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EQUILIBRIUM IN THE SYSTEM LITHIUM CHLORIDE:QUINOLINE

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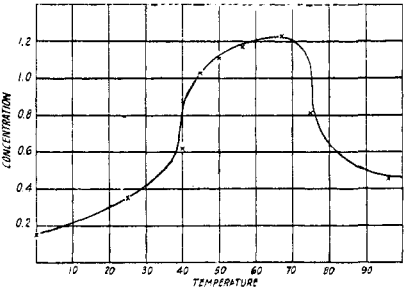
In connection with a series of tests on quinoline as a solvent it was found that the solubility of lithium chloride in this substance decreases markedly with rise in temperature. This difference in solubility is sufficient to produce a fairly voluminous crystalline precipitate when a solution saturated at room temperature is heated to the neighborhood of the boiling point. This paper deals with the solubility of lithium chloride in quinoline at various temperatures.

Experimental

Reagents.—The lithium chloride was the purest obtainable on the market. It was purified by recrystallizing from absolute alcohol and drying at 160°, and was found free from sodium, potassium, and the nitrate and sulfate ions. Analysis of the chlorine content showed the substance to be 99.8% pure.

The quinoline was dried by allowing it to stand over potassium hydroxide, then over barium oxide, from which it was then distilled. The product obtained in this way was amber colored. To obtain an absolutely colorless liquid at least 6 redistillations were necessary. The colorless product obtained in this way distilled at 231.4° at 740.5 mm. The boiling point is given in the literature at 237–239° at 760 mm. On standing in the light, quinoline becomes discolored, but a sample preserved in a bottle coated with asphalt paint showed no change in color after 6 months.

Apparatus.—The samples of the liquid phase were taken in an apparatus described by Walton and Judd[1] which permits the sample to be filtered and collected in a weighing bottle without removing it from the constant-temperature bath. Between 0° and 70° the ordinary type of thermostat was used; above that temperature vapor baths were used, the temperature of the vapors being kept constant by heating them under a pressure that was kept constant by means of an automatic regulator.[2]



Procedure.—The dry lithium chloride and quinoline were placed in the tube and stirred until equilibrium was reached, about 48 hours being necessary. Samples of the liquid phase were taken about every 5 hours and the chlorine content determined by the Volhard method. When this was found to be constant a sample was analyzed for chlorine gravimetrically in the usual way. That the presence of quinoline introduces no error in the determination is

[1] Walton and Judd, THIS JOURNAL, **33**, 1036 (1916).

[2] Mathews and Faville, *J. Phys. Chem.*, **22**, 1 (1918).

shown by the following analyses. The sample of lithium chloride was dissolved in 5 cc. of quinoline; 150 cc. of water and an excess of nitric acid were then added.

Sample G.	AgCl G.	LiCl in sample %	LiCl in absence of quinoline %
0.2455	0.8283	99.91	99.79
0.2506	0.8461	99.76	99.79

In analyzing the solid phase the sample was carefully dried with filter paper and then kept in a desiccator until free from adhering quinoline, and the chlorine content determined gravimetrically.

The following table gives the data obtained in these experiments.

TABLE I

SOLUBILITY OF LITHIUM CHLORIDE IN QUINOLINE

Temperature °C	LiCl per 100 g. of solvent G.	LiCl in solid phase %
0	0.1515	13.92
25	0.3538	13.97
40	0.6175	13.43
45	1.0328	13.90
50	1.1107	14.30
56.4	1.1734	14.22
67	1.2353	14.23
75	0.8180	14.14
96	0.4588	14.33

The composition of the solid phase corresponds to the formula $(C_9H_7N)_2$.LiCl, containing 14.1% of lithium chloride. This compound is very stable at all temperatures between 0° and 97°. A sample standing in a desiccator for 2 weeks showed no change in composition.

Above 67° the length of time necessary to bring about equilibrium resulted in decomposing the quinoline. As a consequence the analyses above this temperature become less accurate. There is evidence of the formation of a new solid phase above 100°, but because of reasons just mentioned its composition was not determined.

The results obtained are shown graphically in the figure. That we have here a single curve and not the intersection of two curves is conclusively proved by the constant composition of the solid phase.

Summary

1. The solubility of lithium chloride in quinoline has been studied between 0° and 97°.

2. The solid phase in equilibrium with the lithium chloride-quinoline solution has the composition, between 0° and 97°, of $(C_9H_7N)_2$.LiCl. This compound has never been reported before.

3. The decomposition of quinoline makes it impracticable to study the solubility above 97°.

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