > 0.0 D). p-Xylene has the lowest boiling point and will vaporize first in the sequence showing less affinity for the solvent.

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