NOMENCLATURE

a = thermodynamic activity
K = equilibrium constant
N = mole fraction
Q = independently measured variable
p = pressure, atm.
q_i = ith measured independent variable
R = probable error in Q
r_i = probable error in q_i measurement
T = temperature, Kelvin
w = weight factor
ΔG° = Gibbs free energy change, cal./gram mole
θ = Bragg diffraction angle
ϕ = complement of Bragg diffraction angle

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RECEIVED for review March 1, 1962. Accepted July 5, 1962. Work supported with assistance of a Michigan Memorial Phoenix Project Grant. Based in part on a thesis by J.R. Piazza, submitted to the Horace H. Rakham School of Graduate Studies of the University of Michigan for part of the Ph. D. degree in metallurgical engineering.

Solubility and Equilibrium Data of Phenol–Water–Isoamyl Acetate and Phenol–Water–Methyl Isobutyl Ketone Systems at 30° C.

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SOLUBILITY and equilibrium data for the system phenol-water-*n*-butyl acetate (system 1) at 30° C. were reported in a previous communication (*4*). The present article deals with the systems phenol-water-isoamyl acetate and phenol-water-methyl isobutyl ketone at 30° C. As in the previous system, the solubility data of the ternary systems were determined first, followed by the determination of the equilibrium data.

MATERIALS

Phenol. 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.

Isoamyl Acetate. Isoamyl acetate was fractionated twice in Tower's fractionating column and the fraction within 2° C, of the boiling point corresponding to 140.1 - 42.1° C. at 760 mm. was used.

Methyl Isobutyl Ketone (MIBK). Commercial methyl isobutyl ketone was similarly fractionated and the fraction corresponding to 113.9 - 15.5° C. at 760 mm. was used.

Solvents Used

	Purified Sample	Lit. Value	Ref.
Isoamyl acetate			
Ester content, %	100	...	...
Specific gravity, 24/4° C.	0.8670	0.8664	(*3*)
Refractive index, 20° C.	1.4005	1.4005	(*3*)
Methyl isobutyl ketone			
Ketone content, %	99.1-99.5	...	...
Specific gravity, 20/20° C.	0.7973	0.8042	(*3*)
Refractive index, 20° C.	1.3960	1.3958	(*3*)

EXPERIMENTAL PROCEDURE

Solubility data were obtained by the turbidity end point method as described by Othmer, White, and Trueger (*6*). The experimental details were similar to those of the earlier system (*4*). Tables I and II give the solubility data in weight fractions for systems phenol-water-isoamyl acetate (system 2) and phenol-water-methyl isobutyl ketone (system 3), respectively. Mutual solubilities of

Table I. Solubility Data for the System Phenol–Water–Isoamyl Acetate at 30° C. (Weight fractions)

Phenol	Water	Isoamyl Acetate	R.I.
	Solvent-Rich Phase		
. . .	0.0058	0.9942	1.3960
0.1248	0.0136	0.8616	1.4425
0.1969	0.0232	0.7799	1.4225
0.2622	0.0234	0.7144	1.4320
0.3265	0.0308	0.6427	1.4399
0.4311	0.0413	0.5276	1.4550
0.4649	0.0497	0.4854	1.4600
0.4968	0.0564	0.4468	1.4640
0.5325	0.0637	0.4038	1.4690
0.5702	0.0713	0.3585	1.4745
0.5772	0.0812	0.3416	1.4755
0.6469	0.1062	0.2469	1.4829
0.7025	0.1479	0.1496	1.4882
0.7221	0.2095	0.0684	1.4862
0.6960	0.3040	. . .	1.4779
	Water-Rich Phase		
. . .	0.9978	0.0022	1.3325
0.0112	0.9874	0.0014	1.3340
0.0217	0.9773	0.0010	1.3360
0.0271	0.9720	0.0009	1.3372
0.0423	0.9573	0.0004	1.3405
0.0608	0.9389	0.0003	1.3442
0.0880	0.9120	. . .	1.3489

Table II. Solubility Data for the System Phenol–Water–Methyl Isobutyl Ketone (MIBK) at 30° C. (Weight fractions)

Phenol	Water	MIBK	R.I.
	Solvent-Rich Phase		
. . .	0.0146	0.9854	1.3912
0.2849	0.0424	0.6727	1.4315
0.3318	0.0486	0.6196	1.4381
0.3538	0.0493	0.5969	1.4415
0.4059	0.0506	0.5435	1.4490
0.4460	0.0563	0.4977	1.4550
0.5050	0.0670	0.4280	1.4630
0.5610	0.0742	0.3648	1.4710
0.5898	0.0800	0.3302	1.4748
0.6383	0.0952	0.2665	1.4825
0.6816	0.1183	0.2001	1.4865
0.7000	0.1399	0.1601	1.4880
0.7386	0.1789	0.0825	1.4918
0.7256	0.2459	0.0285	1.4862
0.6935	0.3065	. . .	1.4779
	Water-Rich Phase		
. . .	0.9913	0.0087	1.3335
0.0123	0.9814	0.0063	1.3352
0.0206	0.9753	0.0041	1.3370
0.0290	0.9681	0.0029	1.3385
0.0374	0.9608	0.0018	1.3400
0.0526	0.9465	0.0009	1.3430
0.0856	0.9144	. . .	1.3490

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

	Soly.,		
	Observed	Lit. value	Ref.
Isoamyl acetate in water	0.0022	0.0020	(*8*)
Water in isoamyl acetate	0.0058	0.0040	(*8*)
Methyl isobutyl ketone in water	0.0087	0.0166	(*2*)
Water in methyl isobutyl ketone	0.0146	. . .	. . .

water and isoamyl acetate, and water and MIBK, with the literature values are compared in Table III. Mutual solubilities between water and isoamyl acetate show close agreement between the observed and literature values; but the solubility of MIBK in water appears to be lower than the reported values (*2*). Tables I and II also give the refractive indices (for the sodium D line) for the ternary saturated mixtures. These were used later for finding the equilibrium data in the analysis of ternary saturated mixtures.

EQUILIBRIUM DATA

The data were determined by the method reported earlier (*4*). The phenol-water-solvent mixtures were well stirred in the apparatus at 30° C. and allowed to settle. The refractive indices of two phases which were in equilibrium with each other were determined. The compositions of the ternary mixtures were obtained with the help of the plots drawn previously connecting refractive index and the composition of ternary saturated mixtures at 30° C. Samples of each layer in equilibrium were also analyzed for phenol concentration by Koppeschar's method (*7*) as a check on the refractive index method. The equilibrium data (in weight fractions) for the two systems are reported in Tables IV and V and are represented in Figures 1 and 2.

OBSERVATIONS

The phase behavior of these two systems is similar to that of the phenol-water-butyl acetate system, in which two pairs are partially miscible. Binodal curves for all three systems are compared in Figures 3 (solvent-rich

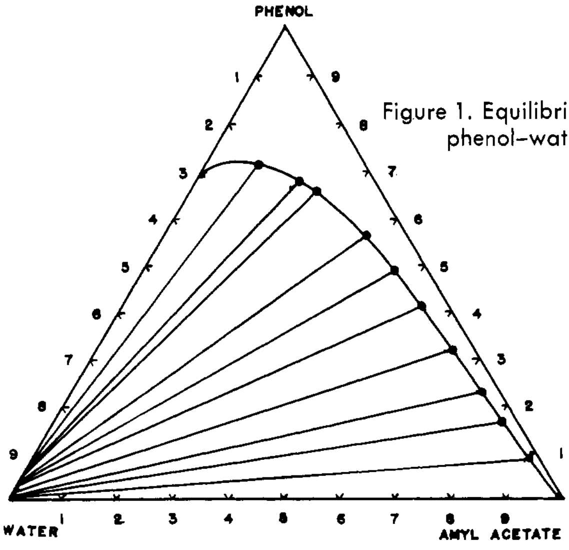

Figure 1. Equilibrium data for the system phenol-water-amyl acetate

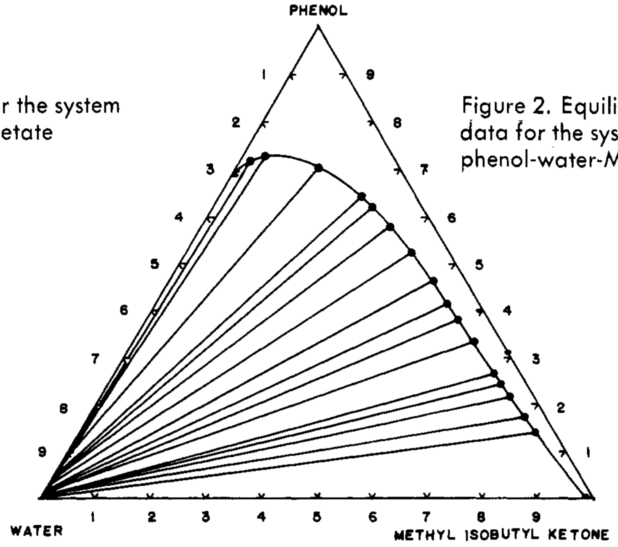

Figure 2. Equilibrium data for the system phenol-water-MIBK

Table IV. Equilibrium Data for the System Phenol–Water–Isoamyl Acetate at 30° C. (Weight fractions)

Phenol	Water	Isoamyl Acetate	R.I.
	Extract Phase		
...	0.0058	0.9942	1.3960
0.0875	0.0125	0.9000	1.4080
0.1675	0.0225	0.8100	1.4190
0.2300	0.0275	0.7425	1.4275
0.3200	0.0375	0.6425	1.4395
0.4150	0.0450	0.5400	1.4525
0.4900	0.0550	0.4550	1.4625
0.5650	0.0700	0.3650	1.4728
0.6600	0.1100	0.2300	1.4845
0.6800	0.1325	0.1875	1.4865
0.7175	0.1875	0.0950	1.4872
0.6960	0.3040	...	1.4779
	Raffinate Phase		
...	0.9978	0.0022	1.3325
0.0025	0.9955	0.0020	1.3328
0.0050	0.9932	0.0018	1.3331
0.0085	0.9899	0.0016	1.3335
0.0165	0.9822	0.0013	1.3350
0.0252	0.9739	0.0009	1.3368
0.0308	0.9684	0.0008	1.3380
0.0425	0.9570	0.0005	1.3405
0.0570	0.9426	0.0004	1.3435
0.0595	0.9402	0.0003	1.3440
0.0685	0.9313	0.0002	1.3455
0.0880	0.9120	...	1.3489

phase) and 4 (water rich phase). A tangent drawn from the solvent point to the binodal curve, shows that the maximum concentration to which dilute phenol solution can be enriched using amyl acetate as solvent is over 91%; using MIBK, it is 89% at 30° C. (Table VI).

During determination of the equilibrium data for the system phenol–water–butyl acetate, it was observed for phenol concentration between 59.25 and 65.05% in the extract phase that the densities of the two phases were very near to each other. A similar observation was made in the present data. The densities of the two phases were found to be almost equal in the range 56.5 to 66.0% for the system phenol–water–isoamyl acetate and 64.5 to 70.8% for the system phenol-water-MIBK.

Table V. Equilibrium Data for the System Phenol-Water-Methyl Isobutyl Ketone (MIBK) at 30° C. (Weight fractions)

Phenol	Water	MIBK	R.I.
	Extract Phase		
...	0.0146	0.9854	1.3912
0.1400	0.0350	0.8250	1.4115
0.1725	0.0390	0.7885	1.4165
0.2150	0.0420	0.7430	1.4222
0.2425	0.0430	0.7145	1.4260
0.2650	0.0440	0.6910	1.4290
0.3325	0.0480	0.6195	1.4388
0.3800	0.0520	0.5680	1.4456
0.4150	0.0540	0.5310	1.4505
0.4675	0.0590	0.4735	1.4580
0.5250	0.0660	0.4090	1.4659
0.5800	0.0770	0.3430	1.4735
0.6225	0.0890	0.2885	1.4790
0.6450	0.0980	0.2570	1.4822
0.7075	0.1410	0.1515	1.4889
0.7300	0.2320	0.0380	1.4885
0.7175	0.2620	0.0165	1.4839
0.6936	0.3065	...	1.4779
	Raffinate Phase		
...	0.9913	0.0087	1.3335
0.0035	0.9880	0.0085	1.3339
0.0045	0.9875	0.0080	1.3340
0.0052	0.9870	0.0078	1.3341
0.0060	0.9865	0.0075	1.3342
0.0067	0.9860	0.0073	1.3343
0.0080	0.9845	0.0075	1.3345
0.0112	0.9825	0.0063	1.3350
0.0140	0.9802	0.0058	1.3355
0.0187	0.9767	0.0046	1.3365
0.0237	0.9725	0.0038	1.3375
0.0315	0.9655	0.0030	1.3390
0.0370	0.9610	0.0020	1.3400
0.0422	0.9560	0.0018	1.3410
0.0555	0.9440	0.0005	1.3435
0.0690	0.9307	0.0003	1.3460
0.0790	0.9209	0.0001	1.3475
0.0856	0.9144	...	1.3490

Table VI. Comparison of Three Solvents

Solvent	B.P., ° C.	Soly., Wt. % in water	Soly., Wt. % of water in,	Enrichment of Phenol Concn., Wt. %
Methyl isobutyl ketone	115.9	0.87	1.46	89.0
n-Butyl acetate	126.0	0.29	1.45	91.0
Isoamyl acetate	142.1	0.22	0.58	91.5

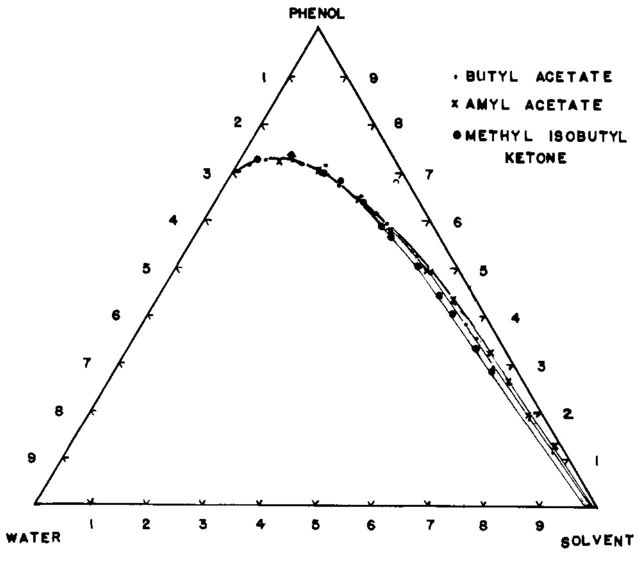

Figure 3. Binodal curves for the systems in solvent rich phase

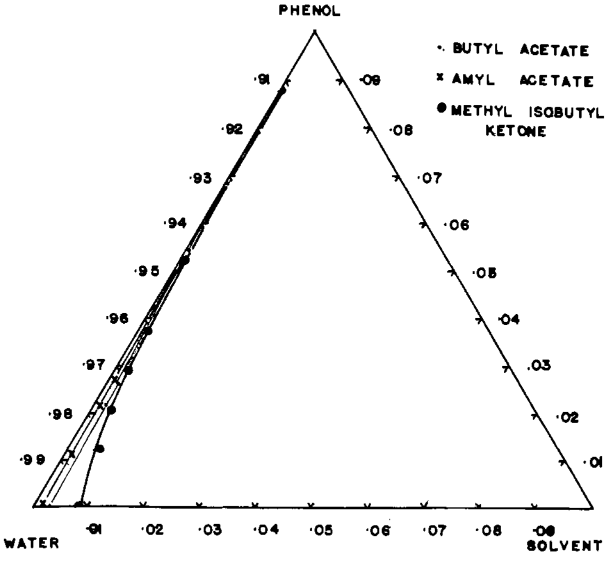

Figure 4. Binodal curves for the systems in water rich phase

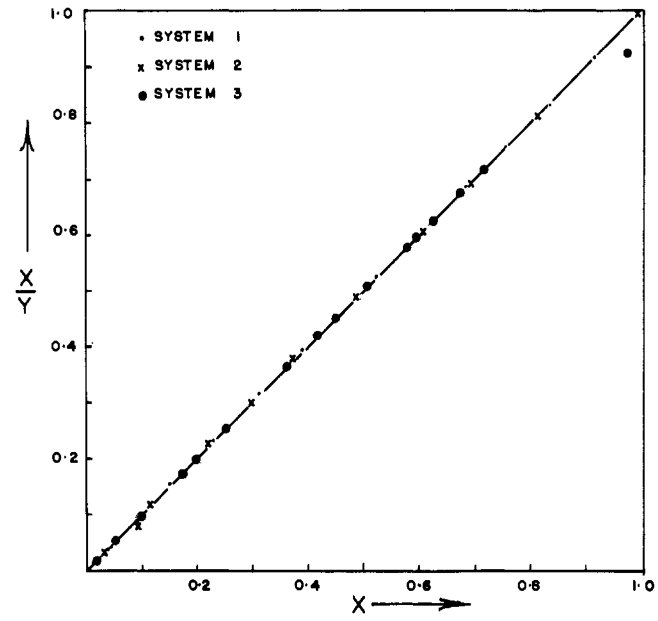

Figure 5. Bachman's correlation for the systems

CORRELATION

The present data were analyzed by a number of methods to check their consistency and to ascertain the methods for their interpolation. The correlation suggested by Othmer and Tobias (*5*)

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

did not yield a straight line for the present data. but correlation suggested by Bachman (*1*) did.

$$X = C_3\frac{X}{Y} + C_4 \qquad (2)$$

Figure 5 gives Bachman's correlation for all three systems. The data for all the three systems could be represented by a single straight line.

The modified Dryden's relation

$$\frac{P}{Q} = C_5 P + C_6 \qquad (3)$$

which was successfully used to correlate the data for the system phenol-water-butyl acetate was applied to the present system (Figure 6). Each system has yielded a separate straight line.

Figure 7 represents a plot of P *vs.* Q for the three systems, which is useful for the interpolation of data and theoretical stage calculations.

CONCLUSIONS

n-Butyl acetate and isoamyl acetate give slightly better enrichment for phenol than MIBK, and are less soluble in water.

Bachman's method as well as the modified Dryden's method appear to be useful for interpolation of the data for systems studied.

ACKNOWLEDGMENT

The authors express their sincere thanks to S. Husain Zaheer, Director, Regional Research Laboratory, for his keen interest in the work.

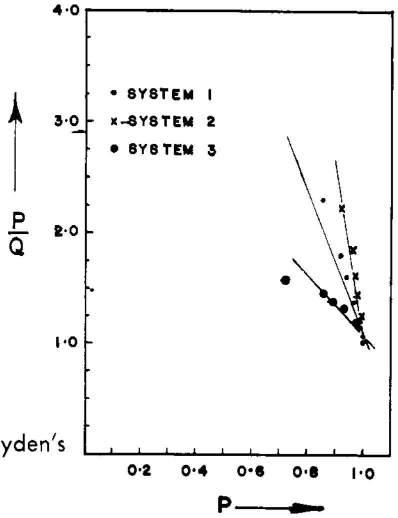

Figure 6. Modified Dryden's correlation

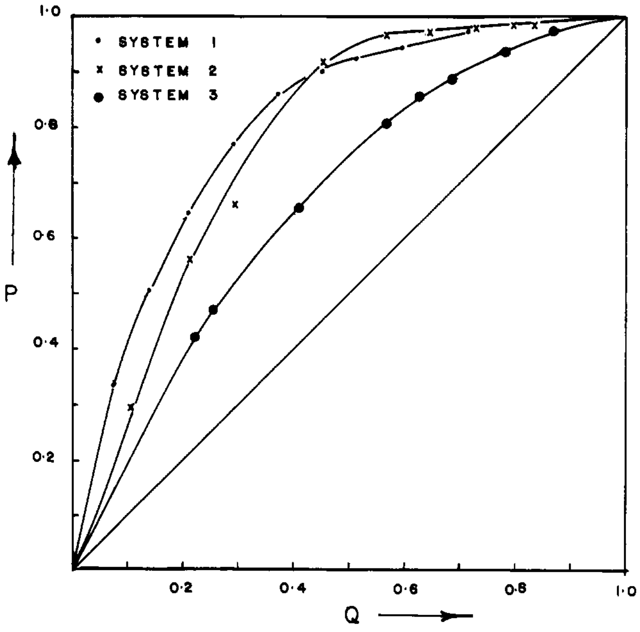

Figure 7. Equilibrium relationships for the three systems on water-free basis

NOMENCLATURE

X = mole fraction of solvent (isoamyl acetate or MIBK) in the extract phase
Y = mole fraction of residue (water) in the raffinate phase
P = mole fraction of solute (phenol) in the raffinate on water free basis
Q = mole fraction of solute (phenol) in the extract on water free basis
C_1 to C_6 = constants

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Received for review April 19, 1962. Accepted June 25, 1962.