Isobaric Vapor−Liquid Equilibria for Ternary Mixtures: Saturated Hydrocarbons, Xylenes, and Ethylbenzene with Sulfolane at 101.325 kPa

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Isobaric vapor−liquid equilibria have been determined for the partially miscible systems octane + *p*-xylene + sulfolane, nonane + *o*-xylene + sulfolane, nonane + *p*-xylene + sulfolane, and nonane + ethylbenzene + sulfolane at 101.325 kPa. The data have been compared with those calculated by the UNIFAC-group-contribution model. The calculated vapor-phase compositions and activity coefficients have been compared with the experimental values.

Introduction

Xylenes are important petrochemicals and are mainly produced by catalytic reforming of feedstock of boiling range (125−140) °C. Apart from aromatics, reformed naphtha feeds invariably contain C8−C9 saturated hydrocarbons (or saturates) as impurities. These saturates either form close-boiling mixtures or azeotropes with one or more aromatic components present that make separation by ordinary distillation difficult.

The addition of a third component such as sulfolane, *N*-methylpyrrolidone (NMP), or tetraethylene glycol can enhance the relative volatilities of saturate components. The separation of these saturates and aromatics from the extract phase is achieved in a stripper or extractive distillation column using the above solvents to produce pure aromatics.

The vapor−liquid equilibrium (VLE) data needed for the design of such processes are scarce in the literature and are of importance. These data have, therefore, been determined in the present study for alkanes + xylenes with sulfolane under isobaric conditions. To the authors' knowledge VLE data on these systems have not been reported in the literature.

Experimental Section

Chemicals. Octane and nonane (Fluka, AG, Switzerland, 99+% GC), ethylbenzene, *o*-xylene, and *p*-xylene (Aldrich Chemical Co., United States, 99+% GC) were used as such without further purification. Sulfolane (Philips Petroleum Co., United States) was vacuum-distilled, and a heartcut was used.

Procedure. The VLE studies for the four ternaries were carried out in a still (Smith and Bonner, 1949) provided with a magnetic stirrer. The details of the procedure have been described by Gupta and Rawat (1991).

Analysis. Because of the large differences in the boiling points between sulfolane (286.8 °C) and the hydrocarbons, the vapor phase contained a very small concentration of sulfolane. The condensed vapor sample was, therefore, divided into two parts. One part was used for the determination of sulfur content using a Microcoulometer (Doh-

man Envirotech, United States), and the other part was washed with water for sulfolane removal. In the determination of sulfur content, the amount of sulfur was found to be around 60% of the total sulfur present in the sample on the basis of several synthetic measurements. The total sulfur present in the sample was therefore calculated by applying this correction factor. The sulfolane content in the representative vapor phase was finally calculated on the basis of the corrected sulfur content. The water-washed portion of vapor sample was analyzed for composition by a refractive index (RI)−composition calibration curve. Traces of water present in washed hydrocarbons did not affect the RI values. The accuracy of results obtained in both the cases was within ±0.5 and ±0.3 mass %, respectively.

Results and Discussion

The four ternary systems octane + *p*-xylene + sulfolane, nonane + *o*-xylene + sulfolane, nonane + *p*-xylene + sulfolane, and nonane + ethylbenzene + sulfolane are partially miscible systems. The VLE studies for these systems were taken up in the miscible region by selecting appropriate liquid compositions from their respective solubility envelopes (binodal curves) drawn from liquid−liquid equilibrium (LLE) data generated in our laboratory using the procedure as reported earlier (Rawat and Gulati, 1976). These are given in Table 2. The experimental VLE data for these ternaries are presented in Table 1. The liquid-phase activity coefficients for all the four systems have been calculated using the relation (Van Ness, 1964)

$$\gamma_i = \frac{P y_i}{x_i p_i^s} \exp\left[\frac{(B_i - V_i^L)(P - p_i^s)}{RT}\right] \tag{1}$$

where x_i, y_i are the liquid and vapor phase mole fractions, P and p_i^s are the total pressure and pure component vapor pressures, V_i^L is the liquid molar volumes of component i, B_i is the second virial coefficient, R is the universal gas constant, and T is the temperature in K.

The second virial coefficients for all the five hydrocarbons required in eq 1 for the calculation of activity coefficients were computed from Pitzer and Curl's correlation (1957)

Table 1. Experimental VLE Data for the Ternary Systems

$t/°C$	x_1	x_2	x_3	y_1	y_2	y_3
		Octane (1) + *p*-Xylene (2) + Sulfolane (3)				
131.8	0.3430	0.6100	0.0470	0.4812	0.5161	0.0027
132.5	0.2845	0.6407	0.0748	0.4501	0.5468	0.0031
134.5	0.1888	0.7186	0.0926	0.3454	0.6520	0.0035
140.0	0.0460	0.6243	0.3297	0.1720	0.8204	0.0076
		Nonane (1) + *o*-Xylene (2) + Sulfolane (3)				
147.5	0.1224	0.6415	0.2361	0.2154	0.7660	0.0186
149.6	0.0763	0.5348	0.3889	0.2104	0.7688	0.0208
150.4	0.0588	0.4815	0.4597	0.2178	0.7609	0.0213
154.0	0.0455	0.5280	0.4265	0.1247	0.8482	0.0271
		Nonane (1) + *p*-Xylene (2) + Sulfolane (3)				
140.8	0.3180	0.6510	0.0310	0.2638	0.7324	0.0038
142.0	0.2018	0.6821	0.1161	0.2020	0.7910	0.0070
142.2	0.1311	0.6895	0.1794	0.1614	0.8310	0.0076
143.4	0.0869	0.6475	0.2656	0.1398	0.8523	0.0079
144.0	0.0442	0.5959	0.3599	0.0999	0.8918	0.0083
		Nonane (1) + Ethylbenzene (2) + Sulfolane (3)				
147.0	0.0670	0.4292	0.5038	0.2165	0.7654	0.0181
149.5	0.0429	0.3264	0.6306	0.2332	0.7436	0.0232
155.2	0.0240	0.2165	0.7595	0.2518	0.7188	0.0294
171.4	0.0141	0.1057	0.8802	0.3249	0.6240	0.0511
195.0	0.0077	0.0566	0.9357	0.3121	0.5907	0.0972

Table 2. Liquid−Liquid Equilibrium Data (for Binodal Curves)

extract phase			raffinate phase		
saturate	aromatic	solvent	saturate	aromatic	solvent
	Octane (1) + *p*-Xylene (2) + Sulfolane (3) at 333.15 K				
0.0105	0.0282	0.9613	0.9038	0.0877	0.0085
0.0146	0.0718	0.9136	0.7147	0.2704	0.0149
0.0166	0.1336	0.8498	0.5319	0.4376	0.0304
0.0245	0.2556	0.7200	0.2883	0.6204	0.0913
	Nonane (1) + *o*-Xylene (2) + Sulfolane (3) at 373.15 K				
0.0103	0.0327	0.9570	0.8936	0.0938	0.0126
0.0121	0.0985	0.8894	0.7047	0.2669	0.0285
0.0138	0.1645	0.8217	0.5114	0.4523	0.0363
0.0208	0.2945	0.6847	0.2836	0.6275	0.0889
	Nonane (1) + *p*-Xylene (2) + Sulfolane (3) at 313.15 K				
0.0165	0.2176	0.7660	0.3147	0.6198	0.0655
0.0102	0.0741	0.9157	0.6905	0.2933	0.0162
0.0129	0.1371	0.8500	0.3724	0.5970	0.0306
0.0093	0.0248	0.9658	0.8854	0.1020	0.0126
	Nonane (1) + Ethylbenzene (2) + Sulfolane (3) at 373.15 K				
0.0215	0.0384	0.9401	0.8834	0.1020	0.0147
0.0204	0.1030	0.8766	0.6919	0.2767	0.0314
0.0276	0.1755	0.7969	0.5074	0.4257	0.0669
0.0604	0.3542	0.5854	0.2259	0.5350	0.2392

Table 3. Experimental and Calculated Activity Coefficients

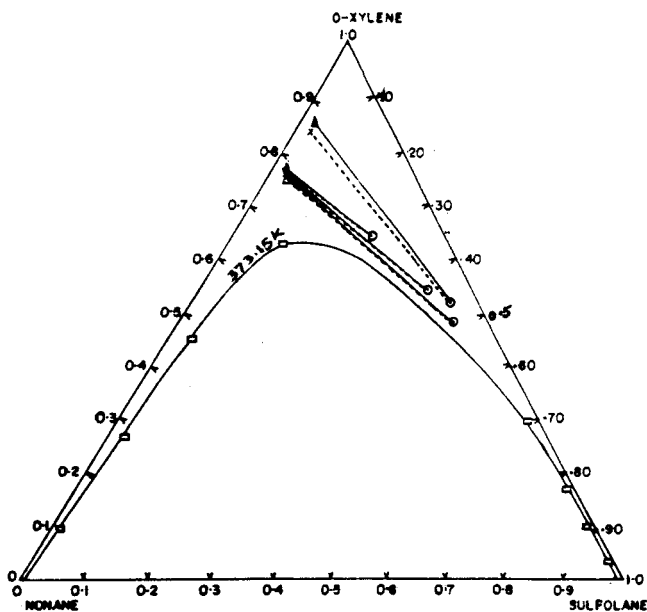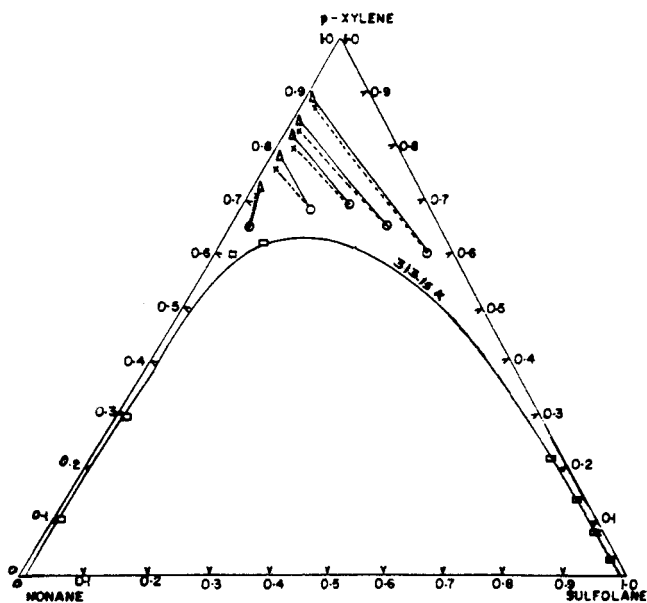| experimental			calculated[a]		
γ_1	γ_2	γ_3	γ_1	γ_2	γ_3
	Octane (1) + *p*-Xylene (2) + Sulfolane (3)				
1.20	1.00	6.25	1.20	1.01	7.46
1.33	0.99	4.10	1.28	1.00	6.24
1.46	1.00	3.35	1.38	0.99	5.12
2.62	1.26	1.63	2.29	1.13	2.54
	Nonane (1) + *o*-Xylene (2) + Sulfolane (3)				
1.91	1.11	4.11	1.82	1.03	3.34
2.84	1.26	2.57	2.65	1.17	2.30
3.74	1.36	2.16	3.27	1.30	1.98
2.74	1.27	1.63	2.99	1.25	2.07
	Nonane (1) + *p*-Xylene (2) + Sulfolane (3)				
1.07	1.06	8.37	1.18	1.02	7.48
1.25	1.06	3.92	1.41	0.99	4.96
1.53	1.09	2.73	1.63	1.01	3.87
1.94	1.16	1.83	1.99	1.06	3.03
2.69	1.30	1.39	2.55	1.16	2.38
	Nonane (1) + Ethylbenzene (2) + Sulfolane (3)				
3.56	1.36	1.91	4.77	1.46	1.69
5.61	1.64	1.77	8.13	1.90	1.34
9.42	2.09	1.50	15.02	2.66	1.14
14.25	2.62	1.25	27.48	3.82	1.03
15.50	2.93	1.04	34.77	4.47	1.01

[a] By UNIFAC.
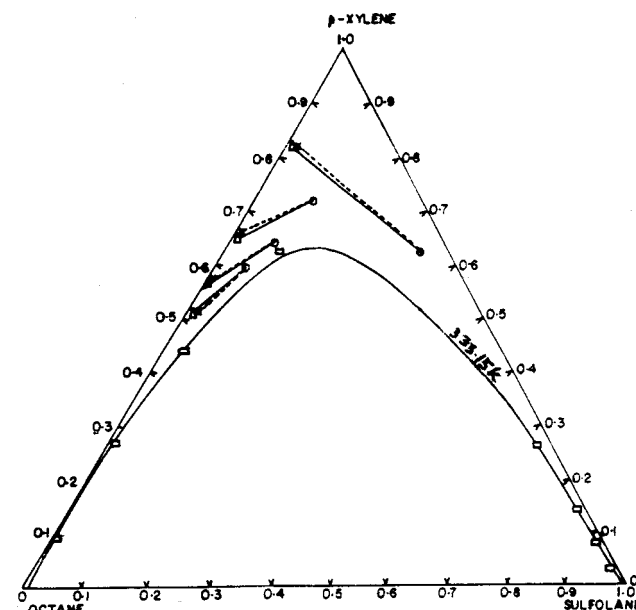
Figure 1. Experimental and calculated liquid and vapor mole fractions for the octane (1) + *p*-xylene (2) + sulfolane (3) system at 101.325 kPa. Symbols: □, points on binodal curve; ○, liquid compositions (exptl); △, vapor compositions (exptl); ×, vapor compositions (calc).

as modified by Tsonopoulos (1974). In the case of sulfolane, however, the Abbott correlation as described by Walas (1985) was used. The pure-component vapor pressures for all the five hydrocarbons were calculated by using Antoine vapor pressure constants as reported by Rossini (1953), and for the sulfolane the constants are taken from DECHEMA (Gmehling et al., 1980; Benoit and Charbonneau, 1969) (Table 6). The values of molar volumes for all the hydrocarbons were calculated from the molar volume equation using their density values at three different temperatures as reported by Timmermans (1950). For the sulfolane these molar volumes were calculated from the constants reported in the literature (Mamata Mukhopadhyay, 1979). The critical constants and acentric factors for all the hydrocarbons were taken from Rossini (1953) and API Technical Data Book (1976). The critical constants for the sulfolane were calculated by the procedure as described by Hakuta and Hirata (1970) as reported by Mamata Mukhopadhyay and Sahasranaman (1982). The vapor−liquid equilibrium tie-line data and solubilty limits (binodal

curves) are represented in Figures 1, 2, 3, and 4. The ternary data have been compared by the UNIFAC (1975, 1977, 1982) model (Table 5) using the interaction parameters as reported by Mamata Mukhopadhyay and Dongaonkar (1983) and Hansen et al. (1991). The experimental data were also tested for their thermodynamic consistency using McDermott and Ellis (1965) point-to-point consistency test. The values of deviations *D* vary from 0.001 to 0.07.

It is clear from the Tables 1, 3, and 4 that the ternary data for the systems octane + *p*-xylene + sulfolane, nonane + *o*-xylene + sulfolane, and nonane + *p*-xylene + sulfolane compare fairly well with those calculated by the UNIFAC

Figure 2. Experimental and calculated liquid and vapor mole fractions for the nonane (1) + *o*-xylene (2) + sulfolane (3) system at 101.325 kPa. Symbols as in Figure 1.

Figure 3. Experimental and calculated liquid and vapor mole fractions for the nonane (1) + *p*-xylene (2) + sulfolane (3) system at 101.325 kPa. Symbols as in Figure 1.

model. The root-mean-square deviations (RMSD) as reported in Table 4 have been calculated as

$$\text{RMSD} = \sqrt{\sum (y_i^{\text{exptl}} - y_i^{\text{calc}})^2 / n}$$

between experimental and calculated *y*-values for the respective systems, where y_i^{exptl} and y_i^{calc} are the experimental and calculated vapor-phase mole fractions. The vapor-phase compositions from calculated γ_i-values were calculated using the following relation

$$y_i^{\text{calc}} = \gamma_i^{\text{calc}} x_i \frac{p_i^s}{P} \exp\left[\frac{(V_i^L - B_i)(P - p_i^s)}{RT}\right] \qquad (3)$$

where γ_i^{calc} is the calculated value of the activity coefficient. The results are compared in Table 4.
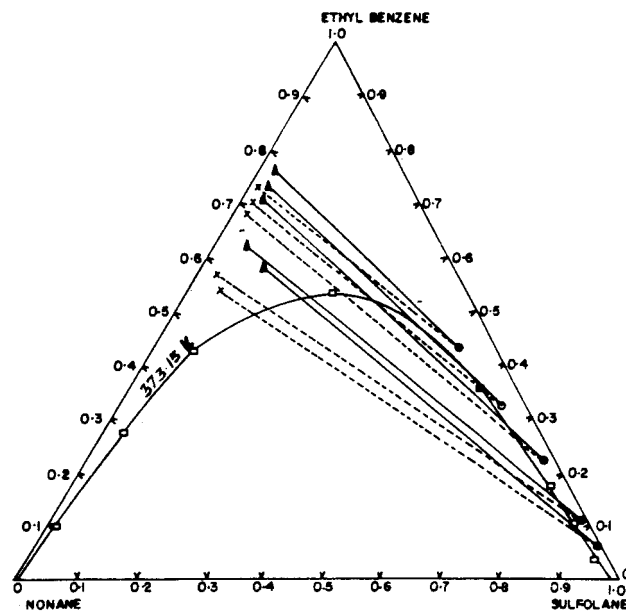
Figure 4. Experimental and calculated liquid and vapor mole fractions for the nonane (1) + ethylbenzene (2) + sulfolane (3) system at 101.325 kPa. Symbols as in Figure 1.

Table 4. RMSD in *y*-Values

systems	y_1	y_2	y_3
octane + *p*-xylene + sulfolane	0.0085	0.0067	0.0031
nonane + *o*-xylene + sulfolane	0.0094	0.0109	0.0026
nonane + *p*-xylene + sulfolane	0.0210	0.0237	0.0047
nonane + ethylbenzene + sulfolane	0.0652	0.0440	0.0226

Table 5. List of UNIFAC Parameters Used

A. Group of Volume and Surface Area Parameters

group	R_k	Q_k
CH$_3$	0.9011	0.8480
CH$_2$	0.6744	0.5400
ACH	0.5313	0.4000
ACCH$_2$	1.0396	0.6600
ACCH$_3$	1.2663	0.9680
sulfolane	3.8702	3.0276

B. Interaction Parameters

group	CH$_3$	CH$_2$	ACH	ACCH$_2$	ACCH$_3$	sulfolane
CH$_3$	0.0	0.0	61.13	76.50	76.50	469.9
CH$_2$	0.0	0.0	61.13	76.50	76.50	469.9
ACH	−11.12	−11.12	0.0	167.0	76.50	222.6
ACCH$_2$	−69.70	−69.70	−146.80	0.0	0.0	−46.8
ACCH$_3$	−69.70	−69.70	−146.80	0.0	0.0	−46.8
sulfolane	52.90	52.90	−40.12	476.0	476.0	0.0

Table 6. Antoine Constants Used

component	A	B	C
octane	6.923 74	1355.126	209.517
nonane	6.935 13	1428.811	201.619
o-xylene	6.998 91	1474.679	213.686
p-xylene	6.990 52	1453.430	215.307
ethylbenzene	6.957 19	1424.255	213.206
sulfolane[a]	7.408 0	2255.469	211.393

Form of Antoine Equation Used
log p_i^s/mmHg = A − B/(C + t), where t is in °C

[a] DECHEMA, Vol. 1, Part 7, Frankfurt, 1980 (Benoit and Charbonneau, 1969).

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