Chemistry. — Ernst Cohen and Saburo Miyake : *"The influence of minute traces of Water on Solution Equilibria."* II

Introductory.

In the first paper under the above title [1]) it was shown that the solution equilibrium between salicylic acid and benzene is shifted by the presence of minute traces of water, the solubility of salicylic acid markedly increasing by the addition of water. We also stated that the phenomenon in question can manifest itself in consequence of the presence of occluded water, so that, if the solubility of substances must be determined with accuracy, great care should be taken to work with pure (dried) substances. At the time we pointed out that the minute quantity of occluded water can be accurately determined by solubility determinations. The experiments which are described in this paper, have been made in order to become acquainted with the influence of minute traces of water in other solution equilibria, and moreover — the measurements which refer to this part of the problem will be described first — to prove, more directly than was done in the first paper, that the phenomena which are investigated here, are indeed (true) equilibria.

As the method of procedure was fully explained in the first communication we need not go into details here.

All the solubility determinations have been carried out at 30°.50 C.

1. The Equilibrium in the System Salicylic acid — Benzene.

1. We used the salicylic acid (preparation Kahlbaum "für kalorimetrische Bestimmungen", vide our first communication under A. § 1a), which, according to the method described there (B. § 2. 2) was recrystallized from dry ether (vide first communication under A. § 1. c). The acid had been kept for a long time in vacuo over P_2O_5, and had been powdered every day until the smell of ether had totally disappeared.

2. The benzene (free from thiophene) had been treated in the way previously described (vide first communication under A. § 1. b.). Whereas in our first investigation we simply poured the liquid out of the flask into the shaking bottles, so that it came in contact with the moist air in the laboratory, we now pressed it from the flask by means of air which had been carefully dried over sulphuric acid and then over P_2O_5. After having used the apparatus for a month we ascertained that practically the benzene

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[1]) These Proceedings **28**, 702 (1925); Zeitschr. f. physik. Chemie **118**, 37, (1925).

had remained unchanged : the solubility of the salicylic acid which had been determined at 1.00 ; 1.02 ; 1.01 ; 1.02 *), was found to be 1.02 at the end of that period (vide first communication § 13).

3. In order to prove that the phenomena, described in the first communication, are indeed equilibria, we set to work as follows : In each of two shaking bottles about one gramme of dry acid and about 40 gms. of dry benzene is weighed ; then these bottles are sealed. One of the bottles is immediately put into the thermostat, the temperature of which has been set to the temperature of the experiment (30°.50 C.). The second bottle, with its contents, is heated in a water bath to such a temperature that the solute has been almost, but not wholly, dissolved. Then this bottle is also placed in the thermostat, and both bottles are shaken for the same length of time, at the temperature of the experiment.

The same manipulations are carried out with two bottles, the contents of which differ from those mentioned above in that they contain moist benzene (of an accurately determined water percentage) instead of dry benzene.

In this way the final condition is reached in both cases (dry and moist benzene), as well from the side of supersaturation as from that of under-saturation.

TABLE 1.
Solubility of Salicylic acid in Benzene.
Temperature 30°.50 C.

Number of the experiment	Period of shaking in hours	Thousandths of weight % of water	Solubility in weight %
1	4	0	1.00 1.02*
2	3	0	1.01 1.02*
3	3	66	1.16 1.17*
4	4	71	1.19 1.18*

As we see from Table 1 we find identical values for the solubilities, within the errors of the experiment, in other words : in the dry system, as well as in the wet, we have indeed true equilibria.

Weight % means gms. of solute in 100 gms. of solution.

2. *The Equilibrium in the System Salicylic acid — Chloroform.*

4. When the chloroform had been for a long time on P_2O_5, it was distilled from fresh P_2O_5, in the way previously described (vide first

*) Means that equilibrium is reached from the side of supersaturation.

communication A. § 1*b*.). The tapping from the flask was done as described in § 2.

When tapping the saturated solutions of salicylic acid we placed the bulb E (Fig. 1 first communication) always in ice water, so as to keep the tension of the vapour over the solution as low as possible.

The following figures prove that the analysis by evaporation of the solvent (vide first communication § 5) gives good results, whether dry chloroform is taken or moist : 0.2631 gms. of dry salicylic acid dissolved in about 17 gms. of dry chloroform gave 0.2629 gms. after the solvent was evaporated. When the residue had been in vacuo over sulphuric acid and salicylic acid for the night, the weight proved to be 0.2629 gms. Further 0.3681 gms. of the acid, which had been dissolved in about 20 gms. of moist chloroform (water-content of the chloroform 0.0354 gms. of water in 100 gms. of chloroform) gave 0.3676 gms. after being treated in the same way.

Table 2 contains the results of the experiments with chloroform.

TABLE 2.

Solubility of salicylic acid in Chloroform.

Temperature 30°.50 C.

Number of the experiment	Period of shaking in hours	Thousandths of weight %/0 of water	Solubility in weight %/0	
5	3	0	1.55	1.56*
6	5	0	1.56	1.55*
7	3	35.4	1.64	1.63*
8	3	60.8	1.69	1.68*
9	3	108.1	1.72	1.71*
10	3	saturated	1.73	1.72*

For further elucidation of the term "saturated" in this table and the following ones, we wish to observe that the solvent had previously been shaken with excess of water at 30°.50 C. and after separating it from the excess of water was used for the determination of solubility.

3. *The Equilibrium in the System Salicylic acid — Carbon Tetrachloride.*

5. The carbon tetrachloride we used was free from sulphur ; when it had been on P_2O_5 for a week, it was distilled from a fresh quantity of P_2O_5. The method of keeping it and of transferring it to the shaking bottles is described in § 2.

In this case too the analysis of the saturated solutions can be made by evaporation of the solvent, as may be seen from the following figures :

0.0432 gms. of salicylic acid, dissolved in about 15 gms. of CCl_4, gave, after evaporation of the solvent, 0.0426 gms. of acid.   In the second experiment we weighed 0.0321 gms. into the bottle and found back 0.0321 gms.

Table 3 gives a summary of the results.

TABLE 3.

Solubility of Salicylic acid in Carbon tetrachloride.
Temperature 30°.50 C.

Number of the experiment	Period of shaking in hours	Thousandths of weight % of water	Solubility in weight %	
11	3	0	0.36	0.35*
12	5	0	0.35	0.35*
13	3	8.7	0.35	0.36*
14	3	22.7	0.36	0.36*
15	3	65.9	0.36	0.37*
16	3	saturated	0.36	0.36*

4.   *The Equilibrium in the System o-Nitrobenzoic acid — Benzene.*

6.   With a view to some experiments on the metastability of this acid as a consequence of enantiotropy or monotropy, we had acquired a rather large quantity.   We used preparations supplied by different factories. After having been recrystallized from water they gave identical results. This was seen f.i. when determining their solubility in water.

TABLE 4.

Solubility of o-nitrobenzoic acid in Benzene.
Temperature 30°.50 C.

Number of the experiment	Period of shaking in hours	Thousandths of weight % of water	Solubility in weight %	
17	3	0	0.35	0.35*
18	3	37.7	0.43	0.43*
19	3	66.3	0.49	0.49*
20	3	89.1	0.49	0.50*
21	3	saturated	0.50	0.50*

Also in this case we found the evaporation method, when determining the solubility, very useful.   Thus 0.0327 gms. of acid, dissolved in 15 gms.

61*

of moist benzene (water content 0.2226 gms. of water in 100 gms. of benzene) gave 0.0327 gms. of acid after evaporation of the solvent. When the residue had been for 24 hours in vacuo over P_2O_5 and o-nitrobenzoic acid, we found 0.0327 gms. In a second experiment in which 0.0558 gms. had been weighed into the bottle, we found in the same way 0.0559 gms.

Table 4 contains the results of these measurements.

5. *The Equilibrium in the System o-Nitrobenzoic acid — Chloroform.*

7. As the experiments in this case were carried out in exactly the same way as in the system salicylic acid—chloroform, it will suffice to point out that the evaporation process yields accurate results. Thus, after weighing 0.0906 gms. of acid into the bottle, we found 0.0907 gms. after evaporation. In another experiment 0.0414 gms. instead of 0.0418 gms.

TABLE 5.

Solubility of o-nitrobenzoic acid in Chloroform.
Temperature 30°.50 C.

Number of the experiment	Period of shaking in hours	Thousandths of weight % of water	Solubility in weight %	
22	3	0	0.45	0.45*
23	5	0	0.45	0.45*
24	$3^1/_4$	25.6	0.51	0.52*
25	3	31.2	0.56	0.56*
26	3	saturated	0.55	0.56*
27	3	„	0.56	—

6. *The Equilibrium in the System Anthracene — Benzene.*

8. We have also investigated the influence of minute traces of water on the equilibrium between a non-electrolyte and benzene. We chose anthracene as a non-electrolyte.

A so-called pure preparation (resublimated) gave in the solubility determination in dry benzene (period of shaking 3 hours) the values of 2.05 ; 2.09. When the period of shaking was five hours we found 2.08 ; 2.09. When this preparation had been recrystallized from dry benzene we found 2.00 ; 2.00. To check the result we recrystallized this preparation from dry ether, left the mass thus obtained for some days in vacuo over P_2O_5, and then determined the solubility again in dry benzene. Now we found 2.00 ; 2.00. We used this preparation for our final solubility determinations in benzene.

In this investigation we also made use of the evaporation method in

order to analyze the saturated solutions, when the following experiments had proved that, in this case too, accurate results were obtained ; 0.1646 gms. of anthracene gave 0.1648 gms. after evaporation of the dry benzene in which they had been dissolved. In a second experiment we dissolved 0.1603 gms. of anthracene in moist benzene ; we found 0.1605 gms.

TABLE 6.
Solubility of Anthracene in Benzene.
Temperature 30°.50 C.

Number of the experiment	Period of shaking in hours	Thousandths of weight %₀ of water	Solubility in weight %₀	
28	3	0	2.00	2.00*
29	3	0	2.00	2.00*
30	3	38.9	2.00	2.00*
31	3	88.8	1.98	1.99*
32	3	saturated	1.98	1.98*

9. We shall not dwell upon the older literature about the solubility of the substances we investigated, as it refers to preparations, the purity (dryness) of which had not been closely examined. Therefore it is of no importance for the problem which occupies us here.

Summary.

Minute traces of water have great influence on solution equilibria in the systems salicylic acid — benzene, salicylic acid — chloroform, o-nitro-benzoic acid — benzene, o-nitrobenzoic acid — chloroform. No influence could be ascertained in the systems salicylic acid — carbon tetrachloride, and anthracene — benzene.

We intend to treat further conclusions in a subsequent communication.

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Utrecht, September 1925.