water mixtures is needed to ensure more accurate data and modeling. This work did not attempt to compensate for the difference in D-glucose crystals because of the difficulty in quantifying the amount of each type of crystal present in solution.

Registry No. D-Glucose, 50-99-7; EtOH, 64-17-5.

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Isobaric Vapor–Liquid Equilibrium for the Cumene–*m*-Cresol and Phenol–*m*-Cresol Systems at 13.33 kPa

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Isobaric vapor–liquid equilibrium data are reported for the cumene–*m*-cresol and phenol–*m*-cresol systems at 13.33 kPa. The activity coefficient data were tested for thermodynamic consistency by the methods of Herington, Black, and van Ness and correlated by using the Norrish and Twigg and Wilson equations. The results suggest that *m*-cresol can be used as a solvent for extractive distillation of cumene–phenol mixture with cumene as an overhead product.

Introduction

Cumene can be converted to phenol and acetone via cumene hydroperoxide (*1*). In this process, cumene free of phenol is required for recycling to the cumene oxidation stage because the presence of phenol is detrimental for the oxidation. The separation of the cumene–phenol mixture is difficult because it presents an azeotropic point at atmospheric pressure (*2*) and low pressures would be necessary to make it disappear. Extractive distillation can be used to separate the mixture with an appropriate solvent. Scheibel (*3*) has suggested that the screening of the solvents might be found between the members of homologous series of the components, and he recommends as the lowest boiling point one that does not form an azeotrope. In this case, we have chosen 1-octanol and *m*-cresol as solvents. The UNIFAC method can be used (*4*) to calculate the selectivity at infinite dilution in the alcohols that we have chosen as solvents.

The selectivity at infinite dilution

$$S_1{}^{\infty}{}_2 = (\gamma_1{}^{\infty}/\gamma_2{}^{\infty})_{\text{solvent}} \qquad (1)$$

was calculated for cumene–phenol in 1-octanol and *m*-cresol by means of Fredenslund programs (*5*), and the results are listed in Table I.

Although 1-octanol seems to be the most adequate solvent for the extractive distillation, its recuperation would be difficult because 1-octanol forms an azeotrope with phenol. This azeotrope, with a mole fraction of 0.335 of phenol, has been predicted with the UNIFAC method at 463.15 K.

Vapor–liquid equilibrium data are necessary to be sure that an azeotrope with cumene does not form. In the present paper, the vapor–liquid equilibria of the cumene–*m*-cresol and phenol–*m*-cresol systems were measured at 13.33 kPa. Data on these systems are not found in the literature at temperatures and pressures comparable to those of the present work.

Table I. Selectivity at Infinite Dilution in Solvents for Cumene (1)–Phenol (2) at 443.15 K

solvent	$S_1{}^{\infty}{}_2$
m-cresol	1.9043
1-octanol	4.3953

Table II. Physical Properties of Pure Compounds: Density, Refractive Index, and Boiling Point

	ρ, g/cm^3		n_D		T_B, K	
	obsd	ref *13*	obsd	ref *13*	obsd	ref *13*
cumene (T = 298.15 K)	0.8574	0.8575	1.4889	1.4889	425.54	425.54
phenol (T = 318.15 K)	1.0542	1.0545	1.5400	1.5402	454.96	454.98
m-cresol (T = 298.15 K)	1.0306	1.0302	1.5399	1.5396	475.5	475.38

Table III. Vapor–Liquid Equilibrium Data for the Cumene–*m*-Cresol System at 13.33 kPa

x	y	T, K	γ_1	γ_2
0.0676	0.4850	398.41	1.9596	1.0000
0.1041	0.6045	392.41	1.9354	1.0000
0.2305	0.8048	377.89	1.9376	1.0171
0.3164	0.8423	373.93	1.6929	1.1004
0.4067	0.8832	370.13	1.6087	1.1387
0.4870	0.9010	368.85	1.4383	1.1848
0.6273	0.9265	366.68	1.2492	1.3416
0.7106	0.9401	365.36	1.1426	1.5357
0.8379	0.9568	363.20	1.1056	2.1685
0.9210	0.9805	362.53	1.0583	2.1290
0.9642	0.9922	362.15	1.0373	1.9137

Experimental Section

Measurements were made in a vapor recirculating type equilibrium still. The experimental apparatus and procedure have been described in a previous paper (*6*).

Cumene was supplied by Merck, phenol was supplied by PANREAC, and *m*-cresol was supplied by Scharlau. They are analytical-grade reagents and were purified by distillation under vacuum in a laboratory column. Physical properties of these components are listed in Table II along with their literature values.

Table IV. Vapor–Liquid Equilibrium Data for the Phenol–*m*-Cresol System at 13.33 kPa

x	y	T, K	γ_1	γ_2
0.0486	0.0904	409.45	1.0276	1.0184
0.1252	0.2561	406.95	1.2378	1.0000
0.2206	0.3811	404.45	1.1467	1.0258
0.2960	0.4757	403.02	1.1256	1.0177
0.3107	0.4935	402.55	1.1323	1.0230
0.4284	0.5910	400.55	1.0611	1.0788
0.4842	0.6557	399.55	1.0825	1.0477
0.5503	0.7071	398.63	1.0643	1.0611
0.6266	0.7593	397.66	1.0423	1.0925
0.6880	0.8022	396.94	1.0315	1.1065
0.7317	0.8338	396.45	1.0277	1.1032
0.7821	0.8680	395.8	1.0269	1.1081
0.8236	0.8881	395.35	1.0157	1.1822
0.8889	0.9344	394.75	1.0140	1.1281

Table V. Correlation Constants and Correlation Coefficients

		cumene–*m*-cresol	phenol–*m*-cresol
Norrish and Twigg	M	2.6547	0.8527
	C	−1.5920	−0.3503
	r^2	0.994	0.9860
Wilson	Λ_{12}	1.0000	1.3595
	Λ_{21}	0.1700	0.5235
	σ	0.0450	0.0053

Compositions of the liquid and condensed vapor samples were determined by analysis with a Perkin-Elmer 3920 gas chromatograph utilizing a thermal conductivity detector, with a Carbobax 20M column.

Results and Discussion

The vapor–liquid equilibrium data for the cumene–*m*-cresol and phenol–*m*-cresol systems at 13.33 kPa are reported in Tables III and IV, respectively.

Fugacity coefficients became close to unity so we have taken $\phi = 1.0$ for all compositions, and the activity coefficients are calculated by

$$\gamma_i = y_i P / x_i P^\circ \qquad (2)$$

where x_i and y_i are the liquid and vapor mole fractions, P is the pressure, and P° is the vapor pressure. In this paper, the temperature dependence of the vapor pressure is given by the Antoine equation, and the constants of this equation are

	A	B	C
cumene (*2*)	7.25009	1671.459	230.000
phenol (*13*)	7.13457	1516.072	174.569
m-cresol (*13*)	6.35980	1572.471	73.230

The values of the activity coefficients are shown in Tables III and IV.

The thermodynamic consistency of the data was examined by using the point to point test originated by van Ness et al. (*7*) and modified by Fredenslund et al. (*5*) using a fifth-order Legendre polynomial. According to this test, the data point is considered consistent if the average absolute deviation is $y \leq 0.01$. The estimated standard deviations for vapor-phase compositions were 0.0091 for the cumene–*m*-cresol system and 0.0062 for the phenol–*m*-cresol system. The data for these systems were also assessed at thermodynamic consistency by applying the Herington (*8*, *9*) and Black (*10*) tests. The data satisfied the criteria of all the tests, thereby showing them to be thermodynamically consistent.

The activity coefficient data were fitted to the Norrish and Twigg (*11*) and Wilson (*12*) correlations. The constants in these correlations are given in Table V. The Wilson equation gave the best fit for the two systems; the Norrish and Twigg equation correlated the composition data properly, but the activity coefficients calculated with it are greater than the experimental ones. In Figures 1 and 2 the experimental values of composition and their fit to the Norrish and Twigg and Wilson equations are plotted.

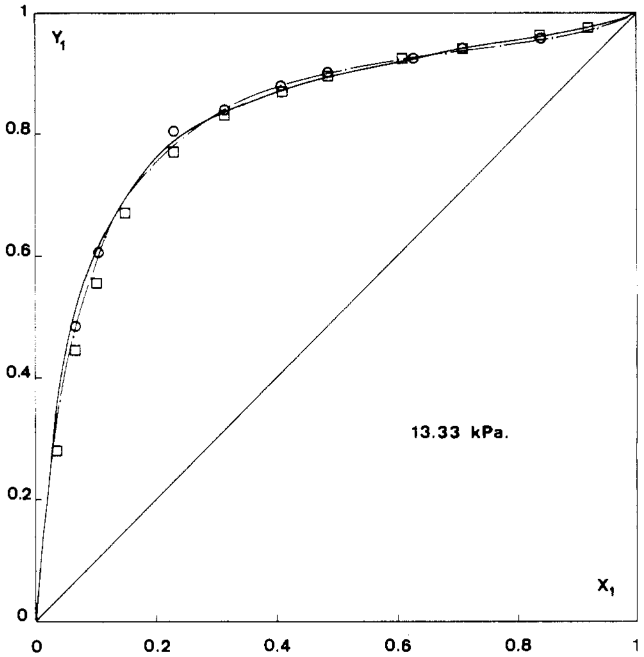

Figure 1. x–y phase equilibrium diagram for cumene (1)–*m*-cresol (2) at 13.33 kPa: (○) experimental data; (□) values obtained by means of UNIFAC method; (—) Norrish–Twigg's correlation, (- - -) Wilson's correlation.

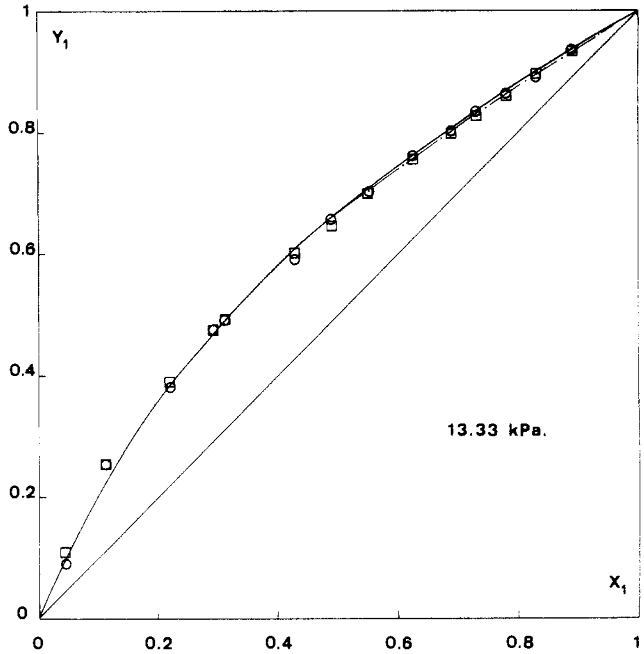

Figure 2. x–y phase equilibrium diagram for phenol (1)–*m*-cresol (2) system at 13.33 kPa. Legend as in Figure 1.

The activity coefficients have also been calculated by the UNIFAC method (*5*), and it is found that the experimental values are lower than the predicted ones. Data obtained with this method are plotted in Figures 1 and 2.

Conclusions

New liquid–vapor equilibrium data for the cumene–phenol and phenol–*m*-cresol systems are reported. This suggests that *m*-cresol can be used as a solvent for extractive distillation of cumene–phenol mixture with cumene as an overhead product.

Acknowledgment

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Glossary

C, M	constants in Norrish and Twigg equation
n	number of points
n_D	refraction index
P	pressure, kPa
r^2	correlation coefficient
S^∞	selectivity at infinite dilution
T	temperature, K
T_B	boiling point, K
x	liquid-phase mole fraction
y	vapor-phase mole fraction

Greek Letters

γ	activity coefficient
ϕ	fugacity coefficient
Λ_{12}, Λ_{21}	constants in Wilson model
ρ	density, g/cm^3
σ	average deviation $(\sum(y_{\text{exptl}} - y_{\text{calcd}})/n)$

Suscripts

1	more volatile component
2	less volatile component
calcd	calculated
exptl	experimental

Registry No. Phenol, 108-95-2; *m*-cresol, 108-39-4; cumene, 98-82-8.

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PVTx Properties of the Binary System R 115 + R 114 and Its Thermodynamic Behavior

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This paper reports the *PVTx* properties of the R 115 + R 114 system in a wide range of temperatures from 296 to 443 K, of pressures from 0.4 to 9.8 MPa, and of densities from 149 to 1313 kg/m^3. Five hundred ninety-seven *PVTx* measurements for four compositions, i.e., 25, 50, 75, and 100 wt % R 115, have been measured along the 41 isochores. The uncertainties of the temperature, pressure, and density measurements are less than ±8 mK, ±2.2 kPa, and ±0.1%, respectively. On the basis of the experimental measurements of 100 wt % R 115, we confirmed the reliability of our experimental apparatus and measurements. From *PVTx* measurements for 75 wt % R 115, 50 wt % R 115, and 25 wt % R 115, we have established the thermodynamic behavior of this binary mixture. We have also compared the critical curve of the R 115 + R 114 system observed in the present experimental study with those of other binary fluorocarbon mixtures that have been reported by us.

Introduction

The *PVTx* properties of binary refrigerant mixtures must be known accurately for system design and for reliable assessment of cycle performance (*1*, *2*).

Although the binary refrigerant mixture of the R 115 ($CClF_2CF_3$; monochloropentafluoroethane) and R 114 ($CClF_2CClF_2$; 1,2-dichloro-1,1,2,2-tetrafluoroethane) system is one of the technically important mixtures, experimental measurements of the thermodynamic properties of this system are not available. Continuing our own project of *PVTx* measurements of refrigerant mixtures, the R 12 + R 22 system (*3*), R 22 + R 114 system (*4*), R 13B1 + R 114 system (*5*), and R 152a + R 114 system (*6*, *7*), this paper reports the *PVTx* properties of the R 115 + R 114 system over a wide range of temperatures from 296 to 443 K, of pressures from 0.4 to 9.8 MPa, and of densities from 149 to 1313 kg/m^3, respectively. Five hundred ninety-seven *PVTx* measurements for four compositions, i.e., 25, 50, 75, and 100 wt % R 115, have been measured along 41 isochores. On the basis of these experimental data, we have determined dew points, bubble points, and the critical point for each composition.

Experimental Section

The method, apparatus, and procedure of the *PVTx* measurements used here have been described in detail in our previous publications (*9*, *10*). In principle, the *PVTx* measurements of this work were made by the constant-volume method coupled with isothermal expansion.

The mass fraction of the mixture charged to the sample cell was determined by weighing the mass of each component on a chemical balance before mixing. The density of the sample was determined to be the ratio of the mass of the sample to the volume of the sample cell. The temperature of the sample was measured by a 25-Ω platinum resistance thermometer which was mounted near the cell in a thermostated fluid bath. The pressure of the sample was transmitted through the diaphragm of the differential pressure indicator (DPI) to an external pressure measuring system by balancing it with the pressure of nitrogen gas, the pressure transmitting gas. The fact that

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