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Vapor–Liquid Equilibria: Systems Methyl Ethyl Ketone–*p*-Xylene and Chlorobenzene–*p*-Xylene

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Vapor–liquid equilibrium data have been measured for the binary systems methyl ethyl ketone–*p*-xylene and chlorobenzene–*p*-xylene, at 685 mmHg pressure. The activity coefficients have been evaluated taking into consideration the vapor-phase nonideality. The *t–x–y* data have been subjected to a thermodynamic consistency test and the activity coefficients have been correlated by the Wilson equation.

Introduction

In continuation with our attempts to separate a *p*-xylene and *m*-xylene mixture by azeotropic distillation techniques, the vapor-liquid equilibria of the systems methyl ethyl ketone–*p*-xylene and chlorobenzene–*p*-xylene have been determined at 685 mmHg pressure.

Experimental Section

p-Xylene "Labchem" grade, obtained from E. Merck, and chlorobenzene, supplied by M/s. Sarabhai M. Chemicals, were purified by repeatedly shaking with concentrated sulfuric acid until the acid layer was no longer colored. These were washed with water, alkali, and water and then dried over anhydrous calcium chloride. Methyl ethyl ketone, supplied by M/s. B.D.H. Chemicals, was purified by the bisulfite method. All the liquids purified by chemical methods were distilled in a 30-mm glass column packed with 10-mm Raschig rings to a height of 1 m. The column was operated at total refulx for 30 min. The low boiling impurities were drawn off at a very low rate as rejects. When the desired boiling temperature was reached and remained constant for 15 min, the fraction was collected, while the column was operated at nearly total reflux. The physical properties of the materials used are listed in Table I.

Apparatus and Analytical Procedure

A vapor-recirculation type equilibrium still described by Brown (*2*, *3*) was used to study the vapor-liquid equilibrium. The still was operated for 3 h after recirculation was stabilized. A mercury-in-glass thermometer with an accuracy of ±0.1 °C calibrated against vapor pressure measurements was used for temperature measurements. The pressure was maintained at 685 ± 0.5 mmHg. The pressure was measured with a precision of ±0.1 mm. After the attainment of equilibrium, the vapor and liquid samples were withdrawn without disturbing the operation of the still.

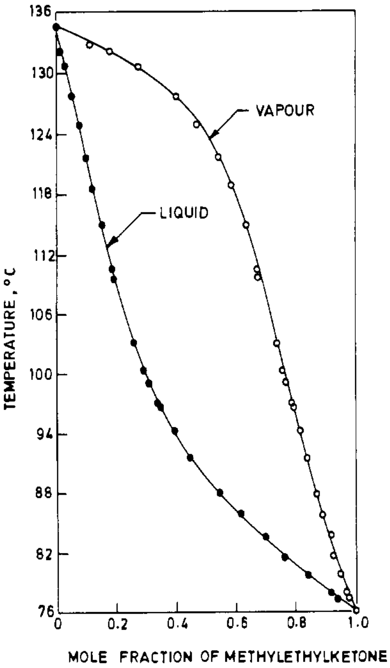

Figure 1. Boiling point-composition diagram for the methyl ethyl ketone–*p*-xylene system.

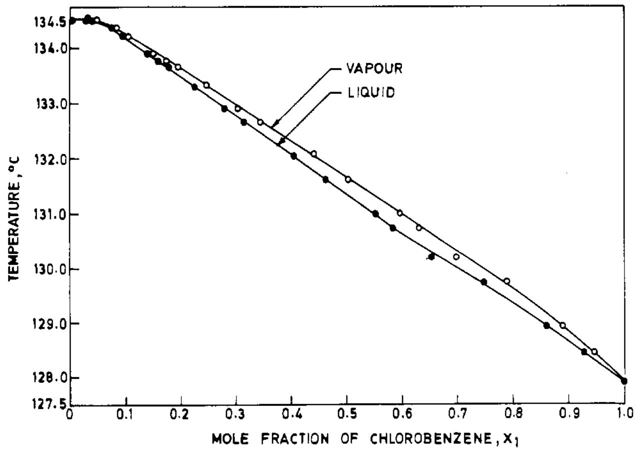

Figure 2. Boiling point-composition diagram for the chlorobenzene–*p*-xylene system.

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Table I. Physical Properties of Materials

	methyl ethyl ketone	chlorobenzene	*p*-xylene
mol wt	72.10	112.56	106.16
density at 30 °C, g/cm^3			
exptl	0.7946	1.0955	0.8524
lit.	0.7954 (*11*)	1.0957 (*12*)	0.8525 (*12*)
refractive index at 25 °C			
exptl	1.376 85	1.521 36	1.493 21
lit.	1.376 10 (*12*)	1.521 38 (*7*)	1.493 25 (*12*)

Table II. Density-Composition Data

methyl ethyl ketone–*p*-xylene		chlorobenzene–*p*-xylene	
mole fraction methyl ethyl ketone	density (30 °C), g/cm^3	mole fraction chlorobenzene	density (35 °C), g/cm^3
0.0000	0.8523	0.0000	0.8481
0.0326	0.8515	0.0539	0.8593
0.0837	0.8496	0.0892	0.8666
0.1225	0.8481	0.1104	0.8750
0.1565	0.8467	0.1453	0.8783
0.1922	0.8454	0.1807	0.8859
0.2243	0.8437	0.2021	0.8905
0.2769	0.8413	0.2403	0.8988
0.3011	0.8402	0.2886	0.9095
0.3430	0.8381	0.3053	0.9132
0.3863	0.8359	0.3448	0.9221
0.4232	0.8333	0.3893	0.9324
0.4762	0.8311	0.4195	0.9395
0.5018	0.8297	0.4505	0.9469
0.5536	0.8266	0.4971	0.9579
0.5673	0.8260	0.5301	0.9659
0.5963	0.8241	0.5669	0.9749
0.6306	0.8219	0.5735	0.9765
0.6668	0.8197	0.6021	0.9836
0.6912	0.8181	0.6448	0.9943
0.7158	0.8167	0.6664	0.9997
0.7412	0.8149	0.6972	1.0077
0.7739	0.8125	0.7205	1.0137
0.8033	0.8104	0.7465	1.0208
0.8441	0.8075	0.7715	1.0348
0.8671	0.8059	0.8362	1.0442
0.8903	0.8042	0.8809	1.0563
0.9125	0.8025	0.9136	1.0685
0.9408	0.8003	0.9485	1.0749
0.9711	0.7980	0.9806	1.0839
1.0000	0.7956	1.0000	1.0903

Table III. Vapor-Liquid Equilibrium Data at 685 mmHg for the Methyl Ethyl Ketone-*p*-Xylene System

t, °C	x_1	y_1	γ_1	γ_2
76.30	1.0000	1.0000	1.0000	0.0000
77.60	0.9402	0.9769	1.0000	2.4840
78.10	0.9195	0.9730	1.0020	2.1170
79.90	0.8372	0.9517	1.0190	1.7400
81.70	0.7630	0.9340	1.0410	1.3240
83.70	0.6966	0.9170	1.0540	1.3870
85.90	0.6218	0.8964	1.0830	1.2780
88.10	0.5522	0.8766	1.1200	1.1850
91.70	0.4495	0.8366	1.1850	1.0960
94.20	0.3994	0.8186	1.2210	1.0430
96.60	0.3495	0.7961	1.2710	0.9956
97.00	0.3425	0.7923	1.2760	0.9893
99.20	0.3075	0.7708	1.3020	0.9594
100.30	0.2957	0.7627	1.3050	0.9432
102.90	0.2602	0.7401	1.3450	0.9010
109.60	0.1923	0.6818	1.4180	0.8151
110.40	0.1852	0.6749	1.4290	0.8046
115.00	0.1574	0.6382	1.4230	0.7518
118.50	0.1189	0.5787	1.5770	0.7532
121.60	0.1001	0.5425	1.6370	0.7316
124.90	0.0749	0.4729	1.7700	0.7436
127.60	0.0525	0.3961	2.0030	0.7707
130.60	0.0275	0.2702	2.4600	0.8347
132.00	0.0150	0.1768	2.8770	0.8932
132.60	0.0081	0.1095	3.3100	0.9421
134.5	0.0000	0.0000	0.0000	1.0000

Table IV. Vapor-Liquid Equilibrium Data at 685 mmHg for the Chlorobenzene-*p*-Xylene System

t, °C	x_1	y_1	γ_1	γ_2
127.9	1.0000	1.0000	1.0000	0.0000
128.4	0.9274	0.9457	1.0040	0.8904
128.9	0.8603	0.8884	1.0040	0.9369
129.7	0.7502	0.7906	1.0030	0.9598
130.2	0.6532	0.6979	1.0070	0.9833
130.7	0.5860	0.6301	0.9988	0.9928
131.0	0.5505	0.5941	1.0000	0.9956
131.6	0.4619	0.5014	0.9881	1.0040
132.0	0.4034	0.4392	0.9815	1.0050
132.6	0.3125	0.3418	0.9714	1.0070
132.9	0.2775	0.3037	0.9665	1.0070
133.3	0.2242	0.2450	0.9561	1.0060
133.6	0.1775	0.1931	0.9423	1.0030
133.7	0.1593	0.1731	0.9414	1.0030
133.9	0.1375	0.1486	0.9387	1.0030
134.2	0.0974	0.1042	0.9232	1.0020
134.3	0.0745	0.0791	0.9078	0.9993
134.5	0.0419	0.0439	0.8995	0.9989
134.5	0.0252	0.0262	0.8869	0.9993
134.5	0.0000	0.0000	0.0000	1.0000

The mixtures were analyzed by density measurements. The density measurements were made with an accuracy of ±0.0001 g cm^{-3}.

Results and Discussion

The density-composition data for the mixtures are given in Table II. The vapor-liquid equilibrium data collected at 685 mmHg pressure are given in Tables III and IV. Figures 1 and 2 represent the boiling point-composition diagrams for the two binaries studied.

The liquid-phase activity coefficients were calculated from the experimental data using the equation (*13*)

$$\gamma_1 = (y_1P/x_1p_1^\circ)\exp\left[\frac{(B_{11} - V_1^L)(P - p_1^\circ)}{RT} + Py_2^2\delta'_{12}\right] \tag{1}$$

The vapor pressures of the pure components were calculated from the Antoine equation. The Antione constants were taken from the literature (*1*, *7*, *9*).

The gas-phase second virial coefficients for *p*-xylene were estimated by the Pitzer and Curl correlation (*10*) and for methyl ethyl ketone by the O'Connell correlation (*5*).

The gas-phase second virial coefficients for chlorobenzene were calculated from the Berthelot equations (*6*) and were fitted to the O'Connell correlation. The virial cross coefficients were calculated according to the combination rules (*5*). The activity coefficients data satisfied Herington's consistency criteria (*8*):

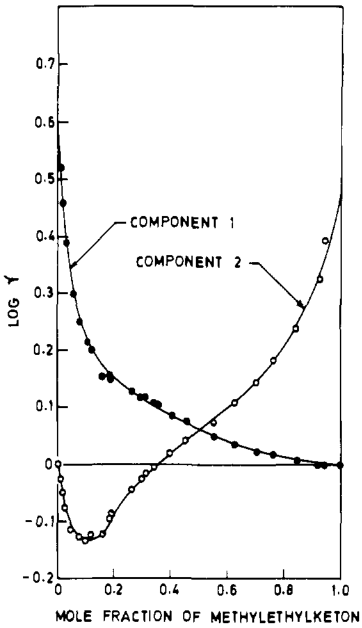

Figure 3. Plot of log γ vs. mole fraction for the methyl ethyl ketone–p-xylene system

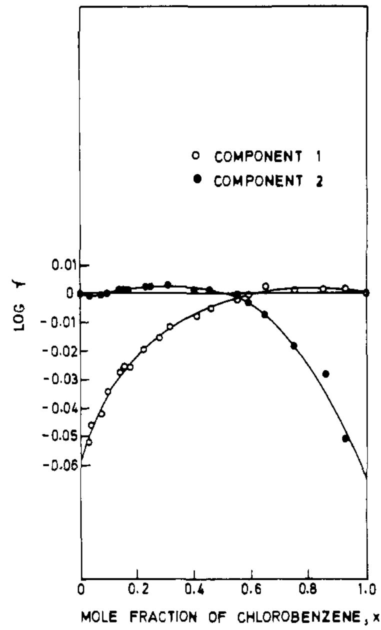

Figure 4. Plot of log γ vs. mole fraction for the chlorobenzene–p-xylene system.

$D \leq J$ for the methyl ethyl ketone–p-xylene system and $D - J \leq 10$ for the chlorobenzene–p-xylene system. The activity coefficients were correlated by the Wilson equations (*14*).

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

$$\ln \gamma_2 = -\ln (x_2 + \lambda_{21}x_1) - x_1\left[\frac{\lambda_{12}}{x_1 + \lambda_{12}x_2} - \frac{\lambda_{21}}{\lambda_{21}x_1 + x_2}\right] \quad (3)$$

The values of the constants λ_{12} and λ_{21} in eq 2 and 3 are the following: methyl ethyl ketone–p-xylene, λ_{12}, 0.3872; λ_{21}, 0.7994; chlorobenzene–p-xylene, λ_{12}, 1.2156; λ_{21}, 0.9075. Tables III and IV also give the activity coefficients of the two components. Plots of log-activity coefficients vs. mole fraction for the two systems are shown in Figures 3 and 4. An observation of Figure 3 indicates that the curve for p-xylene crosses the x axis at x_1 = 0.3750, reaches a minimum at x_1 = 0.1001 and again increases to x_1 = 0. This type of behavior has been observed by Burke et al. (*4*) for the methanol–toulene system. The methanol–toluene system forms an azeotrope at a methanol mole fraction of x_1 = 0.085. However, no such azeotrope formation has been observed in the methyl ethyl ketone–p-xylene system.

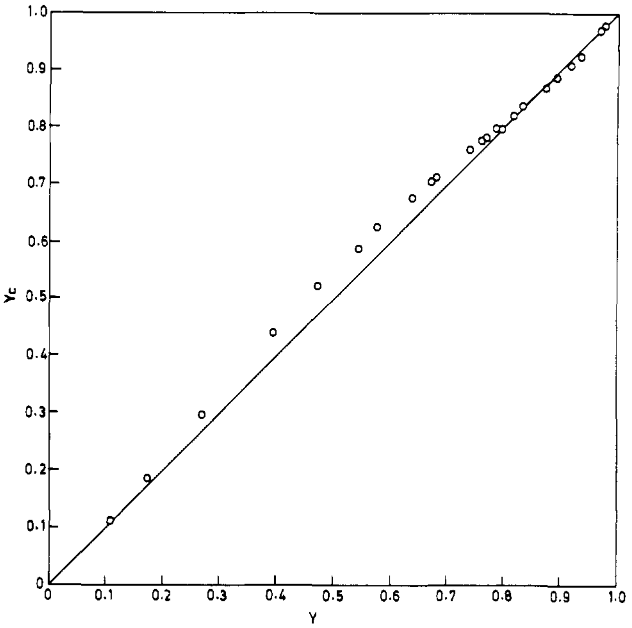

Figure 5. Experimental and calculated vapor compositions for the methyl ethyl ketone–p-xylene system.

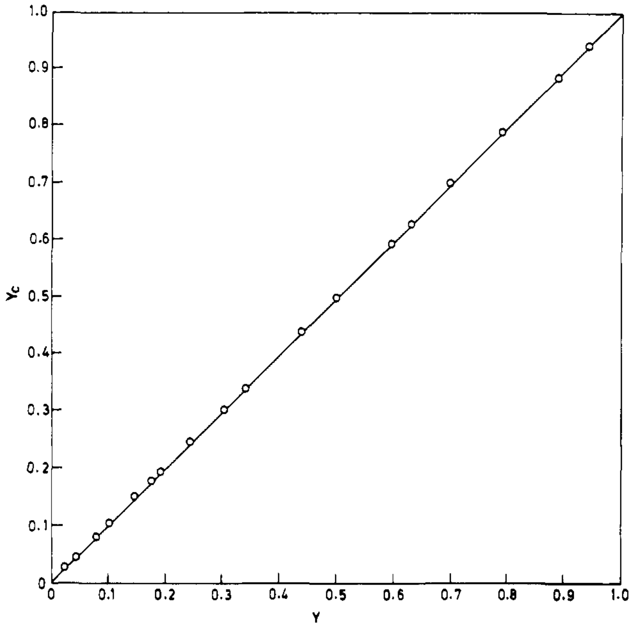

Figure 6. Experimental and calculated vapor compositions for the chlorobenzene–p-xylene system.

Experimental and calculated vapor compositions are compared in Figures 5 and 6. From these figures it is evident that eq 2 and 3 fit the experimental activity coefficients well. In the case of the methyl ethyl ketone–p-xylene system large deviations of calculated vapor-phase compositions from experimental vapor-phase compositions are observed. This is because of the anomalous behavior of the activity coefficients of p-xylene with mole fraction mentioned earlier. From the activity coefficients it is clear that the system methyl ethyl ketone–p-xylene exhibits positive deviations from Raoult's law while the system chlorobenzene–*p*-xylene exhibits negative deviations from Raoult's law.

Glossary

B_{11}, B_{22}	gas-phase second virial coefficient for component 1 and 2, respectively
P	total pressure, mmHg
p_1°	vapor pressure of component 1, mmHg
R	universal gas constant, 82.054 cm^3 atm K^{-1} mol^{-1}
T	absolute temperature, K
V_1^L	liquid molar volume of component 1, cm^3/mol
x_1, x_2	mole fraction of components 1 and 2, respectively, in liquid phase
y_1	mole fraction of component 1 in vapor phase
γ_1	activity coefficient of component 1.
δ_{12}'	$B_{12} - B_{11} - B_{22}$ where B_{12} is the second virial cross coefficient
λ_{12}, λ_{21}	constants in Wilson's equation

Subscripts

1	low boiling component
2	high boiling component

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Salt Effect on the Vapor Pressure of Pure Solvents: Methanol with Seven Salts at 24.9 °C

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Vapor pressure data of methanol at 24.9 °C with seven salts (LiCl, NaBr, $CaCl_2$, NaOH, NaI, KI, and $CuCl_2$) are presented. Attempts to correlate the results to crystallographic radii, or salt solubility in methanol, were inconclusive. For the two salts with I^- as common ion (NaI and KI), increased ΔP values follow decreasing values at the cation radii. This is not the case for the three salts with Na^+ as common ion (NaOH, NaI, NaBr) or for the two salts with Cl^- as common anion (LiCl, $CuCl_2$, $CaCl_2$). Considering salt solubility for the three salts with Na^+ as the common ion, vapor pressure depression effects increase with increasing salt solubility. The same was true for the two salts with I^- as common ion but not for the three salts with Cl^- as common ion (LiCl, $CuCl_2$, $CaCl_2$).

Introduction

While data for the vapor pressure depression of a large number of salts in water are available, see for example Weast (*13*), such data for nonaqueous solvents are rather scarce. Data for methanol with seven salts at 24.9 °C are presented in this paper. This represents part of a more general effort for the development and correlation of data for solvent-salt systems (Bekerman and Tassios (*2*)).

Experimental Section

An experimental study was conducted to determine the concentration effect of seven salts on the vapor pressure of methanol at 24.9 °C. Solutions of varying concentrations were charged to an Othmer still (*7*, *8*). The still was continuously heated while the pressure was adjusted until the liquid solution was boiling at a temperature of 24.9 ± 0.1 °C. When the temperature remained constant for about 30 min, the system was assumed to be in equilibrium and the pressure was measured using a cathetometer and a mercury manometer. The pressure was recorded as the vapor pressure of the system. The pressure in the still was controlled to within ±0.1 mmHg by a control system featuring a Precision Micro Set Manostat (*1*). The temperature was measured with a calibrated mercury-in-glass thermometer immersed in the liquid phase. The pressure in the still was measured with mercury manometer with the use of a cathetometer. Experimental details are given by Bixon (*3*).

Reagents and Chemicals

1. "Baker Analyzed" reagent grade sodium hydrozide was used for the sodium hydroxide runs. The assay was 98.3% NaOH. The largest impurity present was sodium carbonate listed as 0.4%. Before each run, an unknown impurity was filtered out from the NaOH—methanol solution with coarse grade filter paper. The impurity was probably the sodium carbonate since it is insoluble in methanol (*13*). The other impurities were not listed on the label.
2. Two different types of lithium chloride were used in these experiments. The first brand used was from Fisher Scientific Co. while the other brand was "Baker Analyzed" reagent grade. Both grades were listed as being 99.8% pure.
3. The cupric chloride was certified anhydrous grade from Fisher Scientific. The impurities listed on the label totaled 0.06%.

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