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Solubility of Lithium Bromide in Water between -50° and +100° C. (45 to 70% Lithium Bromide)

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The solubility curve between 45 and 70 weight % lithium bromide was studied and compared with published results. Solubility measurements were in good agreement with reported values obtained using the same technique. The addition of a small amount of lithium hydroxide or hydrogen bromide has a minimal effect on the solubility of lithium bromide.

THE SOLUBILITY of lithium bromide in water has been studied by many investigators as listed by Linke and Seidell (*6*), who point out that there is poor agreement among published values, especially in the range of interest to the air-conditioning field (*2*, *9*). The spread of these values is demonstrated in Figure 1, which illustrates why this system has remained a subject for continuing research.

The present study attempts to define the solubility curve, correlate the results with literature values, and show the effects of a small excess of lithium hydroxide and hydrogen bromide on the solubility, in the temperature range between −50° and +100° C. which encompasses a concentration of 45 and 75 weight % lithium bromide.

EXPERIMENTAL

Pure LiBr was prepared in solution from certified ACS HBr (Fisher Scientific Co.) and spectrographically pure Li_2CO_3 (Foote Mineral Co.). Recrystallized $LiOH \cdot H_2O$ or HBr was added to adjust the pH to 7. The pH of the neutral brine was measured on a diluted sample (1 part of brine to 10 parts of distilled water). The desired concentration was finally obtained by evaporation or addition of water to ensure the presence of both a solid and a liquid phase. The bromide ion concentration in the saturated solution was determined by titration techniques using standardized silver nitrate and potassium chromate as an indicator.

The solubility technique involved maintaining the solid and liquid phase together in a sealed polypropylene container submerged in a constant temperature bath for a minimum of 3 hours, with stirring. Samples maintained at constant temperature for a longer time (15 hours) did not give different values, indicating that equilibrium was attained. After the 3-hour period, the temperature of the mixture was measured at 1-hour intervals using copper-constantan thermocouples and a Wheatstone bridge.

Before the liquid phase was sampled, stirring was stopped and solids were allowed to settle. The clear solution was transferred rapidly to a weighing bottle using a pipet. Mixtures maintained above room temperature were sampled with a heated pipet to prevent crystallization from the saturated solution. This precaution assures that the sample weighed for analysis is representative of the solution maintained at constant temperature. Three samples were taken for each determination, weighed in sealed weighing bottles, diluted, and titrated.

RESULTS AND DISCUSSION

In Figure 1 the results given in Table I compare favorably with the published solubility data of Kessis (*5*). The breaks in the curve are due to the changes in the composition of the solid phases—i.e., $LiBr \cdot 5H_2O \rightleftarrows LiBr \cdot 3H_2O$ at −51.2° C. and 45.7% LiBr, $LiBr \cdot 3H_2O \rightleftarrows LiBr \cdot 2H_2O$ at 2.9° C. and 58.2% LiBr, and $LiBr \cdot 2H_2O \rightleftarrows LiBr \cdot H_2O$ at 42.8° C. and 64.7% LiBr (*5*). A small amount of lithium hydroxide or hydrogen bromide in solution is shown in Table II to have a negligible effect on the solubility.

Linke and Seidell (*6*) showed concern for the lack of reproducibility for solutions saturated with lithium bromide dihydrate between 5° and 35° C. Special emphasis was given to the fact that the solubility determination by Scott and Durham (*8*) at 25° C. (60.4% LiBr) is in considerable disagreement with the other results reported. The data listed by Linke and Seidell are illustrated in Figure 1, which shows Scott's determination to be in agreement with the present study.

Lack of consistency may be due to the different techniques each author used to overcome the tendency of saturated lithium bromide solutions to supercool, and methods of determining the liquidus temperature upon heating after the solid phase had formed (*1, 3, 4*).

Solubility determinations at constant temperature, as opposed to the melting point technique, have been shown to be consistent with one another (*5, 8*). This technique ensures that equilibrium is reached between the solid and liquid phases.

The cooling curve method of determining the saturation temperature recently used by Maust (*7*) considers the supercooling property of LiBr solutions. The two samples studied gave saturation temperatures of 31.83°

Table I. Solubility of Pure LiBr in Water

Temp., ° C.	S. D.[a]	LiBr, Wt. %	S. D.[a]
−53.61	0.12	45.20	0.11
−49.32	0.09	48.03	0.07
−42.12	0.19	49.63	0.56
−36.32	0.58	50.09	0.53
−32.96	0.27	50.50	0.12
−29.17	0.20	51.20	0.47
−25.24	0.11	51.70	0.11
−16.11	0.16	51.95	0.17
−13.47	0.05	53.70	0.07
− 8.94	0.04	54.75	0.18
− 4.54	0.01	55.92	0.09
+ 1.11	0.13	56.81	0.55
5.10	0.15	57.22	0.12
9.93	0.03	58.08	0.13
18.99	0.06	58.67	0.02
24.29	0.07	60.63	0.11
33.14	0.05	62.50	0.08
38.26	0.19	63.96	0.01
44.27	0.10	65.17	0.09
50.35	0.03	65.82	0.07
57.58	0.02	66.16	0.04
63.42	0.06	66.55	0.16
70.90	0.21	67.37	0.15
71.69[b]	0.05	67.39	0.09
82.68	0.11	68.32	0.11
83.11[b]	0.08	68.27	0.16
91.36	0.08	68.99	0.06
91.82[b]	0.03	69.05	0.08
102.02	0.05	70.08	0.19
101.05[b]	0.04	70.04	0.19

[a] Standard deviation.
[b] Separate determinations on different sample.

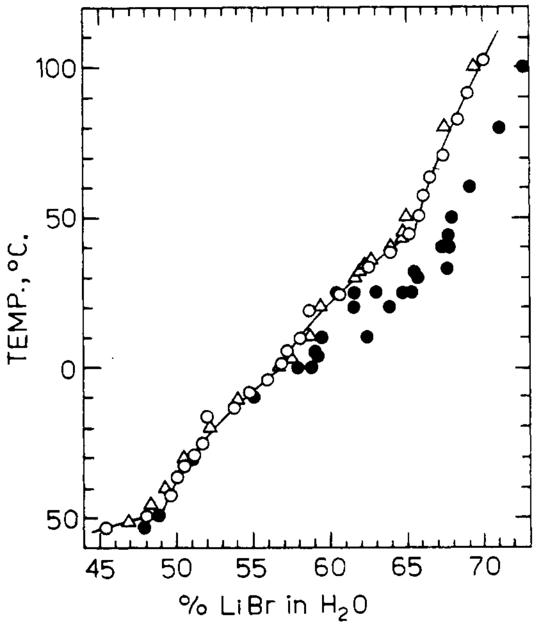

Figure 1. Solubility of LiBr in H_2O

○ Present study
△ Kessis
● Linke and Seidell

Table II. Solubility of LiBr in Solutions Containing Small Amounts of HBr or LiOH

Sample	Temp., ° C.	%LiOH	%HBr	%LiBr
A[a]	43.19	. . .	. . .	64.3
B[b]	43.28	. . .	. . .	64.1
C[c]	43.27	. . .	0.17	63.7
D[d]	43.29	0.11	. . .	63.8
E[e]	43.32	0.27	. . .	63.7
A	10.34	. . .	. . .	58.2
B	10.34	. . .	. . .	58.1
C	10.39	. . .	0.36	57.8
D	10.33	0.14	. . .	58.0
E	10.34	0.23	. . .	58.4
A	−20.47	. . .	. . .	51.6
B	−20.64	. . .	. . .	51.6
C	−20.33	. . .	0.12	51.6
D	−20.49	0.07	. . .	51.5
E	−20.55	0.21	. . .	51.4

[a] Prepared from standard Li_2CO_3.
[b] Prepared from spectrographically pure Li_2CO_3 (Foote Mineral Co.).
[c] Excess H^+.
[d] Excess OH^-.
[e] Excess OH^-.

and 59.6° C. for 62.38 and 66.2% LiBr in water, respectively, in agreement with the present solubility study.

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Liquid Hydrogen Sulfide in Contact with Sulfur

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Sulfur in contact with liquid hydrogen sulfide at equilibrium pressure was studied between −81° and 120° C. The solubility of solid sulfur is 5×10^{-6} mole of S_8 per gram of H_2S at −80° C. and 5×10^{-5} at 80° C. Over this range, log solubility vs. $1/T$ gives a straight line. From a least squares analysis of the data, $\Delta H_8 = 2.1 \pm 0.1$ kcal. per mole. From 80° to −80° C., the solubility can be represented by $\log S = \frac{-4.52 \times 10^2}{T} - 3.00$. In contact with liquid H_2S, sulfur melts at 98° C., below the critical point of H_2S. The melting point depression of sulfur is about 20° C., indicating that H_2S dissolves appreciably in solid sulfur. NMR spectra show that no detectable chemical reaction occurs up to 120° C. Photolysis yields a white, finely powdered precipitate, probably photosulfur, which redissolves or converts to orthorhombic sulfur within 4 weeks after irradiation; no sulfanes are formed. Slow reaction occurs between liquid sulfur and gaseous H_2S above 150° C.

THE MUTUAL SOLUBILITY of sulfur and hydrogen sulfide has been studied under three conditions: gaseous hydrogen sulfide and liquid sulfur; solid sulfur and gaseous hydrogen sulfide; and solid sulfur and liquid hydrogen sulfide. In the first system, Fanelli (*4*) observed that the solubility of hydrogen sulfide goes through a maximum between 150° and 200° C. In this range pure liquid sulfur undergoes a marked viscosity change and its color turns from yellow to red. The presence of hydrogen sulfide suppresses the viscosity increase.

In recent years, Hyne and coworkers (*5*) and Wiewiorowski and Turro (*15, 16*), using NMR and infrared spectra, established that the solution undergoes a slow chemical reaction, yielding long sulfane chains of unknown length. In a study (*14*) of sulfur solubility in gaseous hydrogen sulfide at pressures between 40 and 400 atm., results indicate increased sulfur transport by high pressure gas. It is not yet established whether sulfanes form. In the present work our attention is directed towards the system liquid hydrogen sulfide-solid sulfur, which has been least studied. Several publications (*1, 3, 6, 7, 11*) before 1934 mention it in a vague fashion, without reporting numerical data. No recent data are available.

The purpose of the present study is to determine the general behavior of the system, rather than to record very accurate data. Three types of experiments were performed, to establish solubility limits, to explore the critical region of H_2S in the presence of sulfur, and to study possible reactions and reaction products, especially sulfanes.

EXPERIMENTAL

Dried Matheson C.P. grade hydrogen sulfide was condensed into a reservoir bulb and vacuum-distilled into the sample tubes. High purity filtered sulfur (99.99%) was donated by the Freeport Sulphur Co.

For the solubility determination, sulfur was measured into a glass tube 6 cm. long and 6 mm. in o.d., which was then connected to a vacuum system. After evacuation, a known amount of hydrogen sulfide was condensed in the tube at 77° K., and the tube was evacuated and sealed. The elemental sulfur content was determined in either of two ways: Sulfur crystals were