

In addition to the changes noted above, the value for silicon due to Baxter, Weatherill and Holmes, which was cited in our last report, namely,  $Si = 28.111$  may be adopted now and rounded off to 28.1.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

## SOLUBILITIES IN MIXTURES OF TWO SOLVENTS.

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In a recent paper<sup>1</sup> by one of us on solubilities in mixtures of water and pyridine, it was stated<sup>2</sup> that more extensive and accurate solubility studies of pyridine, quinoline, etc. are to be made, also efforts will be made to prepare the molecular compounds indicated. This paper includes studies of solubilities both in mixtures of water and pyridine and in mixtures of alcohol and quinoline; and the molecular compound  $C_9H_7N_3CO-(NH_2)_2$ , indicated by the curve of solubilities of urea in the alcohol-quinoline mixtures, was isolated and studied.

Although constants of solubility are the most numerous and useful of chemical data, and although solutions themselves afford the media of the vast majority of chemical reactions, little is accurately known concerning either the nature of solutions or the mechanism of chemical reactions in solutions. It is true that the nature of solutions has been studied deeply from the standpoints of the phase rule, the kinetic theory, and the ionic theory, yet it can scarcely be held that the intimate nature of solvent and solute has thereby been elucidated. Cryoscopic and ebullioscopic methods have recently demonstrated the frequent existence in solution of molecular compounds aggregated of the solvent and the solute, and other physical methods have confirmed these demonstrations, but all methods failed, except rarely, to yield the molecular compound itself.

In the present and the earlier paper, the existence of the molecular compound is not only indicated by the solubility curve but the method of mixed solvents can yield the molecular compound itself. For these reasons, and because the method possesses simplicity and ease of application, it is planned to undertake other investigations with mixed solvents, the main objects of which are to study the general problem of solubility, to demonstrate that curved or broken lines of solubility indicate the formation of molecular compounds, and to separate the molecular compounds when possible.

<sup>1</sup> THIS JOURNAL, 39, 1399 (1917).

<sup>2</sup> *Ibid.*, 39, 1404 (1917).

It has been assumed that straightness of line of plotted solubilities indicates a purely physical relation of solute and solvent. This assumption is confirmed by studying the solubilities of hydrated and non-hydrated salts. The former yield curved or broken lines; the latter yield straight or nearly straight lines. Since the latter can be accounted for by a mere physical mingling of solute and water molecules, the former can be, and presumably are, accounted for by states of hydration, that is, by the formation of molecular compounds.

The existence of the most varied types of other molecular compounds in solution is set forth in the literature. These compounds have, however, only rarely been studied in connection with solubility.<sup>3</sup> The lack of study along this line may be explained by the fact that ordinary solubility is conditioned by concentration and temperature and that rising temperature decomposes the molecular compound if present. In studies of solubility in mixed solvents, however, any desired low temperature can be employed and observations and data, not possible by the former method, are obtainable.

### Experimental.

Commercial pyridine was dried with solid potassium hydroxide and metallic sodium, and distilled. The quinoline was freed from nitrobenzene and aniline and then was dehydrated by the same method. Commercial "absolute" alcohol was dehydrated by treatment with calcium carbide and then was distilled into vessels kept free from atmospheric moisture. The materials studied as solutes were taken from the usual laboratory stock and for the most part were not purified.

The determinations of solubilities, unless otherwise stated, were made at the room temperatures of 20° to 25°. The solubilities are largely expressed as grams of solute in 100 g. of the solvent. Excess of the solute and about 5 cc. of the solvent were enclosed in a small vial; the mixture was shaken vigorously or was allowed to stand until equilibrium was established. The solution was then filtered rapidly into a weighed crucible and the latter with contained solution was weighed as quickly as possible. After drying *in vacuo* or on a water-bath, the crucible was again weighed. The weight of the residue and of the solvent lost yielded the desired data. No high degree of accuracy is claimed for the solubilities given in Table I, because merely a preliminary survey of the field was made in order to find compounds behaving abnormally in the alcohol-quinoline mixture.

The first column indicates solubilities in absolute alcohol; the second, in equimolecular mixture of alcohol and quinoline; the last, in absolute quinoline. The plus sign given with the figures indicates that the solute

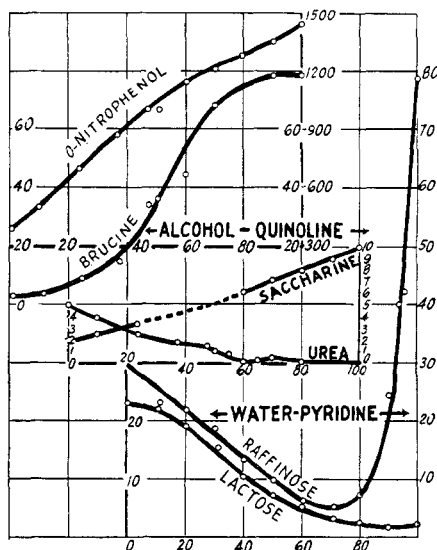
<sup>3</sup> The limited bibliography on solubilities of organic compounds in mixed solvents is indicated in the former paper. Ref. 1.

had partially volatilized; the  $\infty$  sign indicates that only a solid phase had formed.

TABLE I.  
SOLUBILITIES IN MIXTURES OF ALCOHOL AND QUINOLINE.

Solute.	Alcohol.	Equimolecular mixture.	Quinoline.
Acetamide	31.50	.....	.....
Acetanilide	21.30	23.69	12.67
Antipyrine	74.09	36.55+	19.00+
Asparagine	0.02	0.18	0.11
Azobenzene	9.29	22.88+	.....
Benzamide	17.03	18.55+	6.27+
Benzidine	7.68+	47.23+	43.07+
Borneol	175.50	.....	.....
Brucine	2.35	43.51	79.00
Caffeine	1.88	3.93	3.56
Carbazole	1.30	9.86	33.40
Casein	0.28	0.92	0.38
Chloral hydrate	215.00	0.58+	12.56+
Cinnamic acid	22.03	132.40	1.85+
Coumarine	12.57	0.80+	0.56+
Diphenyl urea	0.84	3.12	2.50
Ethyl urea	79.95	5.55+	1.13+
Glycocoll	0.06	0.17	0.07
Hemoglobin	0.37	0.59	0.23
Hippuric acid	4.60	23.10	20.41
Hydrobenzamide	1.99	2.56	3.94
Indol	35.85	12.00	11.39
Lactose	0.09	1.32	1.96
Michler's ketone	0.63	6.86	9.72
Naphthalene	9.80	4.69	3.02
Nitrobenzaldehyde	22.14	7.07+	1.96+
<i>o</i> -Nitrophenol	404.00	1000.00	1450.00
<i>m</i> -Nitrophenol	.....	.....	$\infty$
<i>p</i> -Nitrophenol	.....	$\infty$	.....
Papaverine	.....	.....	7.66
Phenacetin	18.80	12.87	7.83
Phenolphthalein	10.24	0.19	0.32
Piperine	6.66	18.81	13.66
Quinine	166.60	30.04	22.28
Raffinose	3.60	5.04	.....
Resorcinol	236.00	99.81+	$\infty$
Saccharine	2.00	.....	10.10
<i>p</i> -Toluidine	110.00	.....	.....
Trilaurine	6.66	16.57	18.22
Tristerine	13.00	$\infty$	5.35
Urea	5.00	$\infty$	0.11
Urethane	96.70	.....	9.72+
Uric acid	0.68	0.61	1.13
Vanillin	67.22	64.30	5.51
Xyloquinone	1.12	4.69	3.02

It will be observed in many cases that the solubilities in the mixtures of the two solvents are often either higher or lower than the solubilities in the respective pure solvents. These peculiarities are most marked in the cases of urea, saccharine, *p*-nitrophenol, acetanilide, resorcinol, piperine, cinnamic acid, and chloral hydrate. The first three gave definite



evidences of molecular-compound formation, either by the evolution of heat in mixing, or by the solidifying of the solutions at certain concentrations, or from the form of the curves obtained. Six compounds were studied in selected concentrations of mixed solvents and the data obtained are given in Tables II and III.

TABLE II.  
SOLUBILITIES IN MIXTURES OF ALCOHOL AND QUINOLINE.

%C <sub>7</sub> H <sub>9</sub> N.	Urea.	Saccharine.	Brucine.	<i>o</i> -Nitrophenol.
0.0	5.00	2.00	3.50	404
10.0	4.00	2.50	3.86	504
23.2	2.50	3.30	10.87	720
37.5	1.80	....	15.09	864
47.5	1.50	....	34.60	1008
50.0	1.05	....	36.50	1005
55.0	0.64	....	....	....
60.0	0.26	6.00	44.60	1152
65.0	0.32	....	....	....
70.0	0.50	7.01	68.20	1224
80.0	0.19	8.05	75.00	1296
90.0	0.10	8.80	78.70	1367
100.0	0.11	10.10	79.00	1450

The urea was estimated by the hypobromite method. The *o*-nitrophenol was estimated colorimetrically in 10% sodium hydroxide solution.

The solubilities of these, therefore, are expressed as grams of solute in 100 cc. of solutions.

TABLE III.

%C <sub>8</sub> H <sub>7</sub> N.	SOLUBILITIES IN MIXTURES OF WATER AND PYRIDINE.		
	Lactose at 1°.	Lactose at 25°.	Raffinose at 25°.
0.0	19.18	23.04	29.83
10.0	17.84	22.35	23.12
20.0	15.29	19.24	22.16
30.0	12.93	15.48	18.88
40.0	9.48	10.56	13.42
50.0	6.87	7.75	9.94
60.0	4.61	5.62	6.51
70.0	2.85	3.22	5.32
80.0	1.62	2.62	7.40
81.4	2.22	2.50	4.49
90.0	1.75	1.77	24.50
91.0	1.83	1.82	24.60
92.0	....	....	24.70
94.0	....	....	36.90
96.0	....	....	41.90
98.0	....	....	45.70
100.0	1.61	2.22	79.08

It will be observed that the solubilities of urea decrease quite regularly as the concentrations of quinoline increase, but at 60% a definite break occurs. At this concentration a molecular compound is formed, as shown by the following method of its preparation.

**Quinoline Tri-urea.**—To 100 cc. of absolute alcohol, sufficient urea was added to saturate at room temperature, then 110 cc. of quinoline was added while the mixture was shaken vigorously. The precipitate first formed was dissolved by gentle warming; on cooling to room temperature and standing for some hours, a white crystalline mass separated. It was filtered and washed with absolute ether. To be certain that the product contained no free urea, it was redissolved by warming in a 60% solution of quinoline in alcohol, and a little alcohol was added. The volume of the latter used was made sufficient to yield on cooling and standing only about one-half of the original precipitate. In this manner short, snow-white needles were obtained. After washing with absolute ether and drying in a desiccator, these crystals gave 31.50% of N. Calc. for C<sub>8</sub>H<sub>7</sub>N<sub>3</sub>CO(NH<sub>2</sub>)<sub>2</sub>: N, 31.70%.

Quinoline tri-urea softens at 150° and melts<sup>4</sup> at 154°. It is insoluble in ether, is easily soluble in alcohol and in hot 60% quinoline solution in alcohol. In moist air it gives off the odor of quinoline; in water it yields an oily layer of quinoline; its ready hydrolysis is indicated here. When heated above 45° ammonia<sup>4</sup> is evolved; at quite elevated temperatures, quinoline is given off. Since quinoline tri-urea and its decomposition products do not yield violet colored salts or solutions with copper sulfate, it is concluded that they do not possess a cyanuric or a biuret structure.

**Quinoline tri-urea chloroplatinate.**—This compound was formed when quinoline tri-urea, dissolved in absolute alcohol, was treated with an alcoholic solution of platonic chloride. The yellow amorphous precipitate upon recrystallization from hot water gave glistening orange needles.

<sup>4</sup> Urea melts at 132° and gives off ammonia only above 110°.

*Analyses.* Calc. for  $C_8H_7N_3CO(NH_2)_2.PtCl_4$ : Pt, 30.00; Cl, 22.01; Found: Pt, 30.07; Cl, 22.26.

This chloroplatinate is quite stable toward hot water, but with alkalis it easily yields free quinoline.

Substituted ureas, such as ethyl urea, diethyl urea, phenyl urea, did not yield by the above method molecular compounds with quinoline. Urea and pyridine also failed to yield a molecular compound.

**Saccharine in Alcohol and Quinoline.**—When the mixtures contained between 20 and 60% of quinoline, they evolved heat and solidified completely. Above 60% concentration, heat was produced and a liquid only was obtained. The indicated molecular compound of saccharine and quinoline was not isolated.

**Brucine in Alcohol and Quinoline.**—The character of this curve indicates a molecular compound. It was not isolated.

**The Nitrophenols in Alcohol and Quinoline.**—The three isomers reveal marked differences.<sup>5</sup> The *para* form gives only a solid in the equimolecular mixture of the two solvents; the *meta* form gives only a solid in pure quinoline; the *ortho* form gives a solubility curve that is nearly straight.

**Lactose in Water and Pyridine.**—The solubility curve indicates the probable formation in solution of a molecular compound.

**Raffinose in Water and Pyridine.**—A remarkable curve was obtained in these solutions and indicates the probable formation of a molecular compound. The original raffinose did not reduce copper solutions; the residues from the solutions, especially those near the 50-50% concentrations did reduce somewhat; the solutions themselves showed little or no reduction. This curve and other problems suggested by this paper will be investigated farther.

### Summary.

In mixtures of alcohol and quinoline and in mixtures of pyridine and water, certain solutes yielded solubility data indicating or demonstrating molecular compounds. Studies of solubilities in mixed solvents seem to offer a convenient method of study of additive tendencies of solute and solvent.

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<sup>5</sup> It was shown by Kerrymann (*Ber.* 39, 1022 (1906)) that *ortho* substituted benzene derivatives form additive compounds much less readily than the *meta* and *para* derivatives. Our data confirm this conclusion.