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Isobaric Vapor–Liquid Equilibrium of the Systems Cumene + Benzyl Alcohol and Phenol + Benzyl Alcohol at 10 kPa

José M. Resa,* Teresita Quintana, and Emilio Cepeda

Departamento Ingeniería Química, Facultad de Farmacia, Universidad del País Vasco, Apartado 450, Vitoria, Spain

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Isobaric vapor–liquid equilibrium data are reported for the binary systems cumene + benzyl alcohol and phenol + benzyl alcohol at 10 kPa. The activity coefficient data were tested for thermodynamic consistency by the methods of Herington, Black, and Van Ness and correlated with the Wilson equation. None of the systems show an azeotrope.

Introduction

The process of cumene conversion to phenol results in a mixture of phenol, other phenols of high molecular weight, acetone, and cumene. The separation of cumene from phenol is necessary because the presence of phenol in the recirculation flow to the reactor is detrimental to the oxidation (*1*). The separation of the cumene + phenol mixture by distillation is difficult because it presents an azeotrope at atmospheric pressure (*2*), and low pressure would be necessary to make it disappear.

In a previous study (*3*), we suggested *m*-cresol as an agent for the extractive distillation, and the vapor–liquid equilibrium was determined. However, *m*-cresol is very toxic by adsorption through the skin, and the odor is persistent and disagreeable. For this reason other solvents should be investigated for the extractive distillation of cumene + phenol mixtures.

In the screening of solvents for the extractive distillation we have selected benzyl alcohol because it associates via hydrogen bonding with phenol, and its boiling point is 34 K higher than that of phenol. In a distillation column the bottom would be a phenol + benzyl alcohol mixture, and the head pure cumene. UNIFAC predicts (*4*) a phenol (1) + benzyl alcohol (2) azeotrope at 10 kPa for $x_1 = 0.247$. In experiments with a laboratory distillation column, this azeotrope was not found.

In the present paper, the vapor–liquid equilibria of the cumene + benzyl alcohol and phenol + benzyl alcohol systems were measured at 10.00 ± 0.13 kPa. Data on these systems are not found in the literature.

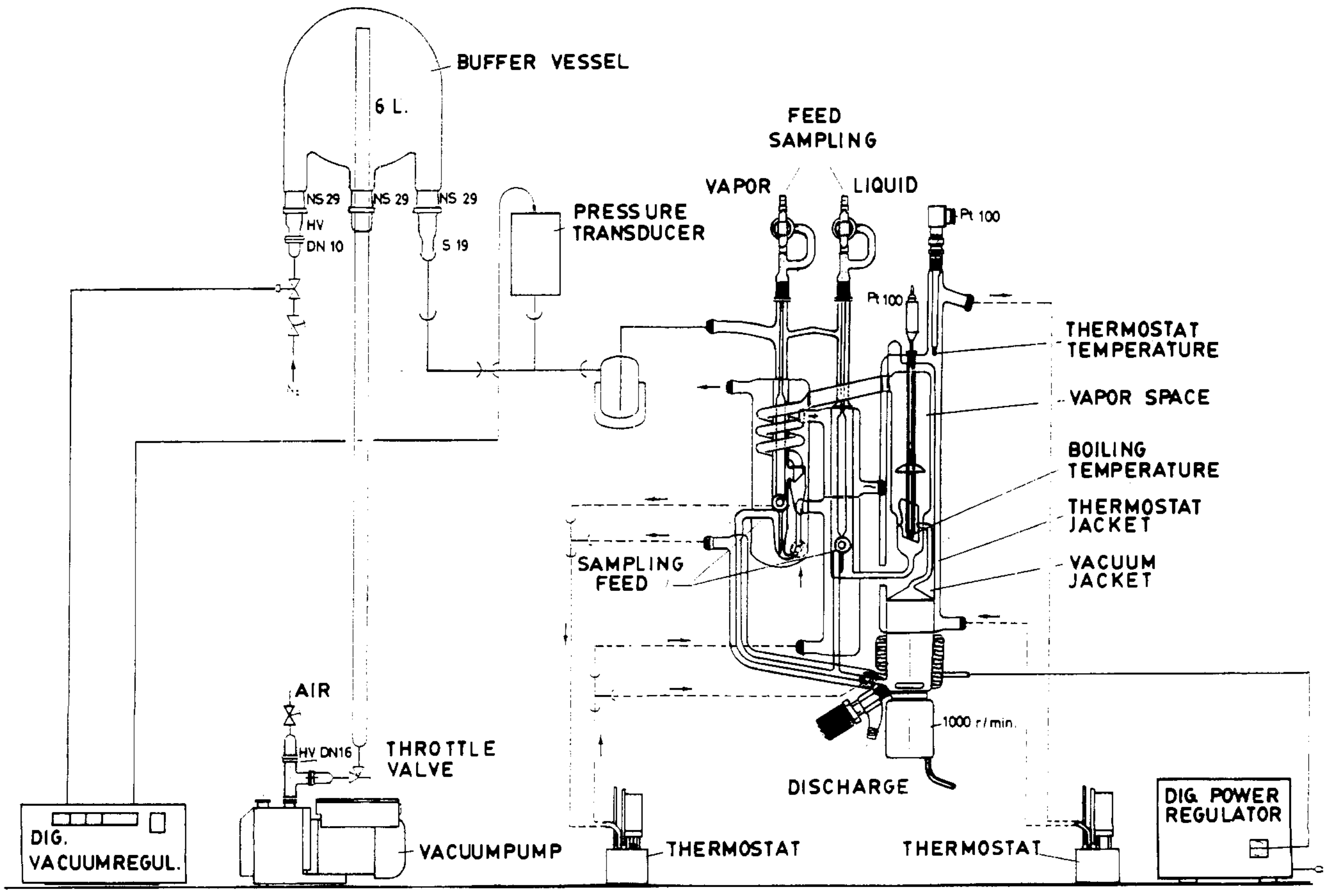

Figure 1. System for the vapor–liquid equilibrium measurement.

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Table I. Physical Properties of Pure Compounds: Density (ρ), Refractive Index (n), Normal Boiling Point (T_b), and Antoine Coefficients (A, B, and C) (Equation 3)[a]

		cumene (T = 298.15 K)	phenol (T = 318.15 K)	benzyl alcohol (T = 298.15 K)
$\rho(T)/(\mathrm{g{\cdot}cm^{-3}})$	obsd	0.8574	1.0542	1.0416
	ref 13	0.85743	1.05446	1.04127
$n(D,T)$	obsd	1.4889	1.5400	1.5385
	ref 13	1.48890	1.54027	1.53837
T_b/K	obsd	425.55	454.95	478.60
	ref 13	425.561	454.989	478.60
		ref 2	ref 7	ref 7
	A	6.37499	6.25945	6.70690
	B	1671.459	1516.074	1904.299
	C	−43.15	−98.59	−73.15

[a] The Antoine constants for cumene are from ref 2, and those for phenol and benzyl alcohol are from ref 7.

Table II. Refractive Index ($n(D)$) of Cumene (1) + Benzyl Alcohol (2) Mixtures as a Function of the Mole Fraction (x) of Cumene at 298.15 ± 0.1 K

x	$n(D)$	x	$n(D)$	x	$n(D)$
0.0000	1.5385	0.3013	1.5209	0.6975	1.5011
0.0484	1.5345	0.3992	1.5153	0.7965	1.4968
0.1027	1.5319	0.4994	1.5103	0.8956	1.4928
0.1984	1.5268	0.5962	1.5059	0.9492	1.4907
				1.0000	1.4889

Experimental Section

Materials. Analytical-grade cumene (Merck, Germany), phenol (PANREAC, Spain), and benzyl alcohol (Scharlau, Spain) were purified by distillation under vacuum in a laboratory column. The physical properties of these components are listed in Table I along with literature values.

Apparatus and Procedure. Measurements were made in an all-glass vapor recirculating type equilibrium still, similar to the apparatus proposed by Gillespie (*5*). In this work we have used an apparatus manufactured by Fritz GmbH (Normag, Germany) described by Röck and Sieg (*6*) with various technical improvements (Figure 1).

In the boiler (1), with a volume of 200 mL vapor bubbles are generated by external heating, producing liquid–vapor transport in the soldered-on Cottrell pump (2). The vapor–liquid mixture empties via the temperature measuring point and separates into vapor escaping upward and liquid flowing downward. The Cottrell pump and vapor space are surrounded by a silver mirror coated high-vacuum jacket, whose external walls are at the boiling temperature with the liquid heat transfer medium; thus, the partial condensation of vapor is avoided. The vapor flows into a cooler and is totally condensed and collected in the receiver (3) from where it flows back into the boiling flask. The liquid is also recirculated into the boiler separately. A shield (4) prevents liquid drops from splashing into the vapor chamber. The boiling point temperature is determined by a Pt 100 resistance thermometer with a four-conductor circuit with an accuracy of ±0.1 K. The temperature of the heat transfer medium is measured as standard at the inlet connection by a grip-type thermometer in combination with a thermostat regulated via a Pt 100 resistance thermometer.

The still is purged with dry nitrogen and the distillation flask filled with the mixture to be investigated. The pressure is preset with a digital vacuum regulator, connected to the upward sloping tube which has a buffer vessel of adequate size, and is measured with an accuracy of ±0.13 kPa. The mixture is heated to the boiling point. Equilibrium is established on the basis of no changes in temperature and constant circulation rates of both vapor and liquid. Each data point requires no more than 45 min.

Table III. Vapor–Liquid Equilibrium Data for the Cumene (1) + Benzyl Alcohol (2) System: Liquid-Phase Mole Fraction (x_1), Vapor-Phase Mole Fraction (y_1), Boiling Temperature (T), and Activity Coefficients (γ_1 and γ_2) at 10.00 kPa[a]

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	406.85		
0.012	0.300	399.50	5.1703	0.9520
0.030	0.421	395.90	3.2405	0.9318
0.049	0.501	392.20	2.6504	0.9588
0.051	0.553	390.60	2.9572	0.9225
0.067	0.633	386.80	2.9124	0.9107
0.097	0.720	381.70	2.7086	0.9045
0.134	0.782	376.55	2.5384	0.9346
0.174	0.818	372.10	2.3904	1.0144
0.209	0.844	370.00	2.2137	1.0073
0.245	0.863	368.05	2.0723	1.0218
0.287	0.879	366.35	1.9177	1.0417
0.325	0.891	364.75	1.8214	1.0760
0.368	0.902	363.45	1.7094	1.1052
0.401	0.914	362.70	1.6351	1.0641
0.415	0.916	362.30	1.6075	1.0868
0.451	0.919	361.80	1.5124	1.1464
0.476	0.921	361.45	1.4553	1.1933
0.532	0.926	360.40	1.3626	1.3230
0.590	0.933	359.60	1.2765	1.4269
0.636	0.938	359.10	1.2136	1.5276
0.678	0.941	358.60	1.1644	1.6880
0.723	0.951	358.10	1.1251	1.6742
0.769	0.958	357.65	1.0844	1.7632
0.820	0.960	357.10	1.0411	2.2203
0.887	0.970	356.30	1.0034	2.7709
1.000	1.000	354.05		

[a] Correlation constants and the correlation coefficient of the Wilson equation: $\Lambda_{12} = 0.4719$, $\Lambda_{21} = 0.4128$, $\sigma = 0.0155$.

Table IV. Vapor–Liquid Equilibrium Data for the Phenol (1) + Benzyl Alcohol (2) System: Liquid-Phase Mole Fraction (x_1), Vapor-Phase Mole Fraction (y_1), Boiling Temperature (T), and Activity Coefficients (γ_1 and γ_2) at 10.00 kPa[a]

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	406.84		
0.044	0.054	406.40	0.5688	1.0068
0.068	0.090	406.35	0.6145	0.9954
0.096	0.126	406.30	0.6105	0.9876
0.122	0.164	406.25	0.6264	0.9745
0.148	0.198	406.10	0.6269	0.9691
0.170	0.236	405.95	0.6541	0.9533
0.192	0.266	405.35	0.6675	0.9635
0.250	0.344	404.95	0.6729	0.9426
0.274	0.386	404.60	0.6979	0.9242
0.305	0.428	404.15	0.7070	0.9157
0.345	0.488	403.40	0.7239	0.8963
0.375	0.532	402.70	0.7547	0.8831
0.405	0.572	402.00	0.7715	0.8727
0.445	0.622	401.15	0.7886	0.8554
0.490	0.676	400.05	0.8119	0.8346
0.545	0.740	398.85	0.8369	0.7887
0.595	0.790	397.65	0.8574	0.7522
0.614	0.816	396.85	0.8856	0.7150
0.635	0.830	396.15	0.8953	0.7194
0.673	0.853	395.20	0.9014	0.7228
0.742	0.894	393.70	0.9097	0.7040
0.772	0.913	393.05	0.9165	0.6723
0.805	0.932	391.90	0.9399	0.6455
0.830	0.944	391.30	0.9462	0.6258
1.000	1.000	386.85		

[a] Correlation constants and the correlation coefficient of the Wilson equation. $\Lambda_{12} = 1.5641$, $\Lambda_{21} = 1.2081$, $\sigma = 0.0011$.

Analysis. Liquid and condensed vapor compositions of the cumene (1) + benzyl alcohol (2) system were obtained from measurements of their refractive index at 298.15 K by using an Abbe-type refractometer with an accuracy of ±0.0002.

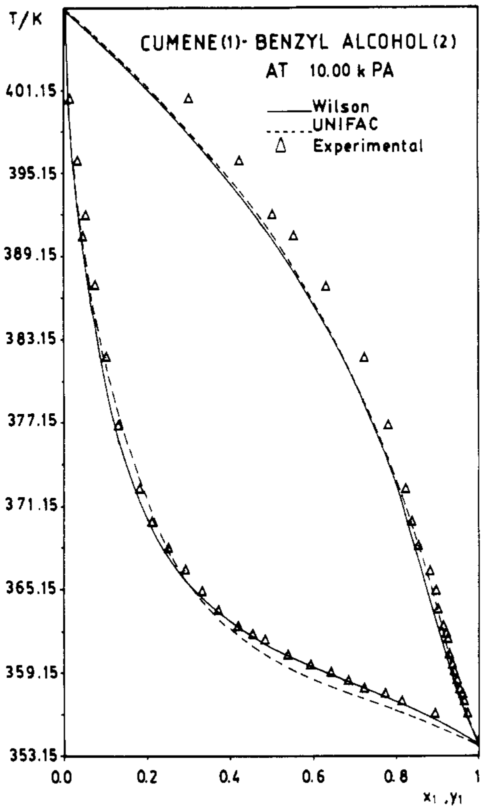

Figure 2. Phase equilibrium diagram for cumene (1) + benzyl alcohol (2) at 10.00 kPa: (Δ) experimental data; (—) Wilson's correlation; (- - -) UNIFAC.

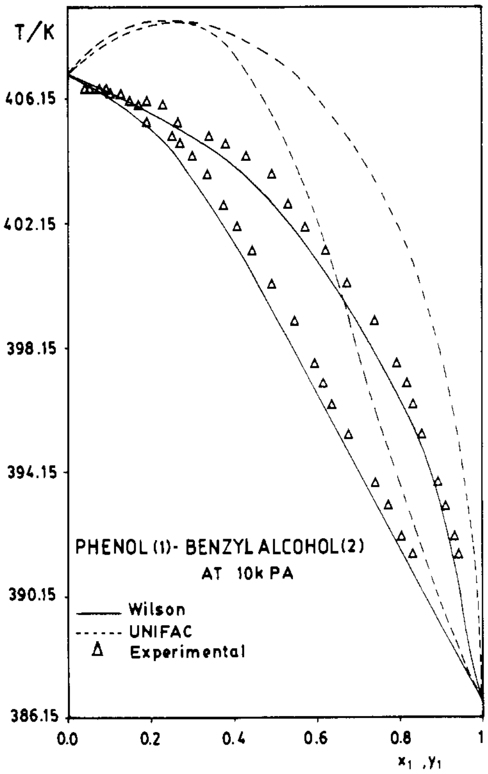

Figure 3. Phase equilibrium diagram for phenol (1) + benzyl alcohol (2) at 10.00 kPa: (Δ) experimental data; (—) Wilson's correlation; (- - -) UNIFAC.

Analysis was made by means of a carefully prepared calibration curve. The data were fitted to the equation

$$n(D,298.15\mathrm{K}) = 0.01129x_1^2 - 0.06034x_1 + 1.53779 \qquad (1)$$

with a correlation coefficient of 0.9999 and a standard deviation in the mole fraction of 0.0003. Table II shows the refractive index–composition values.

The phenol + benzyl alcohol mixtures were analyzed by gas chromatography using a Perkin-Elmer 3920 B apparatus equipped with a thermal conductivity detector. The column used was a 2-m stainless steel tube with Carbowax 20 M, with an accuracy of ±0.0005 in mole fraction.

Results and Discussion

The vapor–liquid equilibrium data for the cumene + benzyl alcohol and phenol + benzyl alcohol at 10.00 kPa are reported in Tables III and IV with an accuracy in the mole fraction of ±0.001.

Fugacity coefficients are close to unity for all compositions, so we have calculated the activity coefficients γ_i by

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

where x_i and y_i are liquid and vapor mole fractions, respectively, P is the pressure, and P_i° is the vapor pressure of pure component i. The cumene + benzyl alcohol system shows positive deviations and the phenol + benzyl alcohol system negative deviations from Raoult's law. No azeotropes are found for these systems at 10.00 kPa. The vapor pressures have been calculated by the Antoine equation; the constants used in this work are given in Table I.

$$\ln(p/\mathrm{kPa}) = A - \frac{B}{(C + T/\mathrm{K})} \qquad (3)$$

The values of the activity coefficients γ_i are shown in Tables III and IV. The data are fitted to the Wilson (*8*) equation by the Marquard method, where the following objective function was minimized:

$$\Delta P = \sum_i^m |P - P_{\mathrm{exp}}|$$

The constants in this correlation are given in Tables III and IV with the mean deviation in y. In Figures 2 and 3 the experimental values of composition and their fit to the Wilson equation are plotted.

The thermodynamic consistency was tested by using the point-to-point method of Van Ness, Byer, and Gibbs (*9*) and modified by Fredenslund (*4*), using a fifth-order Legendre. According to this test, the data point is considered consistent if the average absolute deviation in y is smaller than 0.01. The estimated standard deviations were 0.008 for the cumene + benzyl alcohol and 0.009 for the phenol + benzyl alcohol system. The thermodynamic consistency of the data was also confirmed by applying the Herington (*10*) and Black (*11*) tests.

The activity coefficients have been predicted by the UNIFAC method (*12*), and it is found that the experimental values are very different from the predicted values for the system phenol + benzyl alcohol. UNIFAC predicts an azeotrope for $x = 0.247$, and experimentally we have not found an azeotrope. For the cumene + benzyl alcohol system the predicted results are according to the experimental values (Figures 2 and 3).

Conclusions

New liquid–vapor equilibrium data for the cumene + benzyl alcohol and phenol + benzyl alcohol are reported, and they suggest that benzyl alcohol can be used as a solvent for extractive distillation at low pressures with cumene as an overhead product.

Glossary

$n(D,T)$	refractive index
P	pressure, kPa

T	temperature, K
x	liquid-phase mole fraction
y	vapor-phase mole fraction
γ	activity coefficient
$\rho(T)$	density, g cm^{-3}
Λ_{12},Λ_{21}	constants in the Wilson model
σ	average deviation ($\sum(y_{exp} - y_{calcd})/n$)

Subscripts

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

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