SOME OBSERVATIONS ON THE SYSTEM PHENOL-WATER

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Whilst investigating the depression of the freezing point of water by phenol, two eutectic points were observed, solid phenol-solution-ice and phenol hydrate-solution-ice. The existence of a hydrate of phenol was first described by Calvert[1] who obtained it by cooling a mixture of four parts of phenol and one part of water to 4° C.; and Smits and Maarse[2] definitely showed it to have the formula $(C_6H_5OH)_2.H_2O$. But this compound, it appears, is very difficult to prepare. Paternò and Ampola[3] in their determination of the melting point line of phenol in the system phenol-water, overlooked it, because the formation of the hydrate very often does not take place, and Alexejeff[4] being unable to obtain evidence of a definite compound, concluded that the hydrate described by previous workers was merely a mixture of phenol and water. Smits and Maarse, as well as Rhodes and Markley,[5] were unable to obtain it by the original method of preparation. They state that a solution of 15% of water in phenol must be cooled for an hour at −78°C. before crystals of the hydrate can be obtained, but during the present work, the hydrate occurred spontaneously when the temperature of the solution was not lower than −1°C., which rather supports the view of Calvert and of Lowe and Gill[6] that very low temperatures are not essential for its preparation. Having once prepared a small amount, quantities required for further work were easily obtained by cooling concentrated solutions of phenol below 12°C., and "seeding" with a crystal of the hydrate.

A review of the literature shows that the system phenol-water has been studied by several investigators, but that portion of it below 13°C., not very fully by any of them: more attention has been paid to that part dealing with the concentrations of the phenol and water in the two layers at different temperatures. The temperature given in the literature for the eutectic point, phenol hydrate-solution-ice, varies from −0.85° to −1°C; that of the invariant point, solid phenol—phenol-rich solution—water-rich solution, from 1.5° to 1.7°C. Further, there appears to be no reference to the invariant point, phenol-rich solution—water-rich solution—ice, and figures for the solubility of phenol hydrate are not available.

In view of the rather meagre and contradictory nature of previously published information, and as the hydrate could be easily obtained, it was considered advisable to study a portion of the system more carefully, and to

[1] J. Chem. Soc., **18**, 66 (1865).
[2] Ver. Kon. Akad. Wet. Amsterdam, **20**, 100 (1911-12).
[3] Gazz., **27**, 523 (1897).
[4] J. Soc. Chem. Ind., **1**, 397 (1882).
[5] J. Phys. Chem., **25**, 527 (1921).
[6] Chem. News, **31**, 32 (1875).

attempt to obtain the temperature of the invariant point, phenol-rich solution—water-rich solution—ice. This paper, then, deals with investigations carried out at temperatures below 13°C., and under atmospheric pressure, which has been assumed constant throughout.

Experimental

The phenol used in all the experiments was purified by being fractionally crystallised three times and distilled twice, the second distillation being carried out over anhydrous copper sulphate, and the portion boiling at constant temperature only collected. The final product was pure white, and not hygroscopic. As a criterion of purity, a determination of the freezing point was made. The phenol was distilled directly into the freezing point tube, the necessary precautions to prevent the access of air being taken, and remelted. The tube, containing stirrer, thermometer (calibrated to 0.01°C.), and a tube by means of which a current of dry air could be passed through the apparatus, was then placed in an air jacket in a bath at a temperature not more than 0.5°C. below the true freezing point. The liquid was gently stirred, and temperature readings taken every half minute: a rapid current of dry air was passed through the tube the whole time the phenol was exposed to the air. Several determinations were made, using different samples of phenol. In every case, there was a slight supercooling of about 0.1°C., after which the temperature rose and remained constant for several minutes. The freezing point was also determined in the presence of anhydrous copper sulphate, but no difference was observed. The values obtained were between 40.69° and 40.72°C., and the mean, 40.71°C. is considered to be the true freezing point of phenol. The recorded values for the freezing point vary considerably: Béhal and Choay[1] give a value as high as 42.5°-43°C. Lowe[2] gives the value as 42.25°C. But it is worthy of note that all later workers who have taken special precautions to obtain a pure sample of phenol, favour the lower value, e.g. Hulett,[3] 40.8°C; Tammann,[4] 40.6°C; Rhodes and Markley, 40.8°C.

The concentrations of phenol in solutions in equilibrium with phenol-rich solution at 13°C., with the hydrate and with phenol-rich solution at 9.93° and 4.93°C., as well as those in solutions in equilibrium with the hydrate, phenol-rich solution, and solid phenol at 0°C., have been determined by solubility measurements. Previous investigators have almost invariably used the synthetic method: solutions of known strength were made up and their freezing points determined. But it was considered that solubility measurements would give more reliable information. The solutions, together with excess of hydrate, solid phenol, or phenol-rich solution, as the case might be, were placed in glass-stoppered bottles which were practically immersed in a thermostat kept at the required temperature,—the thermostat wash and regulated to 0.05°C. Vigorous shaking of the bottles to hasten equilibrium

[1] Compt. rend., **118**, 1211 (1894).

[2] Chem. News, **16**, 57 (1867).

[3] Z. physik. Chem., **28**, 663 (1899).

[4] "Kristallisieren und Schmelzen," 308 (1903).

was not possible with solutions containing excess phenol-rich solution, as the emulsion formed by shaking does not readily settle. Hence, these solutions had to be carefully and gently stirred: the time of attaining equilibrium was thus considerably longer, from six to eight hours being required.
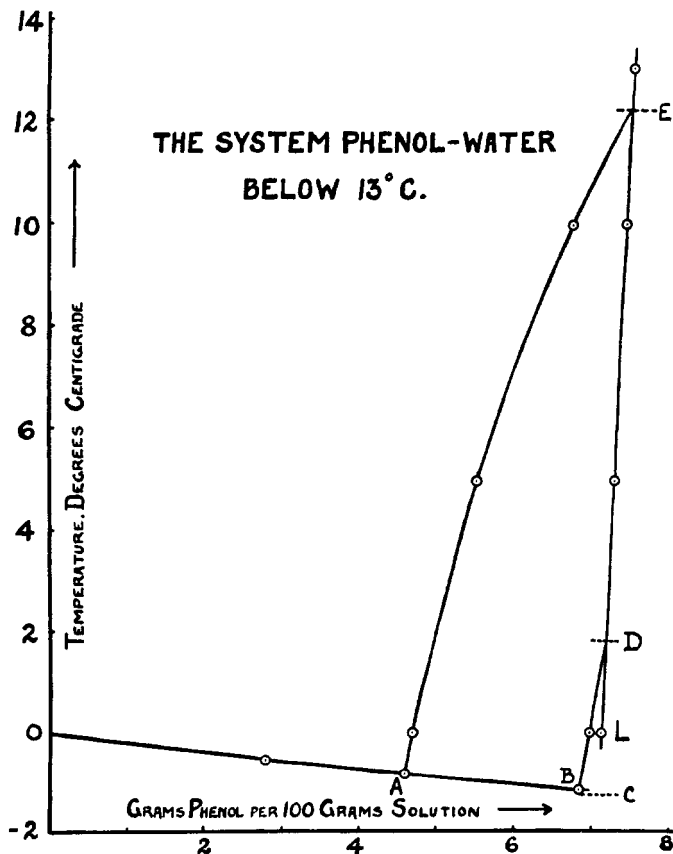

FIG. 1

The phenol solutions were analysed by the method given by Redman, Weith and Brock.[1] It was found, however, that analyses of the necessary accuracy were obtained only when the phenol solutions used were less than N/20, i.e. half the strength recommended by these authors,—solutions of this strength require approximately 40 ccs. of N/10 KBr, KBrO$_3$ solution. All the phenol solutions obtained during this work were stronger than N/20,

[1] J. Ind. Eng. Chem., **6**, 389 (1913).

and so weighed quantities were taken and diluted to a known volume so that the resulting solution was as nearly as possible N/20. Duplicate analyses were done in every case, and these usually agreed to within 0.1%. The solubility measurements were repeated until constant values were obtained.

The results obtained are given in Table I. and illustrated graphically in Fig. 1. AE is the solubility curve of the hydrate, which is the stable form

TABLE I

Grams phenol per 100 grams solution in equilibrium with

Temp. °C.	Phenol-rich Soln.	Phenol Hydrate	Solid Phenol
13.0	7.574		
9.93	7.454	6.771	
4.93	7.308	5.530	
0.	7.147	4.695	7.005

below 12°C. LE, meeting the curve AE at E, the invariant point, phenol hydrate—phenol-rich solution—water-rich solution, is the curve of equilibrium between phenol-rich solution and water-rich solution, and BD represents the solubility of the solid phenol. The liquid phase rich in phenol, and solid phenol, being unstable below E, their solubilities are greater than that of the hydrate.

The melting points, under water, of the hydrate and of phenol have been determined, and are given in Table II. These temperatures are represented

TABLE II

Substance	Phenol	Phenol Hydrate (under water)	Phenol (under water)
Melting Pt. °C.	40.71	12.17	1.80

by the dotted lines in the diagram, cutting the solubility curves at D and E. D is another invariant point, solid phenol—phenol-rich solution—water-rich solution. A thick paste of the hydrate and water was placed in a large test tube fitted with a thermometer and a stirrer. This was warmed up to a temperature of about 16°C., the liquid being stirred to remove all traces of the hydrate, and afterwards cooled to 11.5°-12°C. The test tube was then quickly placed in an air jacket contained in a bath, the temperature of which was kept about 0.2° lower than the melting point, and a small quantity of the hydrate added. The temperature rose fairly quickly, and the highest point reached was taken as the melting point of the hydrate. The mean of several readings has been taken. The same procedure was adopted for the melting point of the phenol (under water), but at the lower temperature, and the seeding being done with solid phenol. The values obtained for these two points agree very closely with those of previous workers.

The observations on the lowering of the freezing point of water were carried out by the equilibrium method previously described,[1] and are represented by the curve OAB in the diagram. The eutectic points A and B, phenol hydrate, solution, and ice, and solid phenol, solution, and ice respectively, were obtained in the usual manner, but the temperature at the invariant point, phenol-rich solution—water-rich solution—ice, represented by the dotted line at C in the diagram, was obtained indirectly. A quantity of finely crushed ice was added to the freezing point flask, into which a saturated solution of phenol, together with an amount of free phenol-rich solution sufficient to be in excess at the equilibrium temperature, had already been placed. The whole apparatus was assembled, and allowed to cool in the bath to a temperature of about $-1.2°C.$, before stirring was attempted. The mixture was then well stirred to ensure thorough mixing, and the temperature, which remained constant for a considerable time, noted. On continuing the stirring, the temperature suddenly rose to that of the eutectic point, solid phenol-solution-ice. This temperature was again noted, and as a further check, the temperature of the hydrate eutectic point determined by inoculating the solution with a little of the hydrate. By difference, it was found that phenol-rich solution, water-rich solution, and ice coexist in metastable equilibrium at $-1.252°C.$ The whole procedure was repeated, and the determinations agreed within the limits of experimental error. A direct determination of the concentration of the phenol at this point was not possible, because the emulsion formed did not settle. By extrapolation from the graph, the concentration at C would be 7.14 grams phenol per 100 grams solution, and the temperature $-1.20°C.$, a value somewhat different from that actually observed. There appear to be three possible explanations to account for this difference. Firstly, the solubility of the unstable phenol may increase below $0°C.$, cf. nicotine and water.[2] Secondly, phenol-rich solution is present as an emulsion, which may be appreciably more soluble than phenol-rich solution in mass: this is scarcely probable, as the temperature is reproducible. Thirdly, there may be a change in the direction of the depression-concentration curve between B and C. Along OB, the concentration increases more rapidly than the depression, and the curve is slightly convex to the axis of concentration, but between B and C, the depression-concentration curve may become concave to this axis. This anomalous behaviour has also been observed with concentrated solutions of butyric acid, which is reported to separate into two layers.

<div align="center">TABLE III</div>

Temperature °C.	-0.534	-0.843*	-1.174*	-1.252
Grams Phenol/100 gms. soln.	2.803	4.607	6.839	

*Eutectic temperatures.

[1] Phil. Mag., (7) 3, 1032 (1927).

[2] Hudson: Z. physik. Chem., 47, 113 (1904).

The results of the freezing point determinations are given in Table III; where the eutectic temperatures are marked with an asterisk.

It will be observed that in this portion of the phenol-water system, there are two eutectic points, A and B, and five invariant points, A, B, C, D, and E; and the region BDLC is doubly unstable,—unstable with respect to the meta-stable curve BD, and the stable solubility curve AE.

Summary

The system phenol-water has been studied below 13°C. Two eutectic points, and the temperature at the doubly unstable invariant point, Phenol-rich solution—water-rich solution—ice, have been observed. Solubility measurements have also been made. The freezing point of pure phenol is given at 40.71°C.

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