Solubilities of Lithium Chloride and Lithium Thiocyanate at Low Temperatures

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FOR SEVERAL problems under investigation it was desirable to have more information than is published on the solubilities of lithium chloride in water and in hydrochloric acid and of lithium thiocyanate in water.

The polytherm of lithium chloride has been investigated in parts by several authors (*1-10, 12-14, 16, 18-20*). The existance of the monohydrate and the dihydrate and their temperature limits are well established. The existence of a trihydrate and of a pentahydrate was first proposed by Bogorodski (*4*) and Hüttig and Steudemann (*9*), respectively. Transition points were found by Hüttig by thermal analysis. But the thermal effects at the transition points are only small, so that this method is not very accurate. Determinations of solubilities yield usually more accurate results. But data found in the literature are also conflicting at very low temperatures. The eutectic point of the system LiCl-H_2O was found by Hüttig at −80° C., by Voskrenskaya (*20*) at −66° C., by Foster D. Snell (*19*) and the Department of Chemical Engineering of the University of Maryland (*13*) below −96° C., by Garrett and Woodlow (*7*) at −73° C. with 28.85% LiCl, and finally by Moran (*14*) at −75.9° C. and 25.2% LiCl. It was therefore desirable to redetermine the system LiCl-H_2O.

No values of the system LiCl-HCl-H_2O were available. Very few scattered data are found in the literature on the system LiSCN-H_2O (*11, 15*).

EXPERIMENTAL

System LiCl-H_2O. The lithium chloride used in the following measurements had been purified by several recrystallizations from water, until it was free from sulfate and contained less than 0.001% of calcium plus barium.

In nearly all cases the solubility was found by determining the temperature at which the solid phase disappeared. A quantity of solution (about 15 cc.) was crystallized quickly by cooling to low temperature. Seeding with the proper hydrates was necessary, because otherwise the entire system turned into a highly viscous or even solid, glass-like mass, which could not be crystallized at all. Very fine crystals were obtained. The temperature of the system was then raised slowly—approximately 1° per 15 minutes. This rate was sufficiently low to obtain reproducible values. In that part of the system, where ice exists as the solid phase, undercooling is less severe. But on the other hand, seeding the undercooled solution with ice had no apparent effect. In view of these conditions, the melting points of the ice and the temperatures of complete dissolution of the salt could be found only with the temperature of the system increasing.

For the analyses of lithium, chloride, and thiocyanate, the usual standard methods were used. Many points had to be determined on the solubility curves of the chloride and the thiocyanate because of the low temperature coefficient of the solubilities. The values found are listed in Table I. From comparative measurements it could be estimated that the temperature readings were correct within ±0.25° C. for the medium and within ±0.5° C. for the very low range. The eutectic temperature was found by thermal analysis using a liquid nitrogen bath and by graphic extrapolation. Both methods gave the same value of −84° ±0.5° C. For temperatures above 0° C., the solubility data of Applebey and coworkers (*1, 2*) tie in best with the values found by the author, while older values reported in the literature fall more or less out of line.

System LiCl-HCL-H_2O. From analogy to the corresponding sodium chloride, system, lithium chloride is not expected to form additional compounds with hydrogen chloride. A point of interest was only whether lithium chloride could be precipitated more or less completely by hydrogen chloride from aqueous solutions as sodium chloride can.

The solubility determinations were made at 25° C. The numerical values of Table II are given in weight per cent. For comparison some values of the system NaCl-HCl-H_2O at 30° C. are added (*11*).

The solid phase was lithium chloride monohydrate throughout, as was found by the wet residue method of Schreinemaker (*17*). When plotted, these points form a straight line, confirming that no addition compounds between lithium chloride and hydrochloric acid are formed. The point at which the hydrochloric acid pressure of the saturated lithium chloride solution was equal to the atmospheric pressure (at 750 mm. of Hg., barometric pressure) had the coordinates (26.1, 19.16). The equilibrium was reached from both sides—i.e., by saturating a saturated solution of lithium chloride solution with hydrogen chloride gas as well as by adding solid lithium chloride to a concentrated hydrochloic acid solution of specific gravity of 1.19.

A solution practically free from lithium chloride cannot be obtained by introducing hydrogen into it under ordinary pressure and temperature, as can be done in the system NaCl-HCl-H_2O. The affinity of lithium chloride for water is greater than that of hydrogen chloride, and vice versa, no dehydrating effect of hydrogen chloride upon lithium chloride monohydrate can be expected.

System LiSCN-H_2O. According to the literature, lithium thiocyanate has been prepared by reacting ammonium thiocyanate with barium hydroxide and precipitating barium sulfate with lithium sulfate. It can be prepared equally well, but somewhat simpler, by reacting lithium hydroxide solution directly with solid ammonium thiocyanate. The solution was boiled until no ammonia could be detected in the escaping vapors; enough ammonium thiocyanate was added to bring the pH of the solution at the end of the reaction between 6.5 and 7.0. The solution was then filtered from insoluble compounds such as lithium carbonate and some other impurites, and concentrated for crystallization preferably under vacuum. The crystallized salt was further purified by recrystallization from water. Lithium thiocyanate crystallized in long colorless needles, which were free from iron, sulfates, and calcium (less than 0.001%). A sample of the solid salt was dried over sulfuric acid and analyzed. It was found to contain 6.81% of Li and 57.40% of SCN. The theoretical values for the dihydrate are 6.87 and 57.47%, respectively. Drying the dihydrate over sulfuric acid for several weeks at room temperature and pressure did not dehydrate the salt further. Over phosphorus pentoxide the dihydrate lost water very slowly in the course of several weeks under partial decomposition into yellow to orange compounds.

Solubility was determined as described for lithium chloride (Table III and Figure 1). In analogy to the chloride it can be said that in the temperature range from +43.3° to 1° C., the solid phase is the dihydrate. The trihydrate exists from +1° to −56° C.; and from −56° to −92° C. a higher hydrate, probably the pentahydrate, is the stable solid phase.

Solubility and transition point determinations of lithium thiocyanate were made only twice in the past, and then

Table I. The System $LiCL-H_2O$

Temp., ° C.	LiCl in Soln., Weight %	Solid Phase
0	0	Ice
−5.1	5.2	Ice (*6*)
−12.2	9.65	Ice (*6*)
−18.75	13.0	Ice
−25.4	15.7	Ice (*6*)
−39.0	18.8	Ice
−48.5	21.2	Ice
−55.0	22.2	Ice
−64.0	23.6	Ice
−65.0	23.8	Ice
−68.0	24.2	Ice
−84.0	25.2	$LiCl\cdot 5H_2O$ + ice[a]
−78.5	25.9	$LiCl\cdot 5H_2O$
−73.0	27.2	$LiCl\cdot 5H_2O$
−70.0	28.2	$LiCl\cdot 5H_2O$
−67.0	29.5	$LiCl\cdot 5H_2O$[b]
−65.0	30.8	$LiCl\cdot 5H_2O$[b]
−67.2	29.3	$LiCl\cdot 5H_2O$ + $LiCl\cdot 3H_2O$[c]
−67.5	29.2	$LiCl\cdot 3H_2O$
−60.0	30.0	$LiCl\cdot 3H_2O$
−54.5	30.6	$LiCl\cdot 3H_2O$
−51.0	30.8	$LiCl\cdot 3H_2O$
−49.5	31.4	$LiCl\cdot 3H_2O$
−41.0	32.45	$LiCl\cdot 3H_2O$
−36.0	33.5	$LiCl\cdot 3H_2O$
−34.5	34.1	$LiCl\cdot 3H_2O$
−29.0	35.0	$LiCl\cdot 3H_2O$
−27.0	35.5	$LiCl\cdot 3H_2O$
−26.0	35.8	$LiCl\cdot 3H_2O$
−25.5	36.15	$LiCl\cdot 3H_2O$
−20.0	37.3	$LiCl\cdot 3H_2O$
−19.0	38.0	$LiCl\cdot 3H_2O$ + $LiCl\cdot 2H_2O$[c]
−25.2	37.3	$LiCl\cdot 2H_2O$[b]
−15.0	38.3	$LiCl\cdot 2H_2O$
−12.0	38.6	$LiCl\cdot 2H_2O$
−8.5	38.9	$LiCl\cdot 2H_2O$
+1.05	40.9	$LiCl\cdot 2H_2O$ (*2*)
+3.0	41.2	$LiCl\cdot 2H_2O$
+10.05	42.71	$LiCl\cdot 2H_2O$ (*2*)
+12.1	43.2	$LiCl\cdot 2H_2O$
+15.2	44.06	$LiCl\cdot 2H_2O$ (*2*)
+18.25	44.86	$LiCl\cdot 2H_2O$ (*2*)
+19.0	45.2	$LiCl\cdot 2H_2O$ + $LiCl\cdot H_2O$ (*1*)[d]

[a] Eutectic points.
[c] Transition points. [b] Metastable points.

Table II. The System $LiCl-HCl-H_2O$

LiCl	HCl	Solid Phase	NaCl	HCl	Solid Phase
45.8	0.	$LiCl\cdot H_2O$	26.47	0	NaCl
42.0	4.6	$LiCl\cdot H_2O$	16.16	6.93	NaCl
35.0	11.0	$LiCl\cdot H_2O$	9.35	12.5	NaCl
26.1	19.16	$LiCl\cdot H_2O$	0.11	35.6	NaCl

Table III. The System $LiSCN-H_2O$

Temp., ° C.	Solid Solid Phase	LiSCN in Solution, Weight %
−7.5	Ice	10.19
−17.9	Ice	18.00
−25.0	Ice	21.34
−33.0	Ice	24.7
−62.5	Ice	33.0
−65.5	Ice	33.75
−92.0	$LiSCN\cdot 5H_2O$ + ice[a]	38.2
−77.0	$LiSCN\cdot 5H_2O$	39.9
−68.5	$LiSCN\cdot 5H_2O$	40.9
−59.0	$LiSCN\cdot 5H_2O$	42.3
−56.0	$LiSCN\cdot 5H_2O$ + $LiSCN\cdot 3H_2O$[b]	43.0
−49.0	$LiSCN\cdot 3H_2O$	43.6
−42.0	$LiSCN\cdot 3H_2O$	44.4
−35.0	$LiSCN\cdot 3H_2O$	45.1
−28.0	$LiSCN\cdot 3H_2O$	45.8
−16.5	$LiSCN\cdot 3H_2O$	47.3
−12.5	$LiSCN\cdot 3H_2O$	47.9
−5.0	$LiSCN\cdot 3H_2O$	48.9
0.0	$LiSCN\cdot 3H_2O$	50.0
+1	$LiSCN\cdot 3H_2O$ + $LiSCN\cdot 2H_2O$[b]	50.2
−2.0	$LiSCN\cdot 2H_2O$[c]	49.8
+3.0	$LiSCN\cdot 2H_2O$	50.3
+6.0	$LiSCN\cdot 2H_2O$	50.96
+12.0	$LiSCN\cdot 2H_2O$	51.68
+16.5	$LiSCN\cdot 2H_2O$	52.52
+24.5	$LiSCN\cdot 2H_2O$	54.1
+27.0	$LiSCN\cdot 2H_2O$	55.4
+28.0	$LiSCN\cdot 2H_2O$	55.5
+32.5	$LiSCN\cdot 2H_2O$	56.3
+40.3	$LiSCN\cdot 2H_2O$	60.5
+43.0	$LiSCN\cdot 2H_2O$	63.8
+43.3	$LiSCN\cdot 2H_2O$[d]	64.3

[a] Eutectic points. [b] Transition points.
[c] Metastable. [d] Congruent melting point with 64.3% LiSCN corresponding to the dihydrate.

Table IV. Comparison of LiSCN Solubilities

Temp., ° C.	LSCN, %	
	Iwase	Author
20	53.2	53.2
25	54.4	54.5
30	55.9	56.7
35	57.7	58.8
40	60.4	60.4

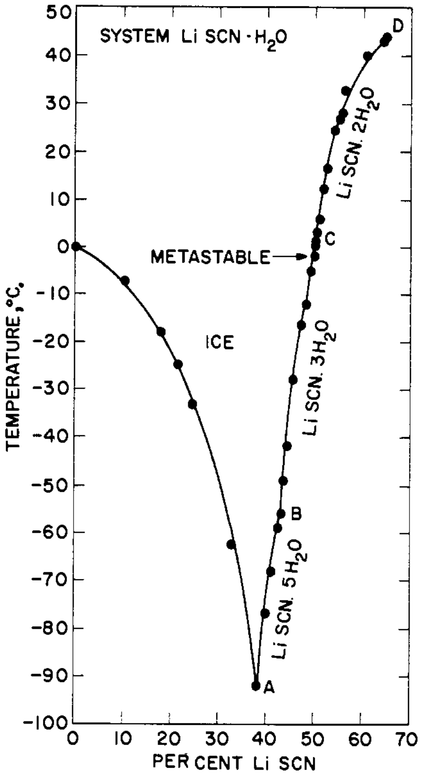

Figure 1. Solubility values for lithium thiocyanate at different temperatures

only over a very limited temperature range, by Nikolaev (*15*) and Iwase (*11*). Nikolaev's value for the solubility of lithium thiocyanate of 63.3% at 17° C. and for the eutectic point of −33° C. are entirely out of line. Iwase found the values listed in Table IV. He concludes that a transition point exists at +34° C. In view of the melting point of the dihydrate at +43.3° C. and the existence of three more transition points at 1°, −56°, and −92° C., another point of transition at +34° C. would require the existence of a greater number of hydrates than with any of the other lithium halides, which is not very probable.

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