Phase Equilibria in Binary Systems Formed by Phenol with Benzene, *n*-Octane, and *n*-Decane

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Isothermal vapor-liquid equilibrium data have been measured for the binary systems benzene-phenol (80 °C), *n*-octane-phenol (110 °C), and *n*-decane-phenol (120 °C). Thermodynamic consistency was checked by two methods, and the parameters in different expressions for the excess Gibbs energy have been fitted. Furthermore, the region of mutual solubility (LLE, SLE) of the binary system *n*-decane-phenol has been investigated.

Introduction

The development of prediction methods for vapor-liquid equilibria, such as ASOG (*1*) or UNIFAC (*2*) requires reliable data. In the case of phenol-alkane or phenol-benzene systems, the number of published data is very limited (*3*). The basic parameters $a_{\mathrm{ACOH,ACH}}$, $a_{\mathrm{ACH,ACOH}}$, $a_{\mathrm{ACOH,CH_2}}$, and $a_{\mathrm{CH_2,ACOH}}$ in the old UNIFAC parameter table (*4*) are thus not very reliable, so that erroneous results are obtained when, for example, the selectivity of phenol as an extractive solvent for the benzene-cyclohexane separation (*5*) is to be predicted. Vapor-liquid equilibrium measurements have now been performed for different binary phenol systems in order to permit an improvement in the results of the UNIFAC method by revising the relevant parameters. The measured data were used to revise the UNIFAC group interaction parameters of the phenol group.

Experimental Section

Purification of the Components. All chemicals used are commercially available. The hydrocarbons were purified by rectification in a packed column. Phenol was purified by fractional crystallization from *n*-octane followed by drying in a vacuum drying oven at 5 mmHg and rectification in a Vigreux column. Table I shows the suppliers of the different chemicals and the degree of purity attained after the purification steps.

Analysis

The composition of the liquid and the vapor phase were obtained by using a digital densitometer (DMA02D, Heraeus/Paar). The densitometer was calibrated by using air and doubly distilled water. The density measurements were carried out at different temperatures, depending on the system (benzene-phenol at 41 °C; *n*-octane-phenol at 60 °C; *n*-decane-phenol at 75 °C). The densities of the pure substances at these temperatures are given in Table I. The precision of measurement at these temperatures is better than 10^{-4} g/cm^3. The calibration curves were attained by measuring weighed samples of the corresponding binary mixture. The measurements of the density (composition) of the equilibrium samples were repeated at least twice.

Vapor-Liquid Equilibrium Measurements

The vapor-liquid equilibrium measurements were performed in an all-glass equilibrium still with circulation of both the liquid and vapor phases; the apparatus has been described previously (*6*). For each data point approximately 45 min elapsed before equilibrium was attained and samples were taken by means of syringes. A precision mercury manometer (Wallace and Tiernan) was used for measurements of pressure.

Table I

component	supplier	grade of purification[a]	density, g/cm^3	temp, °C
benzene	Aral	>99.99	0.859 41	41
n-octane	BASF	>99.99	0.669 56	60
n-decane	Merck AG	>99.99	0.687 59	75
phenol	Bayer	>99.99	1.061 8	41
			1.041 01	60
			1.028 23	75

[a] As shown by GPLC.

Table II. Experimental Data and Fitted Parameters for the System Benzene (1)-Phenol (2) at 80 °C

	A_{12}	A_{21}	α_{12}	mean devn in y
Margules	0.9000	0.9256		0.0011
van Laar	0.9012	0.9251		0.0011
Wilson	308.5931	425.7230		0.0011
NRTL	373.4202	318.1885	0.2986	0.0011
UNIQUAC	72.2429	197.4530		0.0011

exptl data			exptl data		
P, mmHg	x_1	y_1	P, mmHg	x_1	y_1
15.67	0.0	0.0	482.96	0.4666	0.9776
179.80	0.1100	0.9210	506.25	0.5051	0.9793
195.55	0.1265	0.9297	533.32	0.5522	0.9816
220.05	0.1498	0.9391	553.35	0.5946	0.9830
239.02	0.1670	0.9449	575.55	0.6360	0.9845
250.10	0.1755	0.9472	593.47	0.6723	0.9858
271.27	0.2062	0.9539	612.60	0.7150	0.9872
291.60	0.2247	0.9572	631.50	0.7562	0.9886
310.20	0.2459	0.9600	644.00	0.7750	0.9885
335.92	0.2726	0.9644	652.95	0.8036	0.9908
354.60	0.2941	0.9662	690.07	0.8640	0.9931
381.64	0.3342	0.9698	708.04	0.8992	0.9953
405.11	0.3618	0.9725	720.02	0.9225	0.9964
437.00	0.3986	0.9742	740.85	0.9602	0.9982
460.95	0.4294	0.9754	760.31	1.0000	1.0000

Liquid-Liquid (Solid-Liquid) Equilibrium Measurements

The binodal curve and the solubility of solid phenol in *n*-decane were measured by means of the synthetic method, in which known amounts of both components are placed in small test tubes. After the test tubes have been closed by melting off, the phase equilibria (cloud points) of the different samples were determined visually by changing the temperature (heating, cooling) of a transparent thermostat.

Results

The experimental vapor-liquid equilibrium data and the fitted parameters for the excess Gibbs energy are given in Tables II-IV together with the mean deviation of the vapor-phase mole fractions.

The measured pure-component vapor pressures were used for fitting the parameters, and, furthermore, ideality in the vapor

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Table III. Experimental Data and Fitted Parameters for the System *n*-Octane (1)-Phenol (2) at 110 °C

	A_{12}	A_{21}	α_{12}	mean devn in y
Margules	2.0399	2.0368		0.0072
van Laar	2.0392	2.0372		0.0072
Wilson	651.1308	1691.2989		0.0061
NRTL	1153.6643	1156.7889	0.4696	0.0060
UNIQUAC	784.2324	−171.6249		0.0070

exptl data			exptl data		
P, mmHg	x_1	y_1	P, mmHg	x_1	y_1
68.85	0.0	0.0	456.15	0.5282	0.8837
265.88	0.0617	0.7550	460.91	0.6203	0.8836
337.28	0.1002	0.8102	468.08	0.7140	0.8940
390.10	0.1510	0.8430	477.04	0.8430	0.9118
419.95	0.2160	0.8646	479.00	0.9000	0.9225
438.01	0.3013	0.8730	483.23	0.9383	0.9428
448.35	0.3977	0.8789	485.93	1.0000	1.0000

Table IV. Experimental Data and Fitted Parameters for the System *n*-Decane (1)-Phenol (2) at 120 °C

	A_{12}	A_{21}	α_{12}	mean devn in y
Margules	2.1783	1.9897		0.0146
van Laar	2.1950	1.9848		0.0145
Wilson	791.6863	1676.3868		0.0047
NRTL	1041.6904	1367.5677	0.4627	0.0044
UNIQUAC	862.0854	−211.3486		0.0134

exptl data			exptl data		
P, mmHg	x_1	y_1	P, mmHg	x_1	y_1
96.70	0.0	0.0	201.79	0.7520	0.6423
155.78	0.0471	0.3753	200.25	0.7915	0.6602
172.65	0.0802	0.4453	195.26	0.8561	0.6970
190.88	0.1457	0.5247	189.20	0.9042	0.7425
198.82	0.2383	0.5595	181.25	0.9415	0.8050
202.95	0.3421	0.5791	170.45	0.9665	0.8723
204.38	0.4670	0.5805	159.00	0.9884	0.9452
204.83	0.6123	0.6054	150.60	1.0000	1.0000
203.44	0.6931	0.6243			

Table V. Pure-Component Properties

component i	r_i	r_i	q_i
benzene	89.41	3.1878	2.4000
n-octane	163.54	5.8486	4.9360
n-decane	195.92	7.1974	6.0160
phenol	83.14	3.5517	2.6800

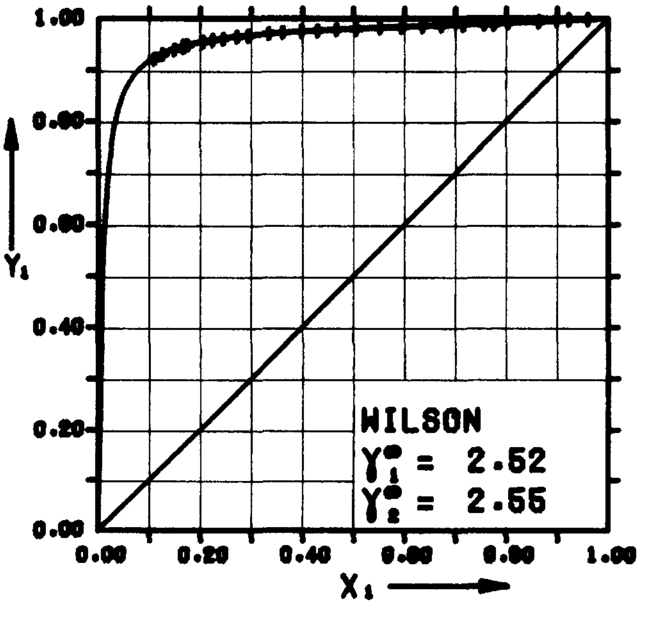

Figure 1. *y*–*x* diagram for the binary system benzene (1)–phenol (2) at 80 °C.

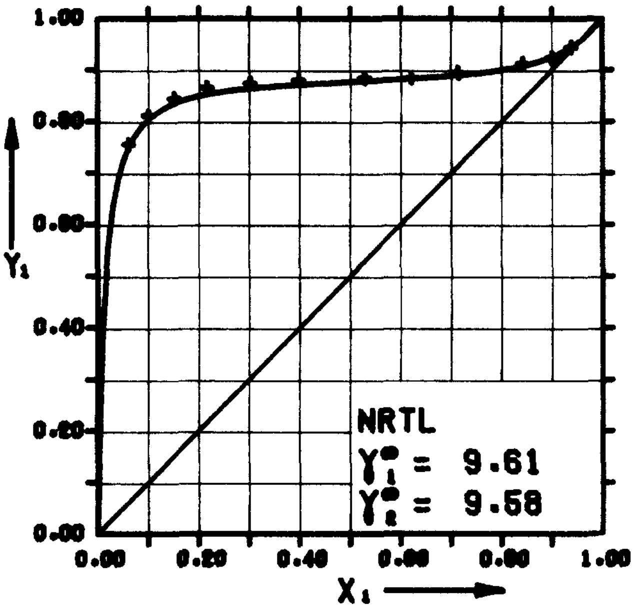

Figure 2. *y*–*x* diagram for the binary system *n*-octane (1)–phenol (2) at 110 °C.

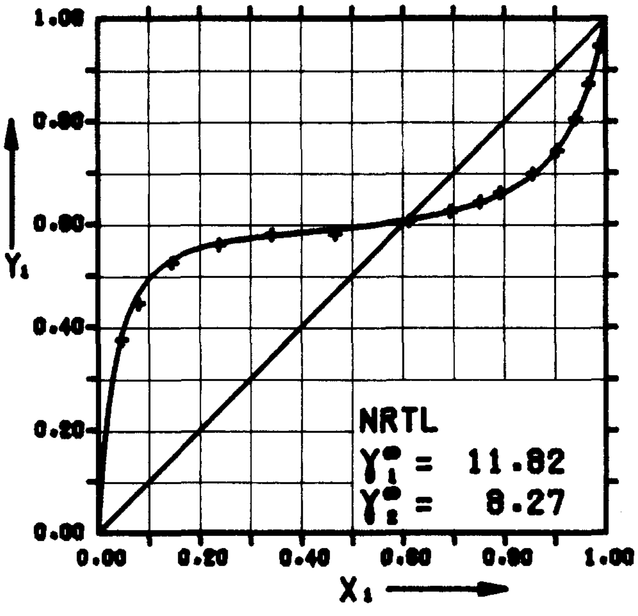

Figure 3. *y*–*x* diagram for the binary system *n*-decane (1)–phenol (2) at 120 °C.

phase was assumed. The sum of the relative squared deviation of the activity coefficients was chosen as an objective function. For expressions based on the local composition concept, A_{12} and A_{21} have the following meanings: Wilson, $A_{12} = (\lambda_{12} - \lambda_{11})$, $A_{21} = (\lambda_{21} - \lambda_{22})$; NRTL, $A_{12} = (g_{12} - g_{22})$, $A_{21} = (g_{21} - g_{11})$; UNIQUAC, $A_{12} = (u_{12} - u_{22})$, $A_{21} = (u_{21} - u_{11})$. The required pure-component properties for the Wilson and UNIQUAC equations are given in Table V (*3*). The experimental data were checked for thermodynamic consistency by using the integral test (*7*) and the point-to-point test developed by van Ness et al. (*8*) and modified by Christiansen and Fredenslund (*9*). All three data sets passed the consistency test with good results.

Figures 1–3 show the y–x diagrams of the different systems; the experimental data are denoted by plus signs and the fitted

Table VI. LLE Data for the System *n*-Decane (1)-Phenol (2)

x_1[a]	temp, °C	x_1[a]	temp, °C
0.0932	38.14	0.3980	63.31
0.1084	44.92	0.4934	62.61
0.1171	47.49	0.5551	61.31
0.1431	52.77	0.6251	58.06
0.1853	58.55	0.6802	54.53
0.2393	61.98	0.7354	49.80
0.2978	63.07	0.7838	45.63
0.3435	63.35	0.8137	42.45

[a] Mole fraction.

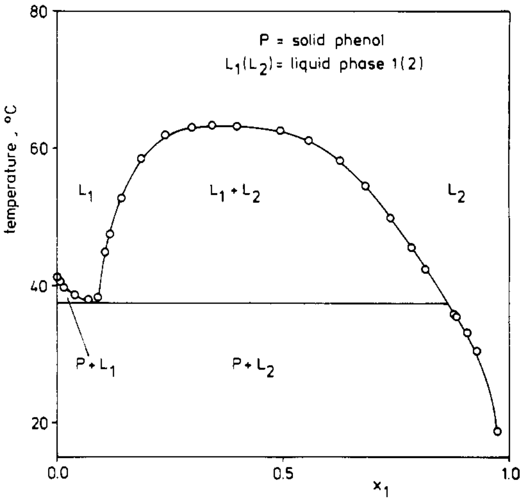

Figure 4. Phase equilibrium diagram for the system *n*-decane (1)-phenol (2).

results are represented by the continuous line. The calculated values were always generated by using the model which gave the lowest mean deviation between the experimental and calculated vapor-phase mole fractions. Furthermore, in all diagrams the calculated activity coefficients at infinite dilution are given for the chosen model.

The systems *n*-octane-phenol and *n*-decane-phenol show much stronger positive deviation from Raoult's law than the system benzene-phenol. For this reason phenol may be used as an extractive solvent for the separation of aliphatic hydrocarbons from aromatics. At the same time the strong positive deviation leads to an immiscibility gap for the systems aliphatic hydrocarbon-phenol at lower temperatures (*10*). Several liquid-liquid equilibria for the binary system aliphatic hydrocarbon-phenol have been published (*11*, *12*).

Because there are no data in the literature for the system *n*-decane-phenol, we have also investigated this system. The results are given in Table VI.

Figure 4 shows our experimental binodal curve for the binary system *n*-decane-phenol. The upper critical solution temperature is 63.35 ± 0.2 °C. The solubility of solid phenol in *n*-decane has been measured in the same way. The results are given in Table VII and also shown in Figure 4.

Table VII. Solubility of Solid Phenol (2) in *n*-Decane (1)

x_2[a]	temp, °C	x_2[a]	temp, °C
0.0272	18.78	0.9588	38.58
0.0685	30.45	0.98329	39.55
0.0910	33.13	0.98463	39.71
0.1187	35.41	0.99255	40.54
0.1231	35.80	1.0000	41.19
0.9291	37.84		

[a] Mole fraction.

Conclusion

Phase equilibria have been measured for aliphatic hydrocarbon-phenol systems. The experimental results were used to revise the old UNIFAC phenol parameters which gave poor results for this kind of system. The new phenol parameters can be found in ref *13*.

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Glossary

A_{12}, A_{21}	parameters used in the Margules, van Laar, Wilson, NRTL, and UNIQUAC equations
λ_{ij}	interaction parameter in the Wilson equation
g_{ij}	interaction parameter in the NRTL equation
u_{ij}	interaction parameter in the UNIQUAC equation
v_i	liquid molar volume of component i
q_i	relative van der Waals surface area of component i
r_i	relative van der Waals volume of component i
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase

Superscripts

∞	value at infinite dilution

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