Solubility and Equilibrium Data of Phenol–Water–*n*-Butyl Acetate System at 30° C.

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LIQUID-LIQUID extraction is a common method used in the recovery of tar-acids from the effluents of carbonization, coke oven, and other plants. Phenosolvan which is a mixture of butyl, propyl, amyl, and hexyl acetates, and boils in the range from 110° to 130° C. (*4*), is a solvent successfully used in industry. Certain other esters and ketones also show high partition coefficients for tar acids (*7*). To select the best solvent or solvent mixture and to assess the performance of liquid/liquid extractors, a detailed knowledge of the phase behavior of the ternary system of pure substances involved is necessary.

Therefore, it was decided to determine solubility and equilibrium data for systems involving different tar acids and solvents like butyl acetate, amyl acetate, methyl isobutyl ketone at a temperature at which extraction operations are normally conducted.

Normally, the solubility data of the ternary systems are determined first, followed by the determination of the equilibrium data, as the analysis of all the components involved is difficult (*1, 3, 13, 18, 19*).

MATERIALS

Phenol. Chemically pure phenol was distilled in a glass Quick-fit distillation apparatus. The fraction obtained at the boiling point corresponding to 181.7° C. at 760 mm. having a purity of 99.93% was used.

Water. Pure distilled water was used

***n*-Butyl Acetate.** Commercial *n*-butyl acetate was fractionated twice in Tower's fractionating column, and the fraction, within 2° C., of the boiling point corresponding to 124°–126° C., at 760 mm. was used. The following were analyses of the butyl acetate:

	For Purified Sample	Literature Value	Ref.
Ester content	98.25–98.56	...	...
Sp. gr., 30°/20° C.	0.8714	0.8725	(*9*)
Refractive index, 25° C.	1.3890	1.3948	(*8*)

EXPERIMENTAL PROCEDURE

Solubility Data. The solubility data were obtained by the turbidity end point method as described by Othmer, White, and Trueger (*11*). To standardize the experimental technique, the solubility data were determined at 44.4° C. and compared with the results of Schuberth and Leibnitz (*15*) in Figure 1. The results agreed fairly closely, confirming the validity of the technique and the purity of the substances used.

Having established the accuracy of the technique used, the solubility data at 30° C. were determined as follows: For the solvent rich phase, mixtures of phenol and butyl acetate of known weights were taken in 100 cc.-stoppered conical flasks and kept in a thermostat at 30° ± 0.1° C. for ½ hour, which was found to be sufficient. Distilled water at 30° C. was then added in the form of drops using a finely drawn capillary tube. The mean weight of each drop was 0.03 gram. Drop-wise addition of water was continued until a permanent turbidity appeared in the solution. By knowing the weight of water added and the composition of the phenol-butyl acetate mixture, the composition of the ternary saturated mixture at 30° C. was calculated. Data for the water-rich phase were obtained by similar titration of phenol-water solutions with butyl acetate at 30° C. The data in weight fractions are reported in Table I. The binodal curve is shown in Figure 2. The data represented in Figure 3 is the enlargement of the solubility curve in the water-rich phase.

The mutual solubilities at 30° C. between water and phenol, and water and butyl acetate were compared with the data available in literature (*8, 16*) and are shown in Table II. There is a good agreement between them.

Refractive indices for sodium D line of the ternary saturated mixtures at 30° C. were determined using an Abbe's refractometer. Plots were drawn connecting the refractive indices and the composition of ternary saturated mixtures. These were used later for finding the equilibrium data in the analyses of ternary saturated mixtures.

Equilibrium Data. The data were determined in an apparatus shown in Figure 4. In principle, it is similar to the one used by Smith and Bonner (*18*). It consists of a jacketed glass unit, 13 cm. long and 4 cm. wide with a variable speed stirrer. Water at 30° C. is circulated in the jacket from a thermostat by a pump, and the temperatures of the contents as well as the water circulated in the jacket were read from two thermometers.

The procedure adopted for the determination of equilibrium data was that mixtures of phenol, water, and butyl acetate were taken in such a way as to give approximately

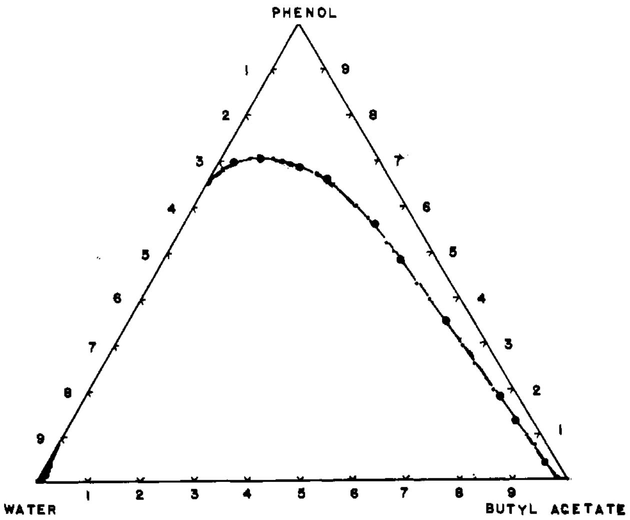

Figure 1. Binodal curve for the system at 44.4° C.

· Schuberth, others
● Experimental

Table I. Solubility Data for the System Phenol–Water–*n*-Butyl Acetate at 30° C.

(In weight fractions)

Phenol	Water	B.A.	R.I.
	Solvent-Rich Phase		
0.6939	0.3061	...	1.4779
0.7151	0.2637	0.0212	1.4840
0.7230	0.2361	0.0409	1.4875
0.7241	0.2209	0.0550	1.4880
0.7145	0.1732	0.1123	1.4890
0.7196	0.1674	0.1130	1.4892
0.6964	0.1369	0.1667	1.4877
0.6736	0.1245	0.2019	1.4865
0.6737	0.1207	0.2056	1.4860
0.6656	0.1098	0.2246	1.4855
0.6503	0.0929	0.2568	1.4835
0.6183	0.0829	0.2988	1.4799
0.5987	0.0780	0.3233	1.4779
0.5265	0.0564	0.4171	1.4665
0.5084	0.0506	0.4410	1.4627
0.4909	0.0513	0.4578	1.4612
0.3881	0.0399	0.5720	1.4457
0.3785	0.0364	0.5851	1.4450
0.3530	0.0351	0.6119	1.4409
0.3161	0.0317	0.6522	1.4355
0.2979	0.0352	0.6677	1.4325
0.1865	0.0256	0.7879	1.4165
0.1580	0.0212	0.8208	1.4124
0.1157	0.0197	0.8646	1.4064
0.0664	0.0140	0.9196	1.3990
...	0.0145	0.9855	1.3900
	Water-Rich Phase		
...	0.9971	0.0029	1.3329
0.0211	0.9759	0.0030	1.3362
0.0260	0.9717	0.0023	1.3375
0.0406	0.9581	0.0013	1.3400
0.0539	0.9454	0.0007	1.3425
0.0680	0.9316	0.0004	1.3451
0.0880	0.9120	...	1.3489

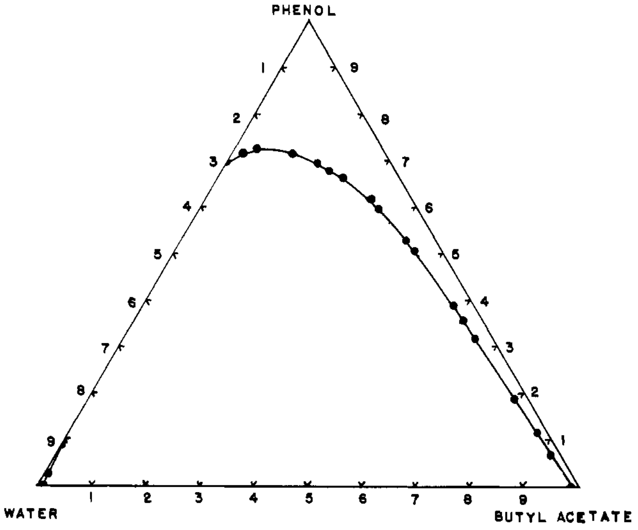

Figure 2. Binodal curve for the system at 30° C.

Table II. Mutual Solubilities as Weight Fractions at 30° C.

Systems	Obsd. Value	Literature Value	Ref.
Phenol in water	0.0880	0.0880	16
Water in Phenol	0.3061	0.3020	16
Butyl acetate in water	0.0029	...	...
Water in butyl acetate	0.0145	0.0255	8

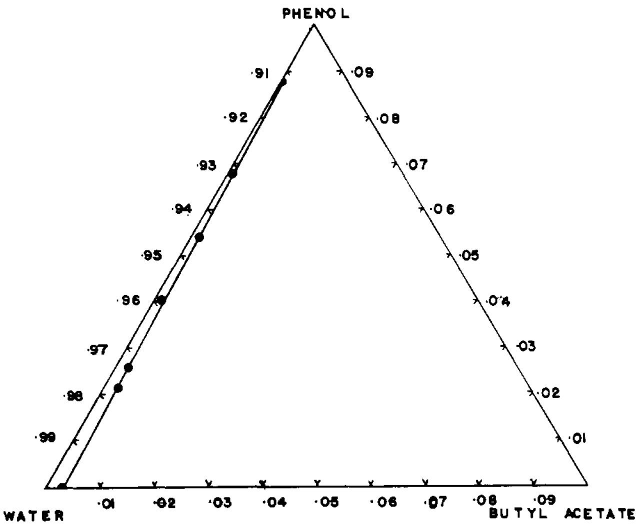

Figure 3. Binodal curve for the water rich phase (enlarged)

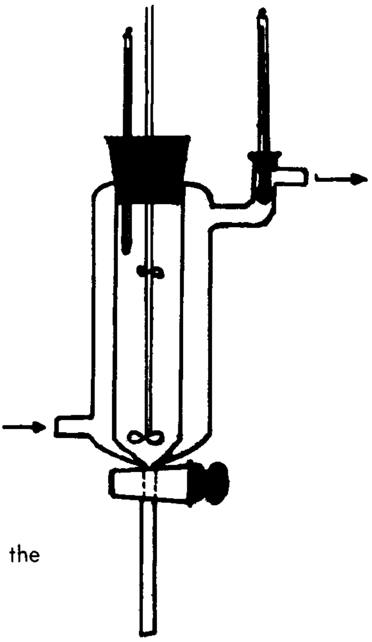

Figure 4. Apparatus used in the determination of the equilibrium data

Table III. Equilibrium Data for the System Phenol–Water–*n*-Butyl Acetate at 30° C.

(In weight fractions)

Extract Phase				Raffinate Phase			
Phenol	Water	B.A.	R.I.	Phenol	Water	B.A.	R.I.
...	0.0145	0.9855	1.3900	...	0.9971	0.0029	1.3329
0.0600	0.0150	0.9250	1.3985	0.0015	0.9955	0.0030	1.3331
0.1200	0.0175	0.8625	1.4070	0.0020	0.9950	0.0030	1.3332
0.1725	0.0275	0.8000	1.4149	0.0040	0.9930	0.0030	1.3335
0.2450	0.0300	0.7250	1.4249	0.0070	0.9900	0.0030	1.3340
0.3175	0.0375	0.6450	1.4355	0.0130	0.9840	0.0030	1.3350
0.3900	0.0400	0.5700	1.4459	0.0185	0.9785	0.0030	1.3360
0.4400	0.0425	0.5175	1.4532	0.0245	0.9730	0.0025	1.3370
0.5125	0.0500	0.4375	1.4639	0.0325	0.9655	0.0020	1.3385
0.5925	0.0700	0.3375	1.4758	0.0450	0.9530	0.0020	1.3410
0.6505	0.1020	0.2475	1.4840	0.0570	0.9415	0.0015	1.3431
0.7050	0.1300	0.1650	1.4879	0.0670	0.9320	0.0010	1.3450
0.7250	0.2150	0.0600	1.4885	0.0725	0.9265	0.0010	1.3460
0.7120	0.2680	0.0200	1.4835	0.0775	0.9215	0.0060	1.3470
0.6939	0.3061	...	1.4779	0.0880	0.9120	...	1.3489

equal volumes of each layer. These mixtures were kept stirred for one hour. The speed of the stirrer was controlled to give proper mixing without emulsion formation. After about an hour of mixing, the contents were allowed to settle, and the refractive index of the top layer was determined at 30° C. This was repeated at subsequent ½-hour intervals until two successive readings were constant, which indicated the attainment of equilibrium. At this stage the bottom layer was sampled, and refractive index determined. From the refractive indices of the two layers, the corresponding compositions were obtained using the plot previously drawn relating the refractive index and composition at 30° C. Samples of each layer were also analyzed for phenol content by the Koppeschar's method (*14*) and the results agreed closely with the values obtained by the refractive index method. The equilibrium data are given in Table III and the tie lines in Figure 5.

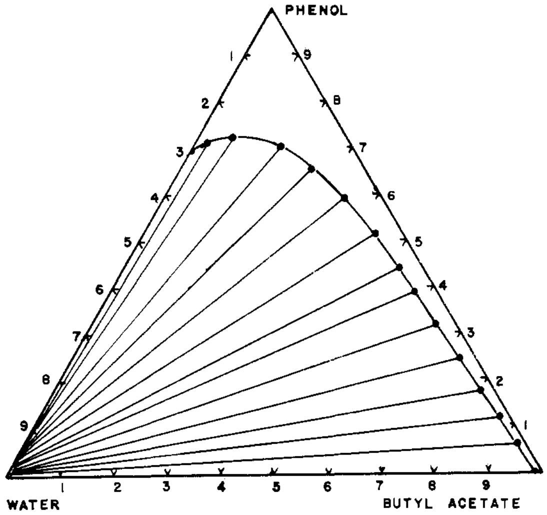

Figure 5. Tie lines for the system

OBSERVATIONS

This is a three component system in which two pairs are partially miscible. By drawing a tangent from the solvent point to the binodal curve in the Figure 2, the maximum concentration to which a dilute phenol solution can be enriched by extraction operation at 30° C, is over 91% by weight compared to 88.5% at 44.4° C. (Figure 1.).

During the determination of the equilibrium data, the extract phase for phenol concentrations below 59.25% by weight was lighter than the raffinate phase; whereas, for concentrations above 65.05% the extract phase was heavier. For phenol concentration between 59.25 and 65.05%, the densities of the two phases are very close. A similar observation was also made at 44.4° C. (*15*).

CORRELATIONS

Various methods of correlations were tried on the data to check the consistency and to find methods for the interpolation of the data.

The International Critical Tables method (*6*) and the Sherwood method (*17*) were not found useful for the system as the points on the water-rich phase are very close (Figure 2). Othmer and Tobias (*10*) have correlated most of the data by the equation

$$\text{Log}\,\frac{1-X}{X} = C_1 \log \frac{1-Y}{Y} + C_2 \qquad (1)$$

The present data could not be correlated by this method and a linear relationship did not result. However, when the correlation suggested by Bachman (*2*)

$$X = C_3\,(X/Y) + C_4 \qquad (2)$$

was used, it has resulted in a straight line (Figure 6). Though doubt has been expressed about the general application of this linear relationship for all systems, it can conveniently be used for the interpolation of the data of the present system.

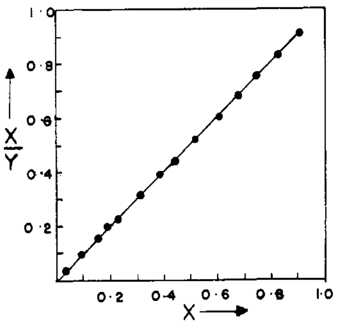

Figure 6. Bachman's correlation for the system

A similar rectilinear relationship was observed by Dryden (5) who gave the relationship

$$M/N = C_5\,M + C_6 \qquad (3)$$

However, when the present data was analyzed according to the Dryden's method, the linear relationship was not obtained. But when the solute concentration was expressed on a water-free instead of a butyl acetate–free basis, a linear relationship was obtained (Figure 7), which can be represented as

$$P/Q = C_7\,P + C_8 \qquad (4)$$

In all normal cases, a plot of M vs. N would give a smooth curve which can be used for theoretical stage calculations (*20*). However, in the present system P vs. Q results in a smooth curve as shown in Figure 8, which can be used for theoretical stage calculations. Schuberth and Leibnitz (*15*) have also observed that when their data was plotted on a water-free basis, a curve similar to Figure 8 resulted. This might be observed for other systems in which two pairs are partially miscible.

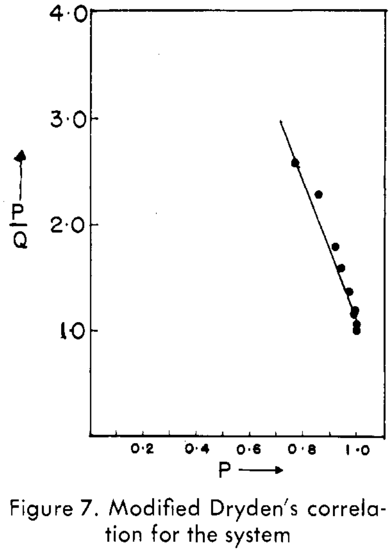

Figure 7. Modified Dryden's correlation for the system

CONCLUSION

General methods of correlation are not useful to the present system; however, methods like Bachman's and modified Dryden's apply better than normal correlations do.

ACKNOWLEDGMENT

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NOMENCLATURE

X = mole fraction of solvent (butyl acetate) in extract phase
Y = mole fraction of residue (water) in raffinate phase
M = mole fraction of solute (phenol) in raffinate phase on solvent-free basis
N = mole fraction of solute (phenol) in extract phase on solvent-free basis
P = mole fraction of solute (phenol) in raffinate on water-free basis
Q = mole fraction of solute (phenol) in extract on water-free basis
C_1 to C_8 = constants

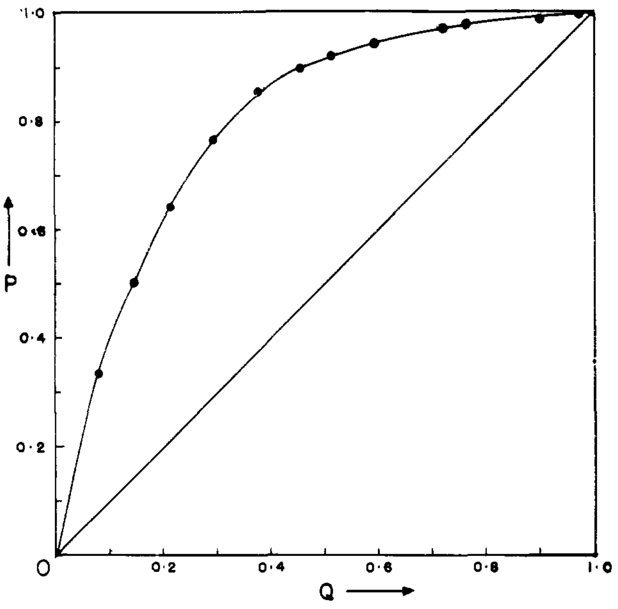

Figure 8. Equilibrium relationship on a water-free basis for the system

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