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Concentrations, Total and Partial Vapor Pressures, Surface Tensions and Viscosities, in the Systems Phenol–Water and Phenol–Water–4% Succinic Acid

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The *T–x* diagram of the system phenol–water has been studied by several investigators.[1] The most complete investigation is that of Rhodes and Markley.[2] These authors show that the stable system involves a compound, $2C_6H_5OH \cdot H_2O$. Using ordinary refrigerants, this compound can only be caused to appear by inoculation with the compound itself, which previously has been prepared by treatment with solid carbon dioxide and alcohol. As in many cases, the normal system is here the partially metastable one, in which the compound does not appear. The partially metastable diagram is shown in Fig. 1, curve ABCDEFG. It is this system that we have investigated and we have used our own data in its construction.

The vapor pressures of certain phenol–water mixtures have been determined by Schükarew and by van der Lee.[3] The *p–x* diagram is shown in Fig. 2 (curve ABCDE); our own figures are used.

We have determined the above diagrams, as well as the compositions of the vapors given off by liquid mixtures in equilibrium with ice, solid phenol, and a second liquid layer, respectively. The latter information is of interest in the light of the theory of solutions. It is pointed out by Hildebrand[4] that a partially miscible liquid pair cannot obey Raoult's law. The partial pressures of phenol observed and calculated by Raoult's law show that in dilute solutions, the fugacity of phenol is much greater than that calculated. This led us to suppose that the solute phenol is driven to the free surface by the solvent and concentrated in the outer layer. Our experiments on surface tension induce us to believe that after addition of 7–10% phenol, this outer layer has a constant composition, while our viscosity measurements indicate that even after the establishment of this layer, further additions of phenol are not distrib-

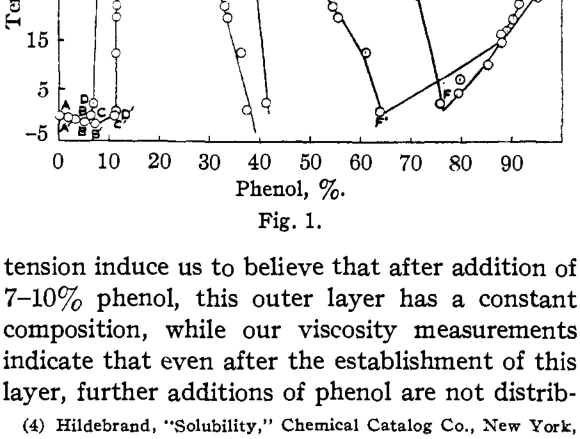

Fig. 1.

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[1] Rothmund, *Z. physik. Chem.*, **26**, 443 (1898); Timmermans, *ibid.*, **58**, 184 (1907); *J. chim. phys.*, **20**, 491 (1923); Hill and Malisoff, THIS JOURNAL, **48**, 918 (1926).

[2] Rhodes and Markley, *J. Phys. Chem.*, **25**, 530 (1921).

[3] Schükarew, *Z. physik. Chem.*, **71**, 90 (1910); van der Lee, *ibid.*, **33**, 622 (1900).

[4] Hildebrand, "Solubility," Chemical Catalog Co., New York, 1924, p. 35.

uted uniformly throughout the body of the solution, but are also, to some extent, distributed with decreasing concentration from the surface inward. The kinetic theory teaches that the vapor pressure is not solely conditioned by the composition of the outer layer but will also be affected by the nature of the layers several molecules deep, since a molecule with high kinetic energy can plunge through these layers and enter the gas phase. The vapor pressure would, however, be independent of the composition beyond this critical depth. Hence, the effective mole fraction of solute increases until these outer layers are established (saturated), further addition being without effect. Hence, the observed partial pressure is at first much too great, increases with addition of phenol but not in proportion to the concentration and finally ceases to increase, while the partial pressure calculated on the total concentration of the solution increases all the time. Hence, the observed increase in $p_{\text{calcd.}}/p_{\text{obsd.}}$ with increasing concentration.

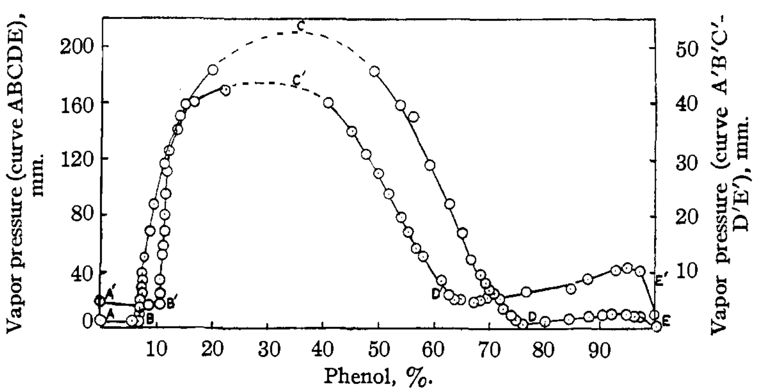

Fig. 2.

Since the outer layer is impoverished with respect to water, one would expect the ratio $p_{\text{calcd.}}/p_{\text{obsd.}}$ for water to be greater than unity and this is the case. That the ratio is not much greater than unity is understandable, when it is remembered that the vapor pressure is not conditioned solely by the outer layer but also by underlying layers, which at first will be almost pure water. It is obvious, from a scrutiny of the subsequent behavior of the ratio $p_{\text{calcd.}}/p_{\text{obsd.}}$, that this view cannot represent the whole truth. It will be necessary to take into account the physical factors mentioned by Hildebrand,[4] the existence in solution of hydrate molecules, and, perhaps, the phases present. If this view is correct, then by the Gibbs–Thomson law, the surface tension of water must be reduced, presumably greatly reduced, by addition of phenol. We, therefore, determined the surface tension of homogeneous phenol solutions relative to that of pure water. The results are shown in Fig. 3.

The surface tension drops rapidly with addition of phenol to a value 0.55 that of water, at a concentration of 7% phenol. After this the relative surface tension remains practically constant to 100% phenol. It seems that the outer layer, which determines the surface tension, consists of almost pure phenol, and this layer of constant composition is established with the first small additions of phenol.

If the above view is correct, it should receive confirmation from an investigation of relative viscosity which we undertook. Since, in viscous flow, the outer layers are motionless, the viscosity should be little affected by the first additions of phenol. The curve is shown in Fig. 4 (curve ABC). The viscosity is not independent of small additions of phenol. It increases steadily to about 1.7 times that of water at 70% phenol. At this concentration there is a strongly marked break in the curve, and the viscosity increases rapidly to the high value of pure phenol. We interpret this to mean that the phenol is accumulated in successive layers from the free surface inward. Only when the rapidly moving central layers are approached, does the true effect on the viscosity show up. In this connection the viscosity determinations of Kremann, Griengl and Schreiner[5] are of interest, although their measure-

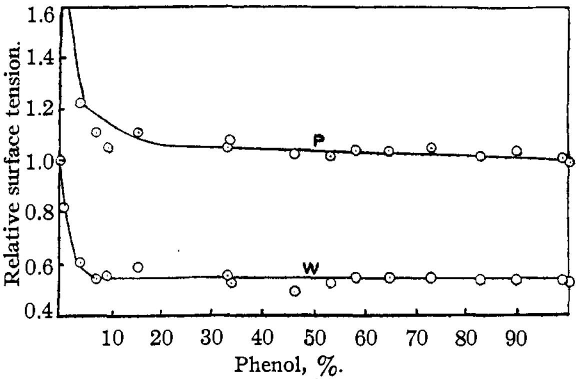

Fig. 3.— Surface tensions: curve P, relative to phenol; curve W, relative to water.

[5] Kremann, Griengl and Schreiner, *Monatsh.*, **62**, 28–46 (1933).

ments refer chiefly to heterogeneous mixtures of phenol and water.

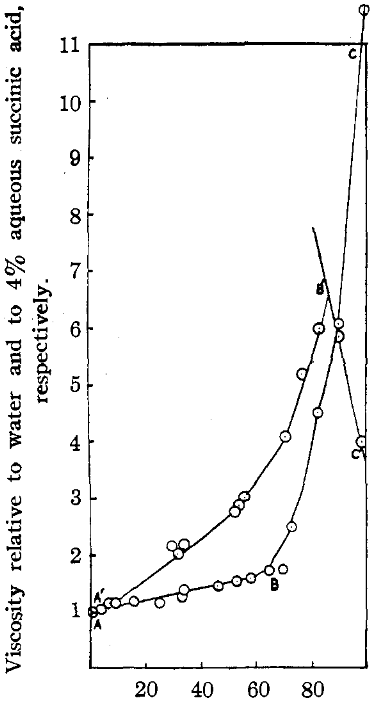

Fig. 4.

The deviation from Raoult's law becomes less with increasing phenol concentration and at a concentration of about 66–67% phenol the observed partial pressure is the same as that calculated. Further addition of phenol causes the ratio $p_{\text{calcd.}}/p_{\text{obsd.}}$ to decrease again and then to vary in a somewhat irregular manner, which may, perhaps, be connected with the presence in solution of molecules of the compound $2C_6H_5OH \cdot H_2O$.

For the system phenol–water–4% succinic acid, we have duplicated all the measurements made on the system phenol–water, using a fixed succinic acid concentration of 4% referred to total weight of mixture. It was known that, corresponding to the fact that succinic acid is soluble both in water and in phenol, the critical solution temperature is lowered, but further details were lacking. The *T–x* and *p–x* diagrams are shown in Fig. 1, curve A'B'C'D'E'F'G', and Fig. 2, curve A'B'C'D'E', respectively.

The vapor phases were also analyzed, and the partial pressures of phenol and of water calculated and compared with the observed values as before. As the effect of the succinic acid is to increase the mutual miscibility, one would expect the increase in fugacity to be less, and, therefore, the deviation from Raoult's law less. This, however, does not seem to be the case. On the contrary, while for the system phenol–water the ratio $p_{\text{calcd.}}/p_{\text{obsd.}}$ does approximately equal unity for a short range of the two-liquid curve, the maximum value for the ratio on the two-liquid curve for the system phenol–water–4% succinic acid is 0.575, after which it falls again. It is noticeable that for both systems, the deviation of water from Raoult's law is much less than that of phenol.

The relative surface tension shows practically the same behavior as before (Fig. 5). The viscosity, however, behaves differently (*cf.* Fig. 4, curve A'B'C'). It increases uniformly up to 85% phenol and then rapidly falls off. This fall is almost certainly due to the fact that while 4% succinic acid can be dissolved in hot concentrated phenol solutions, on cooling, a crystalline precipitate separates. This may merely be unchanged succinic acid, but from the behavior of the refractive indices of concentrated solutions of phenol containing succinic acid, which increase with time, we are inclined to think it a compound of phenol and succinic acid, *e. g.*, phenylsuccinic acid.[6] If so, phenol would be removed from solution and the water content increased, accounting for the decreased viscosity. If succinic acid in phenol exists partly as a compound, the observed effects are not entirely due to succinic acid, although, in the more dilute solutions, judging from the titration values of the two layers, we think the succinic acid is largely free.

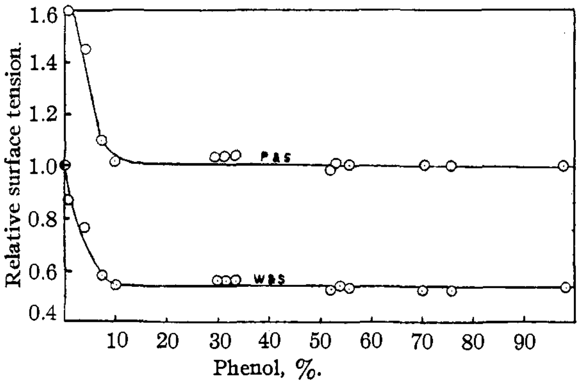

Fig. 5.—Surface tension: curve P & S, relative to phenol and 4% succinic acid; curve W & S, relative to water and 4% succinic acid.

Experimental

The phenol used was distilled; it then had a freezing point of 41.25°. Where solutions were

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[6] According to Kremann, Zechner and Drazil [*Monatsh.*, **45**, 357 (1924)] succinic acid and phenol do not form an addition compound.

TABLE I

REFRACTIVE INDICES OF AQUEOUS SOLUTION OF PHENOL

n_c

Concentration, % phenol	7°	22.5°	25.0°	30°	35°	45°	55°	60°	65°	70°
0.905	1.3336	1.3328	1.3326	1.33215	1.3321	1.3311	1.3288	1.3288	1.3274	1.3262
3.85	1.3396	1.3389	1.3387	1.3387	1.3376	1.3376	1.3350	1.3339	1.3328	1.3321
6.95		1.3466	1.3461	1.3456	1.3456	1.3447	1.3417	1.3405	1.3400	1.3389
9.65						1.3510	1.3465	1.3465	1.3464	1.3402
14.68								1.3580	1.3570	1.3570
24.1									1.3725	1.3640
32.5										1.3890
42.30										1.4114
49.65										1.4225
51.5									1.4265	1.4265
56.0							1.4370	1.4365	1.4355	1.4345
63.5						1.4545	1.4540	1.4506	1.4493	1.4486
68.5					1.4713	1.4679	1.4648	1.4616	1.4612	1.4601
75.2	1.4895	1.4843	1.4829	1.4814	1.4814	1.4815	1.4774	1.4708	1.4695	1.4689
82.0	1.5090	1.5051	1.5038	1.5024	1.5014	1.4977	1.4955	1.4921	1.4910	1.4895
90.0		1.5235	1.5225	1.5212	1.5197	1.5149	1.5149	1.5091	1.5084	1.5062
97.5						1.5323	1.5313	1.5277	1.5245	1.5223

prepared, the concentration was checked by titration by the method of Redman, Weith and Brock.[7]

System: Phenol–Water.—The method of Alexejeff[8] for determining the composition of liquid layers in equilibrium is not very suitable when small changes in concentration produce relatively large changes in temperature of homogeneity. Hill and Malisoff apparently recognized this when they determined the compositions of layers in equilibrium by a volumetric method, for the temperatures 20, 25, 30 and 35°. For higher temperatures, their determinations were made by the method of Alexejeff. We therefore determined the composition of the two layers refractometrically up to a temperature of 60°; from this point the Alexejeff method is preferable. For this purpose the refractive indices of various solutions of phenol in water at different temperatures were required. They are determined with respect to the H_α line (λ = 6563 Å.). These results are contained in Table I.

The curve AB of Fig. 1, along which ice is the stable solid phase, has been determined by Peddle and Turner.[9] We redetermined this, using the ordinary Beckmann freezing point technique. The short curve BD, along which solid phenol is in equilibrium with weak solutions of phenol, is determined by the points B and C. B is the eutectic, ice–phenol; C represents a temperature of 0°, and the corresponding concentration is obtained by placing any solution of phenol, of concentration greater than 7% in a melting ice-bath and determining the concentration of the filtered liquid. B is joined to C and extrapolated to intersect the curve DEF. The point D was also determined directly, as the temperature at which solid phenol disappeared.

Curve FG, along which solid phenol is in equilibrium with concentrated solutions of phenol, was obtained by observing the effect of small additions of water on the freezing point of phenol, and partly by direct determination of the solubility of phenol in water. Our complete data for the *T–x* diagram are contained in Table II.

Comparing our figures for 20, 25, 30 and 35°, with those of Hill and Malisoff, our figures are seen to be in good agreement on the phenol-rich side of the diagram, while on the aqueous side, our figures are lower than theirs by as much as 1%. No doubt, the figures of Hill and Malisoff are more reliable than ours, since the refractometric method is necessarily somewhat coarse (the refractive index of phenol is not greatly different from that of water), but the agreement all around is fair.

Most of the vapor pressure measurements were made by direct manometric observation, using a closed pumped-out system. A few of the lower vapor pressures were determined by the air bubbling method. The composition of the vapor was obtained by slowly bubbling air through the mixture, absorbing in potassium hydroxide and sulfuric acid traps, weighing and ti-

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[7] Thorpe and Whiteley, "Student's Manual of Organic Chemical Analysis," Longmans, Green and Co., New York, 1925, p. 161.

[8] Alexejeff, *Ann. Physik*, **28**, 305 (1886).

[9] Peddle and Turner, *J. Chem. Soc.*, **99**, 691 (1911).

TABLE II

TEMPERATURE–CONCENTRATION DATA

Temp., °C.	Phases present	Concentration of phenol %		
		Weak layer	Concd. layer	Mean
0.00	Ice, vapor, and water	..	..	..
− .3	Ice, vapor, solution	0.9	..	..
− .4	Ice, vapor, solution	1.8	..	..
− .7	Ice, vapor, solution	3.3	..	..
− 1.0	Ice, vapor, solution	4.0	..	..
− 1.2	Ice, vapor, solution	5.0	..	..
− 1.3	Ice, vapor, solution and phenol (eutectic)	5.8	..	..
0.00	Vapor, solution, phenol	6.3	..	..
+ 1.3	Vapor, 2 liquids, phenol (invariant point)	6.8	76.0	41.4
2.6	Vapor, 2 liquids	6.9	75.6	41.3
23.9	Vapor, 2 liquids	7.8	71.2	39.5
29.6	Vapor, 2 liquids	7.5	70.7	39.1
32.5	Vapor, 2 liquids	8.0	69.0	38.5
38.8	Vapor, 2 liquids	7.8	66.6	37.2
45.7	Vapor, 2 liquids	9.7	64.4	37.1
50.0	Vapor, 2 liquids	11.5	62.0	36.8
55.5	Vapor, 2 liquids	12.0	60.0	36.0
59.8	Vapor, 2 liquids	13.6	57.7	35.7
60.5	Vapor, 2 liquids	14.0	55.5	34.8
61.8	Vapor, 2 liquids	15.0	54.0	34.5
65.0^a	Vapor, 2 liquids	18.5	50.0	34.3
+66.8^b	Vapor, one liquid	34.5	34.5	34.5
4.9	Vapor, solution, phenol	..	79.2	..
7.2	Vapor, solution, phenol	..	79.8	..
10.2	Vapor, solution, phenol	..	85.2	..
16.1	Vapor, solution, phenol	..	87.8	..
16.7	Vapor, solution, phenol	..	89.1	..
19.3	Vapor, solution, phenol	..	90.0	..
21.9	Vapor, solution, phenol	..	91.4	..

[a] From the graph obtained by plotting temperatures of homogeneity in this region; these points are indicated by square plots. [b] Critical point deduced from the law of rectilinear diameter.

trating the phenol by the method of Redmann, Weith and Brock.[7] The results are contained in Table III.

Using the data of Table III, the partial pressures of each component in the vapor phase were evaluated and compared with the partial pressures calculated by means of Raoult's law from the respective mole fractions in the liquid and the vapor pressures of the pure components at corresponding temperatures. The vapor pressures of pure phenol have been obtained from an equation in the "International Critical Tables." This, no doubt, represents an extreme extrapolation, but in the absence of experimental determinations at these relatively low temperatures, no other course is open.

The values of the ratio $p_{\text{calcd.}}/p_{\text{obsd.}}$ are collected in Table IV.

TABLE III

VAPOR PRESSURES AND COMPOSITIONS OF THE VAPOR PHASES

Temp., °C.	Phases present	Total vapor pressure, mm.	Composition of vapor % phenol	Composition of layers in equilibrium	
				Weak layer % phenol	Concd. layer % phenol
0.0	Ice and water	4.579 (literature)	0.00	...	..
−1.30	Ice, phenol, soln., vapor	4.113^a	...	6.0	..
0.0	Phenol, soln., vapor	3.6	1.6	6.3	..
3.1	2 liquids, vapor	3.8	...	6.8	75.5
6.2	2 liquids, vapor	5.6	...	6.8	74.8
7.9	2 liquids, vapor	6.7	...	6.8	74.4
10.0	2 liquids, vapor	...	1.7	7.0	74.3
10.6	2 liquids, vapor	8.9	...	7.0	74.0
13.2	2 liquids, vapor	9.4	...	7.0	73.6
15.0	2 liquids, vapor	...	2.2	7.1	72.7
18.1	2 liquids, vapor	13.3	...	7.2	72.5
21.7	2 liquids, vapor	19.7	...	7.3	72.2
22.6	2 liquids, vapor	21.2	...	7.5	72.0
26.2	2 liquids, vapor	24.2	4.3	7.5	70.8
28.3	2 liquids, vapor	27.1	...	7.5	70.2
30.7	2 liquids, vapor	31.7	...	7.5	69.5
34.1	2 liquids, vapor	37.7	...	7.6	68.5
34.3	2 liquids, vapor	38.1	...	7.6	68.3
35.6	2 liquids, vapor	...	5.4	7.7	68.0
38.7	2 liquids, vapor	49.3	...	7.8	66.8
44.5	2 liquids, vapor	67.9	...	8.7	65.0
46.2	2 liquids, vapor	...	6.3	9.0	64.0
49.5	2 liquids and vapor	87.5	...	9.5	62.8
55.0	2 liquids and vapor	...	7.6	11.3	59.5
55.5	2 liquids and vapor	116.2	...	11.5	59.2
59.9	2 liquids and vapor	145.1	7.9	14.0	56.0
62.0	2 liquids and vapor	158.5	...	15.0	53.5
65.0	2 liquids and vapor	...	8.5	18.5	50.0
65.4	2 liquids and vapor	183.2	...	20.0	49.0
1.5	Phenol, solution, vapor	3.5	...	..	76.2
5.3	Phenol, solution, vapor	5.2	...	..	80.2
10.0	Phenol, solution, vapor	...	1.7	..	84.5
10.2	Phenol, solution, vapor	6.4	...	..	84.5
15.7	Phenol, solution, vapor	7.3	...	..	88.0
20.4	Phenol, solution, vapor	9.3	7.7	..	90.6
21.4	Phenol, solution, vapor	9.9	...	..	91.0
22.2	Phenol, solution, vapor	10.2	...	..	91.5
23.6	Phenol, solution, vapor	10.1	...	..	92.0
24.9	Phenol, solution, vapor	10.2	...	..	92.7
25.0	Phenol, solution, vapor	...	8.8	..	92.9
25.8	Phenol, solution, vapor	10.1	...	..	93.2
28.9	Phenol, solution, vapor	10.2	...	..	95.0
29.7	Phenol, solution, vapor	10.0	...	..	95.3
30.0	Phenol, solution, vapor	...	14.3	..	95.5
31.5	Phenol, solution, vapor	9.7	...	..	96.1
33.4	Phenol, solution, vapor	9.3	...	..	97.0
35.0	Phenol, solution, vapor	9.0	...	..	97.2

[a] Taken as the same as that of ice.

The relative surface tensions were determined by the method of capillary rise, using a capillary which gave with water a rise of 6.27 cm. at room temperature. The densities of all solutions were taken as unity, and the determinations were made either at room temperature or at a temperature a few degrees above the temperature of homogeneity. The results are contained in Table V.

The relative viscosities are contained in Table VI.

TABLE IV

VALUES OF $p_{\text{calcd.}}/p_{\text{obsd.}}$

Temp., °C.	$p_{\text{calcd.}}/p_{\text{obsd.}}$			Phases in equilibrium
	Phenol	Water		
0.0		1.00		Ice and water vapor
−1.3	0.0103	1.00		Ice, phenol, solution, vapor
0.0	.0169	1.26		Phenol, solution, vapor
1.3	.0216	1.51	Calcd. on concn. of dilute layer	Phenol, 2 liquids, vapor
5.0	.0263	1.28		2 liquids and vapor
10.0	.0276	1.14		2 liquids and vapor
15.0	.0302	1.13		2 liquids and vapor
20.0	.029	1.14		2 liquids and vapor
25.0	.051	1.02		2 liquids and vapor
30.0	.058	1.04		2 liquids and vapor
35.0	.055	1.05		2 liquids and vapor
40.0	.055	1.01		2 liquids and vapor
45.0	.060	1.02		2 liquids and vapor
50.0	.0665	1.005		2 liquids and vapor
55.0	.070	0.97		2 liquids and vapor
60.0	.0815	.975		2 liquids and vapor
65.0	.108	.97		2 liquids and vapor
66.8	.179	.89		Critical solution temp.
65.0	.42	.845	Calcd. on concn. of concd. layer	2 liquids and vapor
60.0	.505	.82		2 liquids and vapor
55.0	.57	.785		2 liquids and vapor
50.0	.69	.79		2 liquids and vapor
45.0	.815	.78		2 liquids and vapor
40.0	.905	.76		
35.0	1.00	.775		2 liquids and vapor
30.0	1.37	.735		2 liquids and vapor
25.0	1.04	.72		2 liquids and vapor
20.0	0.645	.78		2 liquids and vapor
15.0	.77	.77		2 liquids and vapor
10.0	.69	.75		2 liquids and vapor
5.0	.463	.835		2 liquids and vapor
1.3	.300	.955		Phenol, 2 liquids, vapor
5.0	.84	.74		Phenol, solution, vapor
10.0	1.12	.615		Phenol, solution, vapor
15.0	0.73	.59		Phenol, solution, vapor
20.0	.72	.60		Phenol, solution, vapor
25.0	2.34	.67		Phenol, solution, vapor
30.0	2.80	.655		Phenol, solution, vapor
35.0	0.955	.725		Phenol, solution, vapor
40.0	.975	.805		Phenol, solution, vapor

The System: Phenol–Water–4% Succinic Acid

A constant concentration of 4% succinic acid was used. It was intended to analyze the liquid layers in equilibrium refractometrically, as with the previous system, but it was found that the refractive indices of the more concentrated solutions underwent an anomalous increase on keeping. This behavior inclines us to believe that succinic acid in phenol is partially combined with the phenol, perhaps to give phenylsuccinic acid.

If so, then some doubt attaches to all figures for concentrated solutions of phenol containing succinic acid, since there is no certainty that equilibrium has been attained between free succinic acid and phenol and the hypothetical compound; neither are the equilibrium proportions known. This, however, only applies to solutions of concentration greater than the critical composition.

TABLE V

SURFACE TENSIONS OF PHENOL SOLUTIONS, RELATIVE TO WATER AND TO PHENOL

Phenol, %	Temp. of detn., °C.	Surface tension relative to	
		Water	Phenol
0.8	20.6	0.82	1.66
3.9	18.9	.608	1.22
7.3	20.9	.545	1.11
9.3	54.9	.56	1.05
16.0	73.1	.59	1.11
33.0	70.7	.555	1.05
33.5	75.5	.53	1.08
46.0	74.0	.494	1.03
53.0	63.0	.53	1.02
58.0	56.0	.55	1.04
64.4	64.0	.55	1.04
72.8	42.0	.55	1.05
82.7	51.0	.54	1.02
89.6	49.0	.54	1.04
98.6	49.0	.54	1.01

TABLE VI

VISCOSITIES OF PHENOL SOLUTIONS RELATIVE TO WATER

Phenol, %	Temp. of detn., °C.	Viscosity relative to water
0.8	19.2	1.01
3.9	19.2	1.04
7.3	19.2	1.14
9.2	52.0	1.13
16.0	70.0	1.16
25.0	70.0	1.12
33.0	70.0	1.25
33.5	70.0	1.38
46.0	70.0	1.45
53.0	70.0	1.51
58.0	70.0	1.57
64.4	70.0	1.71
69.5	51.0	1.72
72.8	51.0	2.97
82.7	20.0	4.51
89.6	20.0	6.05
100.0	51.0	11.9

We were obliged, therefore, to determine all points on the two-liquid curve by the method of Alexejeff. Since the depression of this curve is due to the fact that succinic acid is soluble in both layers, a sample from each layer was titrated with sodium hydroxide, in each case where two layers were present. The distribution ratio is given in Table VII.

The data of the *T*–*x* diagram were obtained in the same way as with the system phenol–water, with the exception of the curve for the two liquid

TABLE VII

THE DISTRIBUTION OF SUCCINIC ACID BETWEEN WATER AND PHENOL

Temp. of equil., °C.	C_1 = concn. of succinic acid in phenol layer, %	C_1 = concn. of succinic acid in aq. layer, %	C_1/C_2
19.1	4.08	4.10	1.00
31.0	3.95	4.13	0.955
34.2	3.87	3.79	1.02
29.9	3.82	3.87	0.99
24.5	4.47	4.54	1.00
21.7	4.05	4.04	1.00
14.5	4.10	3.98	1.03
10.5	4.15	3.98	1.04
2.0	4.05	3.95	1.02

layers. The complete data are given in Table VIII.

TABLE VIII

TEMPERATURE–CONCENTRATION DATA

Temp., °C.	Phases present	Concn. phenol, % Weak layer	Concn. phenol, % Concd. layer	Mean
−0.5	Ice, vapor + 4% succinic solution	..	..	..
− .7	Ice, vapor, solution	0.8	..	..
−1.4	Ice, vapor, solution	3.9	..	..
−1.8	Ice, vapor, solution	7.3	..	..
−1.9	Ice, vapor solution, phenol (eutectic)	7.5 (from graph)	..	..
0.0	Vapor, solution, phenol	11.1	..	..
+ .8	Vapor, phenol, 2 liquid layers	11.1 (from graph)	..	..
1.0	Vapor, 2 liquid layers	11.2	63.7	37.5
12.5	Vapor, 2 liquid layers	11.3	60.8	36.1
19.5	Vapor, 2 liquid layers	11.4	55.5	33.5
21.7	Vapor, 2 liquid layers	11.5	54.4	33.0
24.5	Vapor, 2 liquid layers	11.8	52.0	31.9
28.0	Vapor, 2 liquid layers	12.0	50.0	31.0
30.2	Vapor, 2 liquid layers	13.0	48.3	30.7
35.8	Vapor, 2 liquid layers	18.5	37.9	28.2
36.4	Vapor, 2 liquid layers	19.5	37.1	28.3
37.1	Vapor, 2 liquid layers	28.3	28.3	28.3
14.5	Phenol, vapor solution	..	88.0	..
19.3	Phenol, vapor solution	..	90.0	..
23.9	Phenol, vapor solution	..	95.0	..
40.3	Phenol, vapor, liquid phenol + S. A.	..	100.0	..

The vapor pressures and compositions of the vapor phases are given in Table IX.

Using the data of Table IX, the partial pressures of each component in the vapor phase were evaluated and compared with the partial pressures calculated by means of Raoult's law from the respective mole fractions in the liquid and the vapor pressures of the pure components at corresponding temperatures; the presence of the succinic acid was ignored in the calculation.

TABLE IX

VAPOR PRESSURES AND COMPOSITIONS OF THE VAPOR PHASES

Temp., °C.	Phases present	Total vapor pressure, mm.	Composition of vapor, % phenol	Composition of liquid layers in equilibrium Weak layer	Composition of liquid layers in equilibrium Concd. layer
−0.5	Ice, vapor, 4% succinic acid solution	4.395 (lit.)	0.0		
−1.9	Ice, vapor, solution, phenol	3.913 (lit.)		7.5	
−1.6	Vapor, solution, phenol	3.5			
−0.9	Vapor, solution, phenol	3.6			
− .3	Vapor, solution, phenol	3.7			
.0	Vapor, solution, phenol		0.9	11.1	
+ .3	Vapor, solution, phenol	3.7			
2.4	Vapor, 2 liquids	4.7			
5.3	Vapor, 2 liquids	5.8			
9.3	Vapor, 2 liquids	8.0			
12.8	Vapor, 2 liquids		3.1	11.2	60.0
16.0	Vapor, 2 liquids	12.6			
17.5	Vapor, 2 liquids	14.1			
20.5	Vapor, 2 liquids	16.8	4.3	11.5	55.2
22.6	Vapor, 2 liquids	19.5			
25.5	Vapor, 2 liquids	23.5			
28.2	Vapor, 2 liquids	27.3			
30.2	Vapor, 2 liquids	31.0	4.6	12.6	47.8
32.5	Vapor, 2 liquids	34.8			
34.8	Vapor, 2 liquids	39.7	4.8	16.6	41.0
36.9	Vapor, 2 liquids	44.1			
1.4	Phenol, solution, vapor	4.6			
2.3	Phenol, solution, vapor	4.6			
3.0	Phenol, solution, vapor	4.8			
3.4	Phenol, solution, vapor	4.8			
4.0	Phenol, solution, vapor	5.0			
8.1	Phenol, solution, vapor	6.3			
11.2	Phenol, solution, vapor	6.9	3.4		81.7
14.7	Phenol, solution, vapor	8.6			
21.0	Phenol, solution, vapor	10.1	5.0		93.3
23.8	Phenol, solution, vapor	10.8			
26.1	Phenol, solution, vapor	10.5	6.1		96.0
29.4	Phenol, solution, vapor	9.8			

The values of the ratio $p_{\text{calcd.}}/p_{\text{obsd.}}$ are collected in Table X.

Table XI contains the measurements of relative surface tension. Despite the presence of the succinic acid, the surface tension drops to the same value, 0.54 times that of 4% aqueous succinic acid, at about the same phenol concentration, *viz.*, 10%. Apparently the outer layer has an identical structure, whether succinic acid be present or not.

The relative viscosities are contained in Table XII. In contradistinction to the system phenol–water, the viscosities here increased continuously up to 85% phenol, indicating that, apart from the outermost layer, the phenol is more uniformly distributed in the body of the solution. The rapid fall in viscosity after 85% phenol is probably due to the crystallization from solution of a compound of phenol and succinic acid, leaving a solution impoverished in phenol.

TABLE X

VALUES OF $p_{\text{calcd.}}/p_{\text{obsd.}}$

Temp. °C.	$p_{\text{calcd.}}/p_{\text{obsd.}}$ Phenol	$p_{\text{calcd.}}/p_{\text{obsd.}}$ Water		Phases in equilibrium
−0.50		1.00		Ice, vapor, solution of succinic acid
−1.9	0.047	1.00		Ice, phenol, vapor, solution
0.0	.0715	1.20		Phenol, vapor, solution
+ .8	.0635	1.19	Calcd. on concn. of dilute layer	Phenol, vapor, 2 liquids
5.0	.0323	1.10		Vapor, 2 liquids
10.0	.0238	0.995		Vapor, 2 liquids
15.0	.0295	1.03		Vapor, 2 liquids
20.0	.0326	1.04		Vapor, 2 liquids
25.0	.0735	0.99		Vapor, 2 liquids
30.0	.102	1.00		Vapor, 2 liquids
35.0	.15	1.015		Vapor, 2 liquids
36.9	.295	1.03		Vapor, 2 liquids
35.0	.515	0.82	Calcd. on concn. of concd. layer	Vapor, 2 liquids
30.0	.575	.835		Vapor, 2 liquids
25.0	.49	.835		Vapor, 2 liquids
20.0	.248	.95		Vapor, 2 liquids
15.0	.273	.82		Vapor, 2 liquids
10.0	.233	.79		Vapor, 2 liquids
5.0	.325	.84		Vapor, 2 liquids
0.8	.365	.935		Phenol, vapor, 2 liquids
5.0	.385	.75		Phenol, vapor, solution
10.0	.51	.74		Phenol, vapor, solution
15.0	.75	.69		Phenol, vapor, solution
20.0	.127	.53		Phenol, vapor, solution
25.0	3.20	.442		Phenol, vapor, solution
30.0	1.14	.408		Phenol, vapor, solution
35.0	1.20	.400		Phenol, vapor, solution
40.3	1.00	..		Phenol, anhydrous melt, vapor

TABLE XI

SURFACE TENSIONS OF PHENOL SOLUTIONS, RELATIVE TO WATER AND TO PHENOL, CONTAINING 4% SUCCINIC ACID

Phenol, %	Temp. of detn., °C.	Surface tension relative to Water + 4% S. A.	Surface tension relative to Phenol saturated with S. A.
0.8	19.8	0.87	1.66
3.9	19.8	.765	1.45
7.3	19.8	.58	1.10
9.9	25.0	.542	1.03
29.5	40.0	.56	1.04
31.4	40.0	.557	1.04
33.5	40.0	.56	1.04
52.0	31.0	.525	0.98
53.4	31.0	.54	1.01
55.5	31.0	.53	1.00
70.6	25.0	.525	1.00
76.2	25.0	.525	1.00
98.0	40.0	.535	1.00

TABLE XII

VISCOSITIES OF PHENOL SOLUTIONS RELATIVE TO 4% AQUEOUS SUCCINIC ACID

Phenol, %	Temp. of detn., °C.	Viscosity relative to 4% succinic acid
0.8	21	1.02
3.9	21	1.10
7.3	21	1.19
9.9	21	1.26
29.5	40	2.22
31.4	40	2.07
33.5	40	2.23
52.0	40	2.83
53.4	40	2.94
55.5	40	3.09
70.6	21	4.13
76.2	21	5.25
82.7	21	6.05
89.6[a]	40	5.90
98.0[a]	40	4.04

[a] After removal of crystalline precipitate.

Summary

1. The T–x and p–x diagrams of the systems phenol–water and phenol–water–4% succinic acid have been determined.

2. The compositions of the vapor phases in equilibrium with different phases along the above diagrams have been determined.

3. The observed partial pressures ($p_{\text{obsd.}}$) have been compared with the partial pressures calculated by means of Raoult's law ($p_{\text{calcd.}}$).

4. From the observed values of the ratio $p_{\text{calcd.}}/p_{\text{obsd.}}$ it is concluded that the phenol is driven to the free surface of the solution where, at a total concentration of phenol of about 10%, it forms a practically continuous phenol layer, which persists at all higher concentrations of phenol.

5. This conclusion is confirmed by measurements of surface tension and viscosity.

6. The addition of succinic acid appears to be without effect on the establishment of the outer layer of phenol, but, apart from this layer, the phenol appears to be more uniformly distributed in the body of the solution than in the case of phenol–water alone. The values of the ratio $p_{\text{calcd.}}/p_{\text{obsd.}}$ appear, if anything, to deviate still more from ideal behavior; at least they never approach unity, as is the case with phenol–water for a short range of concentration.

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