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The Solubility of Water in Molten Mixtures of LiCl and KCl¹

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The solubility of water in molten mixtures of 50.0, 53.0, 60.0 and 68.6 mole % LiCl in KCl has been determined at 480°, and 50.0 and 60.0% at 390°, over the pressure range 3 to 26 mm. The solubility follows Henry's law to 18 mm. at 480° and 14 mm. at 390°. The reciprocal Henry's law constants are, respectively, 14, 11.8, 11.3 and 10.8 micromoles water per mole LiCl per mm. at 480°, and 30.0 and 30.5 at 390°. Heats of solution of -8 and -11.0 kcal. mole⁻¹ are calculated for the 50 and 60% compositions, respectively. The solubility at 480° exhibits a sharp upward break beyond 18 mm. due to hydrolysis of the LiCl at the higher water pressures. At 390° no such behavior is observed, but only a slight upward deviation above about 14 mm. The uniqueness of the lithium ion in this process, and the unusual tenacity with which water is retained by the melt are discussed.

Introduction

Although the marked hydrolysis of the low molecular weight alkali and alkaline earth halides is a well-known phenomenon, until recently there has been virtually no recognition of the actual retention of water by such molten systems. Laitinen, *et al.*,² found large residual currents due to water in LiCl-KCl melts used for microelectrode polarographic studies, and accordingly developed a procedure that satisfactorily eliminated this impurity. A greater reactivity of LiCl compared to the sodium and potassium salts also has been reported in corrosion studies of nickel, copper, iron and stainless steels by molten alkali^{3,4} and alkaline earth⁵ chlorides. Similar effects have been noted by Jennings.⁶

The retention of water by molten systems containing lithium chloride was noted several years ago in this Laboratory during some qualitative studies on metal displacement series in fused salts, metals such as magnesium, zinc, cadmium, tin, lead, nickel and bismuth displacing hydrogen therefrom. Moreover, the water contained in melts prepared from shelf chemicals was removed only slowly *in vacuo*. Subsequently the solubility of water in molten mixtures of lithium and potassium chloride has been determined directly by measuring the amount of water absorbed by the dry melt.

Results and Discussion

The solubility of water in molten LiCl-KCl mixtures containing 50.0, 53.0, 60.0 and 68.6 mole % LiCl has been determined at 480°, and 50.0 and 60.0%, at 390°. The data shown in Fig. 1 for the 60% mixture at pressures to 18 mm. are representative of the other compositions.

The solubility follows Henry's law to 18 mm. pressure at 480°, and to about 14 mm. at 390°. The values of the reciprocal Henry's law constant, k^{-1} , for the 50, 53, 60 and 68.6% mixtures at 480° are, respectively, 14, 11.8, 11.3 and 10.8 $\mu\text{mole mole}^{-1} \text{mm.}^{-1}$ (micromoles water per mole LiCl per millimeter pressure). The value for the 50%

sample is somewhat in doubt. At 390° the constants are 30.0 and 30.5 $\mu\text{mole mole}^{-1} \text{mm.}^{-1}$ for the 50 and 60% compositions, respectively.

Under proper conditions the technique described in the Experimental section for drying the salts is quite effective, and, as shown in Fig. 1, the data

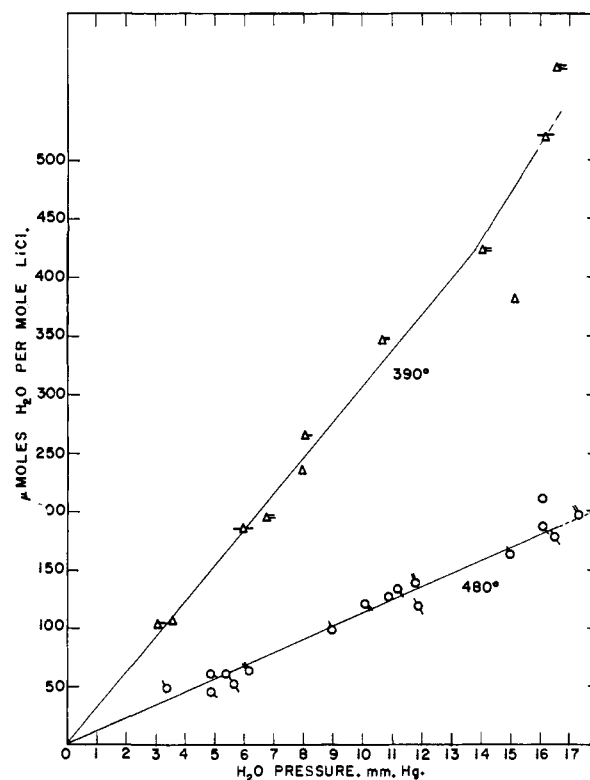


Fig. 1.—Water absorption by mixture of 60 mole % LiCl in KCl at 390 and 480°; 0 to 18 mm.

obtained extrapolate to the origin. As would be expected, failure to remove all the water prior to the equilibration results in a lower line of the same slope. Similar Henry's law dependence of water solubility on pressure also has been observed in work underway in this Laboratory with lithium-containing nitrate and perchlorate mixtures.⁷

The solution of hydrogen chloride in the dry, 60% melt also shows a linear pressure dependence up to 90 mm., with k^{-1} about 1 $\mu\text{mole mole}^{-1} \text{mm.}^{-1}$ at 480°. However, the extrapolated solu-

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) H. Laitinen, W. Ferguson and R. Osteryoung, *J. Electrochem. Soc.*, **104**, 516 (1957).

(3) E. Gurovich, *Zhur. Priklad. Khim.*, **27**, 425 (1954).

(4) V. Kochergin and G. Stolyarov, *ibid.*, **29**, 730 (1956).

(5) V. Kochergin, M. Garpinenko, O. Skornyakova and M. Minulina, *ibid.*, **29**, 566 (1956).

(6) C. Jennings, *J. Electrochem. Soc.*, **103**, 531 (1956).

(7) F. R. Duke and A. S. Doan, unpublished research.

bility at zero pressure amounts to 10 to 45 $\mu\text{mole mole}^{-1}$, indicated a small residual concentration of hydroxide in the dried melts ($< 8 \times 10^{-4} N$). Variations in the hydroxide content of the initial melts had no detectable effect on the water solubility results.⁸

Heats of solution of water of -8 and -11.0 kcal. mole^{-1} are obtained for the 50 and 60% mixtures, respectively. The relationship between $\log k$ and $1/T$ was assumed linear, as data were available at only two temperatures. Again it should be noted that the value for the 50% composition is probably less reliable. Although these heats are comparable with the heat of condensation of water at room temperature, the temperatures used here are considerably above the critical point of water.

Since the constant k^{-1} for the water solubility decreases less than 10% for an increase of 15% in LiCl at 480°, and is essentially invariant at 390°, the other component, KCl, appears to function only as a diluent. In contrast, a much greater change in the opposite direction is found in the ternary alkali nitrate systems.⁷

Appreciable solution of water in molten alkali salts seems to be limited to those systems containing lithium; this, of course, may be attributed to the greater acidity or polarizing power of this ion. Other polar molecules might be expected to show measurable solubilities in molten lithium salts, as does HCl. Fused chlorides containing the smaller alkaline earth ions (Ca^{+2} , Mg^{+2}) also should show appreciable interaction with water.

At 480° the acidic character of the lithium ion causes appreciable hydrolysis at water pressures above 18 mm., and the heretofore simple solubility curve undergoes a sharp break above that point, the apparent slope then being about 140 $\mu\text{mole mole}^{-1} \text{ mm.}^{-1}$. While an amount of HCl corresponding to less than 2 $\mu\text{mole mole}^{-1}$ (the limit of detection) was found in the water vapor in the apparatus after a series of absorptions to a final pressure of 16 mm., considerable quantities of HCl were contained in the water which remained after experiments that extended to higher final pressures. As much as 200 $\mu\text{mole mole}^{-1}$ was found after measurements to a final pressure of 26 mm.

The 390° curve exhibits a slight upward deviation above about 14 mm., but no break below 26 mm. comparable to that found at the higher temperatures. This in itself is evidence that the behavior so pronounced at 480° is not due to a new type of hydration process, since this would be more evident at the lower temperature.

The temperature gradient present in the apparatus used prevents a quantitative treatment of the hydrolysis reaction, since it has been found that water and HCl undergo partial association at room temperature.⁹ Since this interaction is doubtless negligible at 480°, the composition of the gas

(8) Hydroxide rather than oxide is probably present under these conditions. Extrapolation of the data of Gregory and Mohr, *THIS JOURNAL*, **77**, 2142 (1955), gives a dehydration pressure of 2.5 mm. over LiOH(s) at 480°. An ideal solution of 40 $\mu\text{mole LiOH per mole LiCl}$ in the 60% mixture would have an equilibrium pressure of 1×10^{-4} mm. H_2O , approximately the residual pressure in the system.

(9) For example, at 35° 20 mm. H_2O and 3.5 mm. HCl are in equilibrium with about 2.5 mm. of associated products.

above the salt is determined by steady-state diffusion conditions.

Although lithium chloride is unique among the alkali chlorides in forming solid hydrates under ordinary conditions, dehydration of $\text{LiCl} \cdot \text{H}_2\text{O}$ to the anhydrous salt takes place at 94°. The methods reported for drying lithium halides^{2,11} have emphasized the need for removal of water at low temperatures and, in any case, below the melting point of the salt. This condition not only limits the extent of hydrolysis but also takes advantage of the instability of the solid hydrates at moderate temperatures. However, as observed by Briner and Roth,¹² once the melting point has been exceeded, hydrolysis becomes more pronounced, since the hydroxide formed can dissolve in the molten halide. Similarly, a species which can be considered to be the hydrated lithium salt or ion can then also exist in dilute solution, thereby allowing interactions of the sort described here to occur at higher temperatures. As expected, evolution of water from the salt was noted when it solidified.

In addition to the reversible absorption of water in dry LiCl-KCl melts as already described, it has been observed that mixtures prepared directly from commercial chemicals retain larger amounts of water with considerable tenacity. After evacuation of such a preparation for 1 hour at 480° (unstirred), 1.7 to 4 millimoles of water per mole of LiCl are still present, considerably greater than that obtainable by direct absorption at pressures used here. Lesser amounts remain even after evacuation with stirring for 6 to 8 hours, or heating to 800°. As expected, under vacuum conditions such a melt undergoes appreciable hydrolysis; the over-all ratio of evolved water to HCl in one case was 4.5. The hydrolysis rate changes in the expected manner with the addition of basic or acidic salts.¹² In contrast to the behavior of LiCl solutions, a 62 mole % mixture of NaCl in KCl heated to 700° and then evacuated for 1/4 hour showed no detectable water content ($< 16 \mu\text{mole H}_2\text{O per mole NaCl}$).

Experimental

Materials.—LiCl (Baker or Baker and Adamson Reagent) and KCl (Baker) were weighed directly and placed in a 3×5.5 cm. Pt crucible for drying. The weight of the LiCl was corrected for loss of moisture on drying (1.4 wt. % average); no correction was necessary for KCl. HCl (Matheson Anhyd.) was dried by passing through a trap cooled to -80° . Variation of the total sample weight from 20 to 30 g. had no effect on the results.

Drying Procedure.—A modification of the method described by Laitinen and co-workers² was used. The vessel was designed so that alternate evacuation and HCl flushing could be accomplished, and so that the crucible could be transferred to the absorption apparatus after drying. The first evacuation proceeded for 20 hours at room temperature, after which the HCl was passed through the salt and the temperature gradually raised to 345° (LiCl-KCl eutectic, 352°) over a period of 2 to 3 hours. After evacuation for 4 hours the HCl treatment was repeated as the salt was melted and heated to 500°. After another evacuation the hot crucible was rapidly transferred to the preheated absorption vessel which was then evacuated to $< 10^{-4}$ mm.

Shorter periods of evacuation at room temperature gave melts containing residual water, as detected by subsequent

(10) H. Moran, *J. Phys. Chem.*, **60**, 1666 (1956).

(11) H. Gardner, C. Brown and G. Janz, *ibid.*, **60**, 1458 (1956).

(12) E. Briner and P. Roth, *Helv. Chim. Acta*, **31**, 1352 (1948).

solubility measurements. Passage of HCl through such a melt for 1 hour did not completely remove the water.

Solubility Measurements.—The apparatus consisted of a globe of known volume, a water reservoir, a mercury manometer, and the absorption vessel holding the salt crucible. The absorption vessel consisted of two concentric Pyrex tubes, both closed at the top, with space between the upper ends for the crucible. The outer tube was connected through a stopcock to the globe. The open bottoms of the tubes were joined with a 45/50 $\frac{1}{8}$ joint that projected below the furnace. The volume of the vessel was kept as small as possible by using closely fitted tubing.

The total apparent volume of the system was determined for each run under operating conditions by a helium or nitrogen calibration. The globe was filled to about 30 mm. and then was opened to the absorption vessel. The apparent volume was calculated from the two pressures, these being measured to ± 0.1 mm. with an Eberbach cathetometer.

Solubility measurements were made by following a similar sequence of operations with water vapor, the initial pressure in this case being that obtained immediately after H_2O vapor was admitted to the salt vessel. Solubility calculations were made using the ideal gas equation, which was adequate in the temperature and pressure ranges used. About 4 hours was required for equilibrium with a salt sample of 25 g. and a pressure drop of 4 mm. Six to 8 hours was required at final pressures above 18 mm. due to the slow hydrolysis reaction and diffusion of HCl to cooler parts of the apparatus. At least 4 measurements at successively higher pressures were made on each salt sample. Ambient temperatures of 34° were necessary to prevent condensation. The average deviations of solubility results in the low pressure region were 3%.

The furnace was controlled to $\pm 1^\circ$ by a Brown Elec-

tronik proportioning controller. After a run the actual salt temperature was also checked by dipping a thermocouple into the salt.

Distillation of the salt from the crucible was kept to a minimum by avoiding sharp temperature gradients near the salt. The method of stirring, which employed a glass-enclosed, magnetic stirring bar driven by a magnet revolving just below the crucible, introduced no troublesome temperature gradients. The adsorption of small amounts of water by any film of salt that did collect on the container walls was not reflected in the pressure drop used in the calculations since this process took place rapidly before the initial pressure reading was made.

Vacuum Hydrolysis.—A number of experiments relating to the water content and hydrolysis of untreated melts were performed. Nine grams of a 68% mixture prepared directly from bottled chemicals was melted under an argon atmosphere and then evacuated for 1 hour. The subsequent rate of hydrolysis was measured by collection of HCl in one of two parallel traps cooled with liquid N_2 , followed by titration with a mixed brom thymol blue, phenol red indicator. Hydrolysis was enhanced by $PbCl_2$, $NaPO_3$, Pb, Zn and Bi, and eliminated by the addition of 1 mole% LiOH. In some cases the simultaneous loss of water and HCl was measured by weighing the collected sample prior to titration of the acid. Stirring increased the relative rate of water loss.

The results of quantitative measurement of total water content or reactivity toward a given metal of such preparations were found to be somewhat irreproducible and dependent on the history of the sample in an indeterminable manner.

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[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DIVISION, ARGONNE NATIONAL LABORATORY]

The Dissociation Pressure of Sodium Bifluoride—the Free Energy and Enthalpy Change for the Reaction $NaHF_2(s) \rightarrow NaF(s) + HF(g)$ from 157 to 269°¹

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The dissociation pressure of sodium bifluoride has been determined from 157 to 269° in a nickel and Monel system. Equations for the free energy change and the average enthalpy change from 157 to 269° were obtained for the reaction $NaHF_2(s) \rightarrow NaF(s) + HF(g)$.

Sodium fluoride is often used as an absorbant for hydrogen fluoride and sodium bifluoride is used as a source of hydrogen fluoride. Sodium fluoride-zirconium fluoride mixtures are used, in their molten state, as media for the hydrofluorination of uranium in zirconium matrix fuel elements, in a process for the recovery of uranium from spent fuels. The dissociation pressure of sodium bifluoride and the thermodynamic information that can be derived from it are therefore very important.

Experimental

Materials.—Merck reagent grade sodium fluoride was used after volatile impurities were vacuum distilled from the salt. Hydrogen fluoride obtained from the Harshaw Chemical Company was purified by vacuum distillation. Hydrogen and other non-condensable gases were distilled from the solid hydrogen fluoride, contained in a nickel vessel cooled with liquid nitrogen. The hydrogen fluoride was then distilled from the vessel, cooled with "Dry Ice" and collected in a nickel storage vessel. This procedure was repeated several times and the vapor pressure of the hydrogen fluoride prepared in this manner agreed with the literature value at zero degree.² The vapor density of the product de-

termined by the Regnault method at 100° and 657 mm. pressure was 20.3 g./GMV, which is in good agreement with the formula weight of 20.01. The deviation from ideal gas behavior is small and the effect of any impurity would be evident.

Apparatus.—The apparatus was constructed with nickel and Monel components, which were either welded together or joined by Teflon gasketed, flared connectors. The component parts were separated by Monel, Teflon seated, bellows valves. The pressure measurements were made in a Monel vessel 6 inches long made from 1 inch Monel tubing. A thermocouple well extended into the bottom of the tube. The pressure measuring vessel was welded to a 20 inch long, $\frac{3}{8}$ inch nickel tube, which was flared at the open end and connected to a Booth-Cromer pressure transmitter and self-balancing relay.³ The transmitter served to isolate the system containing the reactants from the mercury manometer used to measure the pressure with a precision of ± 0.2 mm. The pressure measuring vessel and transmitter were connected to a manifold, which was connected to a helium supply, hydrogen fluoride storage vessel, traps and vacuum system, that could be evacuated to one micron, as detected with a thermocouple gage. The hydrogen fluoride storage vessel was kept at room temperature. Manifold, gas measuring vessels, pressure transmitters and the line leading to the pressure measuring vessel were kept between 100 and 105° by containing them in an insulated, thermostated box in which air was circulated. The pressure measuring vessel

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) R. L. Jarry and W. Davis, Jr., "The Vapor Pressure, Association, and Heat of Vaporization of Hydrogen Fluoride," Carbide and Carbon Chemical Co., K-25 plant, Oak Ridge, Tenn., K-968, 10, 1952.

(3) S. Cromer, "The Electronic Pressure Transmitter and Self-Balancing Relay," S.A.M. Laboratories, Columbia University, MDDC-803, 1947.