Vapor Pressure Measurements of Hygroscopic Salts

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Vapor pressure measurements of several hygroscopic salts are reported in the temperature range of 20° to 80° C. An experimental method for the determination of the transition point for the hydrates is established. Vapor pressure–composition diagrams are presented for lithium chloride and lithium nitrate salts in the above temperature range. Other salts, such as rubidium fluoride, cesium fluoride, and lithium hydroxide, are also studied and their vapor pressure data reported. The values for the heat of adsorption and entropy change of different salts studied in this work are calculated.

THE MEASUREMENT of the vapor pressure of hydrated crystals has been the subject of controversy and has created and maintained lively interest among many investigators. The many different methods of measurement in use do not give concordant results. Interest has been stimulated by the increasing importance of these salts in many diversified fields.

A great variety of methods for measuring the vapor pressure of hydrates have been developed, and these methods can be classified under three catetories: static methods, dynamic methods, and indirect methods. A critical survey of these methods has been presented by Menzies (*4*), Wilson (*7*), and more recently by Gokcen (*3*).

From the measurements of the vapor pressures of the various salts by the different methods used by the investigators, it has been established that each method had its inherent inaccuracy. The anomaly in the results was attributed mainly to experimental errors and to the necessary corrections.

The problem was to determine with accuracy the vapor pressure of hygroscopic salts. Lithium chloride was of prime interest. Its use in air conditioning, refrigeration systems, etc. has increased its importance in recent years. While many investigators have measured the vapor pressure of saturated solutions of lithium chloride, few have paid attention to solid hydrates. Appleby *et al.* (*1*) determined the vapor pressure of saturated solutions using a static method. His measurements did not agree with similar ones by Gokcen (*3*). The only systematic studies of the solid hydrates of lithium chloride have been made by Slonim and Hüttig (*5*). Although many investigators have measured the vapor pressure of these hydrates near their melting points, very little is known about their vapor pressures at ordinary temperatures.

In the present work an attempt was made to select and develop a simple technique which would measure low vapor pressure of hygroscopic salts with accuracy. The vapor pressure–composition chart for lithium chloride salt is constructed for ordinary temperatures. Vapor pressure is determined as a function of temperature for many hygroscopic salts. These include rubidium fluoride and cesium fluoride, for which very little information is available in the literature, and also lithium nitrate and lithium hydroxide.

APPARATUS FOR DETERMINING VAPOR PRESSURE

The two most widely used methods, such as modified dynamic and static methods, were considered for the measurement of the vapor pressures of hygroscopic salts. However, in the dynamic method used, equilibrium was approached very slowly. Moreover, the temperature of the salt could not be maintained precisely because, with the adsorption of water, a large amount of heat was given out. The results obtained for known salts were not satisfactory. Hence, the static method was employed as described in detail below.

The apparatus, as shown in Figure 1, consisted of the network of borosilicate glass components mounted on an aluminum frame. The initial design for the measurement of the vapor pressure of solid hydrate consisted of: 1, a sample flask; 2, a constant temperature bath with a temperature controller; 3, manometer assembly; and 4, a vacuum pump with a trap.

The sample flask was a round-bottomed 50-cc. borosilicate glass flask with a neck of about four inches. At the end of the neck a 19/38 borosilicate glass male fitting was welded to form a ground joint. There was a corresponding female fitting with a 1/18-inch diameter bore welded at one end of the vacuum stopcock. A 10/30 female fitting was welded at the other end of the stopcock. This vacuum stopcock and the flask formed the sample flask assembly. The long neck was provided to avoid melting the grease.

The constant-temperature bath consisted of a 6½-inch diameter stainless steel beaker, 7 inches deep. It was well insulated and rested on a lab jack so that it could be lowered or removed easily. The bath was stirred vigorously by a high speed motor which was supported on an aluminum

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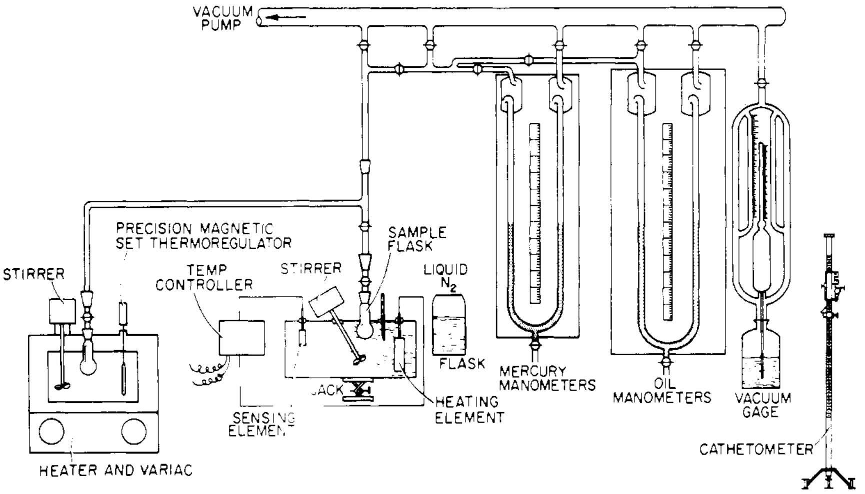

Figure 1. Equilibrium apparatus for the static method

frame. The temperature was controlled by a temperature controller (Bayley Instrument Co., Model 96) which held the temperature to within ±0.01° C. between 20° to 100° C. A Cenco stainless steel immersion heater (450 w) was used as a heating element with a sensing element which was a platinum resistance thermometer. The constant-temperature bath was covered from the top with a wooden cover with corresponding holes for various elements. A precise and standardized mercury in a glass thermometer was inserted in the bath to read the temperature. The temperature was read within ±0.1° C. between 20° C. to 100° C.

The sample flask could be connected directly to either the manifold or the manometer assembly. The assembly consisted of two manometers; one in which mercury was used and one filled with silicone oil (specific gravity 1.04) having a very low vapor pressure. By suitably adjusting the valves the vapor pressure of the hydrate could be read within 0.01 mm. of accuracy on both of these manometers simultaneously or on either of them. The most important step taken before using the manometers was the removal of the inert gases dissolved in the manometer fluid. If this was not done, the vapor pressure measurements were higher than the equilibrium values, owing to the presence of inerts.

The vacuum pump was connected to the manifold through a trap. The trap was always surrounded by liquid nitrogen. The vacuum provided by the pump was of the order of a few microns of mercury.

The connecting tubes were $\frac{3}{16}$ inch in diameter and the manifold was $\frac{3}{4}$ inch in diameter. A McLeod gage was used to measure the pressure. The manometer level readings were taken with a cathetometer.

The major limitation of the apparatus was that its use was restricted to low vapor pressure measurements. For pressures above 30 cm. of water, condensation started and measurements were not reliable. For higher pressures, the whole apparatus needs to be kept in a hot air thermostat to avoid any condensation.

Transition Point Determination. For transition point determination, the salt was exposed to a vapor pressure greater than its higher hydrate and was allowed to equilibrate. This condition requires an additional source of vapor. Two flasks were connected as shown in Figure 1. One of the flasks now served as a sample flask and the other as a reference flask. They were maintained at two different temperatures. Another large heat-capacity, constant-temperature bath with a built-in temperature controller was used for the reference flask.

Solubility Data Determination. The available solubility data of lithium chloride were checked. The sample flask was replaced by a bottle which had an annular space with a 19/38 female fitting at the mouth. The corresponding male fitting contained a hollow tube of the size of the thermometer, was closed at the bottom, and ran nearly to the bottom of the bottle. It was partially filled with glycerin to decrease the time of response of the thermometer by increasing the heat transfer rate. The temperature of the water used as a heating or cooling medium was regulated by a temperature controller with a built-in pump. This equipment simultaneously controlled the temperature of the water in the borosilicate glass jar to within ±0.01° C. and pumped it to the annulus of the bottle.

The stirring of the solution was very important to avoid supersaturation and temperature gradient throughout the bulk phase. A small magnet in the solution was rotated by an external magnetic field which provided vigorous stirring.

EXPERIMENTAL

The sample flask was dried in the oven, cooled, greased, and weighed accurately within ±0.1 mg. About 2 to 5 grams of powdered salt was added and the flask was reweighed. The difference did not give the weight of the salt alone because, being hygroscopic it had some amount of adsorbed water. Depending upon the region in which the vapor pressures were to be measured, an estimated amount of water was added to the salt by a syringe. The flask was closed by a stopcock and reweighed to find the weight of the salt and water.

All the manometers and the lines were opened to the manifold which, in turn, was connected to a pump. The trap was surrounded by liquid nitrogen. The whole system was evacuated for some time. During all this time, the sample flask was closed. The sample flask was then opened for a second or two to remove most of the air above the salt from the flask.

The constant temperature bath was replaced by a Dewar flask which contained liquid nitrogen. When all the water in the flask was frozen, the stopcock was opened to the manifold to remove all the air from the sample flask. The sample flask was then cut off from the manifold by closing the stopcock. The constant-temperature bath replaced the Dewar flask. Before measuring the vapor pressure, the flask was again evacuated for a second or two to remove adsorbed inerts on the surface of the salt or on the glass wall. It was then opened to the manometer for vapor pressure measurements. The readings were taken when steady-state was reached. The above mentioned procedure for removing inerts was repeated until consistent results were obtained.

The temperature of the bath was raised to the next desired value without evacuation. The vapor pressure measurements were then taken. After taking measurements at various temperatures the sample flask was taken out, cleaned, and weighed. The salt in the flask and the solution was titrated to find the Cl^- content, and the lithium chloride content was calculated. As the weight of solution was known, the over-all composition could be calculated. This procedure was repeated for other salts.

Method for the Determination of the Transition Point. The determination of the transition point is one of the crucial steps in the experimental measurement and requires greater attention.

The sample flask was dried, cooled, weighed, and greased. A very small amount of the saturated solution at room temperature was taken to wet the inner surface of the flask. The transition point was determined at 30° C. The vapor pressures corresponding to the equilibrium between the monohydrate and anhydrous salt and the monohydrate and saturated solution were known from the measured data. The reference flask contained the same salt, but it was maintained at a different temperature so that it has a vapor pressure between the two limiting values.

The system was evacuated, and the vapor pressure of the reference flask was measured. The sample flask was evacuated for some time until a thin coating of the salt layer was observed on the inner surface of the flask. The vapor pressure of the sample was measured and found to correspond to the equilibrium between the monohydrate and saturated solution. Then the flask was evacuated for a fixed period of about 10 minutes, and the vapor pressure was measured. This procedure was continued until a step change in the vapor pressure was noted.

The sample flask was allowed to equilibrate. The vapor pressure increased to the value corresponding to the value corresponding to the equilibrium between the monohydrate and the saturated solution. The evacuation time was reduced to about 2 minutes, and the time allowed to equilibrate was increased. Finally, the sample was left overnight (more than 20 hours), and the value corresponding to the equilibrium between the monohydrate and the anhydrous salt was confirmed. At this stage, the sample flask was connected to the reference flask to allow for possible mass transfer. After about 8–10 hours, the vapor pressure measured corresponded to the equilibrium between the anhydrous salt and the monohydrate. The flask was taken out, dried, and weighed, and the composition was determined by titration.

The transition point was approached from the other side also. The same procedure described before was adopted for coating the salt on the flask surface. But this time, the initial evacuation was continued until the vapor pressure corresponded to the equilibrium between the anhydrous salt and the monohydrate. Then the sample flask was connected to the reference flask for more than 50 hours to attain the equilibrium. The vapor pressure of the reference flask was much less than that required to transform the sample to a higher hydrate, but was high enough to provide the driving force for the necessary mass transfer. The two values obtained were cross-checked.

Method for the Measurement of Solubility. An approximately saturated solution was prepared in a flask at the temperature at which the solubility was to be determined. About 75 cc. of this solution was taken into a sample bottle.

The system was evacuated. Most of the air above the solution was removed by evacuation for a second or two. The solution was cooled by liquid nitrogen until the whole mass in the sample bottle solidified. Then all the air above the solution was removed by evacuation while the solution was heated to a temperature about 20° C. higher than that at which the solubility was to be determined. Heating was accomplished by circulating fluid from a constant-temperature bath through the jacketed sample bottle. The solution was stirred vigorously by the magnet to maintain uniformity throughout the bulk of the solution.

The sample bottle was connected to the vacuum; the air which was dissolved in the solution bubbled off. Enough care should be taken to remove all the dissolved inerts from the solution. During this process, some water was lost, thus changing the composition of the solution. The solution was cooled slowly, and the temperature at which crystals started to form was observed. This temperature should be a few degrees lower than the temperature at which solubility is desired. The solution was maintained at this temperature and evacuated until crystals started to form. These crystals were again dissolved in the solution by raising the temperature by a few degrees. The exact crystallization point was determined by cooling the solution very slowly by maintaining the bath temperatures 1° C. lower than the solution temperature. Cooling in this way avoided possibility of supercooling or supersaturation.

The exact point at which crystallization occurred was determined and confirmed by repeating the above procedure. The crystals were dissolved in the solution by raising the temperature. The composition of the solution was determined first, by the gravimetric method, in which a known weight of the solution was dried in a vacuum oven to a constant weight, and the salt content was determined. Secondly, the volumetric method was used in which the salt content was determined by titration. These values were cross-checked.

Table I. Lithium Chloride Monohydrate

Temp., ° C.	In Equilibrium with the Anhydrous Salt ΔH, Cm. of Water	In Equilibrium with the Saturated Solution ΔH, Cm. of Water
22	0.5	3.36
30	0.98	5.15
40	2.18	7.4
50	4.65	13.5
60	9.3	20.4

Table II. Solubility Data for LiCl

Temp., ° C.	Water, Experimental, G./100 G.	Water, Literature Values (2), G./100 G.	% Deviation
30	85.801	85.5	0.355
40	89.33	89.0	0.37
50	93.216	93.1	0.243
60	98.909	98.4	0.515

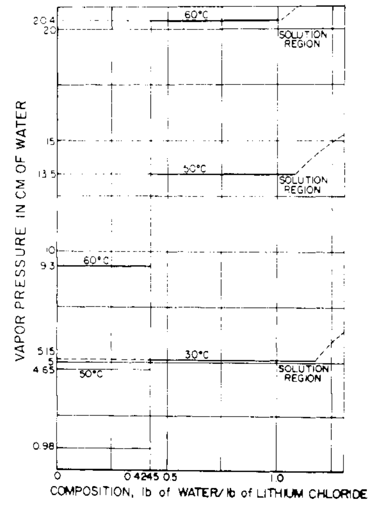

Figure 2. Vapor pressure composition diagram for LiCl

EXPERIMENTAL RESULTS

Lithium Chloride Salt. This salt exists in three hydrated forms; mono-, di-, and trihydrate. But at the ordinary temperature range which is of interest in the present study, only monohydrate exists. Hence the aqueous pressure of monohydrate in equilibrium with the anhydrous salt and with the saturated solution was determined. The averaged data are tabulated in Table I.

The composition-vapor pressure chart for lithium chloride salt for the temperature range of 30° to 60° C. was constructed by using the solubility data as tabulated in Table II and is shown in Figure 2.

Lithium Nitrate Salt. This salt is not as strongly hygroscopic as lithium chloride. It exists in two hydrated forms, $LiNO_3\cdot 3H_2O$ and $LiNO_3\cdot \frac{1}{2}H_2O$.

$$LiNO_3\cdot 3H_2O{-}LiNO_3\cdot \tfrac{1}{2}H_2O + 2\tfrac{1}{2}H_2O$$

$$LiNO_3\cdot \tfrac{1}{2}H_2O \rightarrow LiNO_3 + \tfrac{1}{2}H_2O$$

Because $LiNO_3\cdot 3H_2O$ decomposes at ordinary temperatures, only the vapor pressures of $LiNO_3\cdot \frac{1}{2}H_2O$ in equilibrium with the anhydrous salt and its saturated solution could be measured (Table III). The vapor pressure composition chart for $LiNO_3$ was constructed by using the solubility data reported by Foote (2) (Figure 3).

Lithium Hydroxide Salt. Only the vapor pressure measurements of lithium hydroxide monohydrate in equilibrium with anhydrous salt could be made. Those data corresponding to the equilibrium with the saturated solution could not be taken because at large vapor pressures, condensation took place. Therefore, results were not reliable.

$$LiOH\cdot H_2O \rightarrow LiOH + H_2O$$

Table III. $LiNO_3\cdot \frac{1}{2}H_2O$

Temp., ° C.	In Equilibrium with the Anhydrous Salt ΔH, Cm. of Water	In Equilibrium with the Saturated Solution ΔH, Cm. of Water
30	1.114	4.846
40	2.444	8.242
50	4.94	14.009
60	9.895	22.376
70	18.84	

The results are tabulated in Table IV.

Rubidium Fluoride and Cesium Fluoride. No information is available regarding the stability of the hydrates of these salts in the various temperature ranges. The limiting equilibrium data for the first hydrates of these salts are shown in Tables V and VI.

Table IV. $LiOH\cdot H_2O$ in Equilibrium with the Anhydrous Salt

Temp., ° C.	ΔH, Cm. of Water
30	7.322
35	10.514
40	15.554
45	21.998
50	28.553

Table V. Rubidium Fluoride

Temp., ° C.	In Equilibrium with the Anhydrous Salt ΔH, Cm. of Water	In Equilibrium with the Saturated Solution ΔH, Cm. of Water
30	0.468	1.76
40	1.014	3.04
50	2.111	5.13
60	4.300	8.37
70	8.120	13.03
80	15.408	20.20

Table VI. Cesium Fluoride

Temp., ° C.	In Equilibrium with the Anhydrous Salt ΔH, Cm. of Water	In Equilibrium with the Saturated Solution ΔH, Cm. of Water
30	. . .	0.892
35	0.074	. . .
40	. . .	1.544
50	0.187	2.704
60	0.374	4.470
70	. . .	6.921
80	1.362	10.750
90	2.621	. . .
100	4.722	. . .

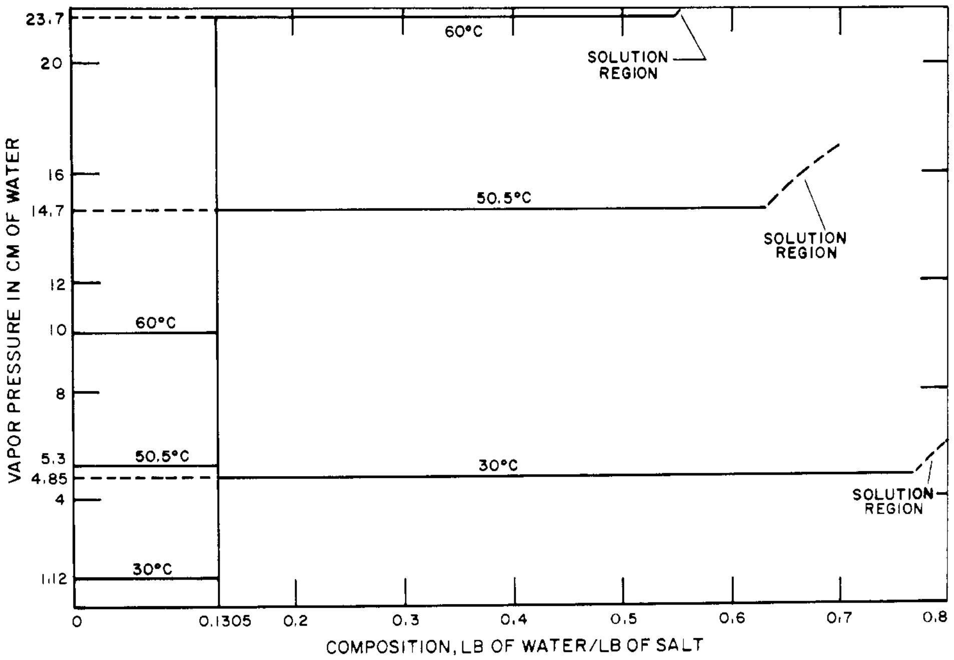

Figure 3. Vapor pressure composition diagram for $LiNO_3$

DISCUSSION OF RESULTS

The variations of vapor pressure of various salts and their hydrates studied in this work were plotted on a log $P - 1/T$ plot in accordance with the familiar Clausius-Clapeyron equation

$$\ln P = A + B/T \tag{1}$$

and all the present data were found to lie on a straight line on this plot (*6*). A least squares analysis of these data was carried out, and the calculated values of A and B together with the standard deviations of the logarithmic vapor pressure equations for different salts are tabulated in Table VII.

Figure 4 compares the present data for the lithium chloride salt with the data available in the literature. The authors' data for the equilibrium between the anhydrous salt and monohydrate show excellent agreement with those of Slonim and Hüttig (*5*). The present data corresponding to the equilibrium between the monohydrate and the saturated solution agree well with those of Foote (*2*). Many other investigators have also reported the vapor pressure data of the saturated solutions. At high temperatures, Gokcen's data (*3*) (which were measured with a dynamic method) do not agree with the present data as well as with the data of Foote. This is not surprising, because in general, the data measured with the dynamic methods are always higher than those determined with the static methods.

Table VII. Values of *A* and *B* in Equation 1 Calculated by a Least Squares Fit to Experimental Data for Various Salts

Salt	*A*	*B*	Std. Dev.
LiCl-LiCl·H_2O	27.05	-82.52×10^2	0.138
LiCl·H_2O-Satd. Soln.	18.35	-51.03×10^2	0.0936
$LiNO_3$·½H_2O	24.32	-73.41×10^2	0.0099
$LiNO_3$·½H_2O, Satd. Soln.	18.63	-51.71×10^2	0.0102
LiOH-LiOH·H_2O	24.37	-67.83×10^2	0.0107
RbF-RbF·nH_2O	23.89	-74.76×10^2	0.0117
RbF·nH_2O, Satd. Soln.	17.79	-52.23×10^2	0.0051
C&F-C&F·nH_2O	17.51	-53.45×10^2	0.0169

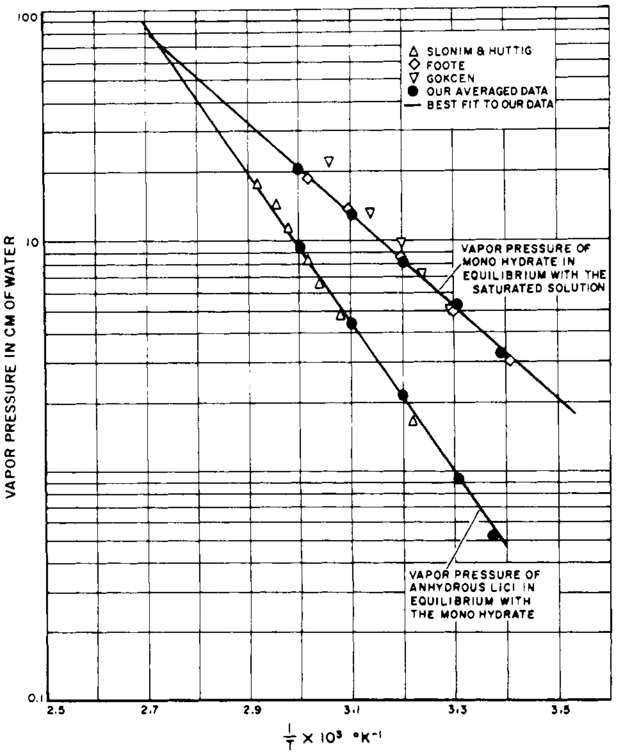

Figure 4. Comparison of LiCl data with the literature values

The intersection of the two straight lines on the plot log P *vs.* $1/T$ should give the transition temperature at which the monohydrate changes to the anhydrous form. The present data show this transition point to be at about 95° C. which agrees well with the Appleby's values (*1*) found to be between 93° and 98° C.

The solubility data for LiCl salt as tabulated in Table II show a good agreement when compared with the literature values (*1*).

The method for determining the transition point has been standardized, and the results obtained for lithium chloride (approaching from both sides) are 0.4363 and 0.424 pound of water per pound of salt. These agree with the value of 0.4241 pound of water per pound of salt reported by Slonim and Hüttig (*5*).

Figure 5 compares the present data for the vapor pressure of lithium hydroxide monohydrate in equilibrium with anhydrous salt with those of Foote (*2*). The data of Foote are slightly lower and do not give a straight line on a log $P - 1/T$ plot.

As no literature data for the vapor pressure of lithium nitrate, rubidium fluoride, and cesium fluoride salts are available, comparison is not possible.

The values for the heat of adsorption and the entropy of different salts studied in this work were calculated and tabulated in Table VIII. The heat of adsorption of different salts was calculated from the slope of a log $P - 1/T$ plot and the entropy changes were calculated from the following relationship:

$$\frac{\Delta S^0}{R} = \ln P^0 + \frac{\Delta H^0}{RT} \tag{2}$$

Table VIII. Calculated Values of the Heat of Adsorption and the Entropy for Various Salts

Salt	Calculated Heat of Adsorption, B.t.u./Lb. Water	Calculated Entropy Change, B.t.u./Lb. Water °R.	Standard State *T*, °C.	Standard State $P \times 10^3$, atm.
LiCl-LiClH_2O	1490	6.361	25	0.625
$LiNO_3$-$LiNO_3$·½H_2O	1439	6.068	25	0.653
LiOH-LiOH·H_2O	1353	6.256	25	4.71
CsF-First hydrate	1496	5.216	25	0.023
RbF-First hydrate	1477	6.020	25	0.300

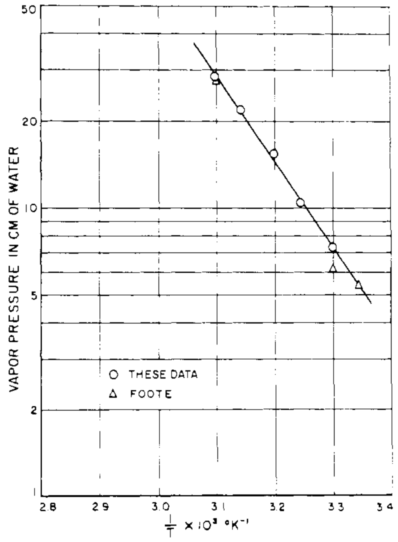

Figure 5. Vapor pressure of LiOH

The heat of adsorption of $LiCl \cdot H_2O$ given by Slonim and Hüttig (5) as 1465 B.t.u. per pound by water, which agreed with the present calculated value of 1490 B.t.u. per pound of water. The heats of adsorption for other salts could not be compared because of the lack of data in the literature. Also the entropy changes for the salts studied could not be compared with the third law entropy changes because of the lack of absolute entropy data.

ACKNOWLEDGMENT

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Some Base-Catalyzed Reactions of Diethyl Phthalate with Aromatic Amines

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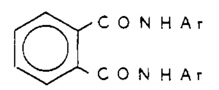
The reaction of diethyl phthalate with aromatic amines in the presence of sodium ethoxide has been examined. Several new *N,N'*-diaryldiamides of o-phthalic acid have been synthesized and characterized. Complicating factors have been investigated.

SOME TIME AGO, the authors reported syntheses of the previously unknown di-*o*- and di-*p*-toluides of *o*-phthalic acid (1a and 1b) via reaction of diethyl phthalate with the appropriate amines in the presence of sodium or sodium ethoxide (*7*). Extension of this synthetic method to synthesis of other *N,N'*-diaryldiamides of *o*-phthalic acid has met with varying degrees of success.



Diethyl phthalate was treated with each of 15 aromatic amines in ethanolic sodium ethoxide. Amines employed were the *o*, *m*, and *p* isomers of phenylenediamine, anisidine, toluidine, chloroaniline, and nitroaniline. No diamides were isolated from reaction mixtures containing the phenylenediamines or the nitroanilines.

In view of the expected low acidities of the phenylenediamines (*10*), it is not surprising that reaction did not take place under the mild conditions employed. Sufficient concentrations of the sodium salts of the phenylenediamines necessary for the diamide synthesis (*7*) could, probably, be generated in the presence of a stronger base.

Conversely, the nitroanilines would be expected to be the strongest acids of all the amines used (*10*), and they should react with sodium ethoxide to form comparatively high concentrations of the corresponding sodium salts. However, the lack of concentration of nucleophilicity on the amine nitrogen atom might well render these comparatively stable anions ineffectual in the reactions under consideration. The nitroanilines were recovered unchanged from all reaction mixtures. The failure of this synthetic method in these cases is not particularly serious, inasmuch as the dinitroanilides are among the few *N,N'*-diaryldiamides of *o*-phthalic acid available by other synthetic methods (*5, 9*).

Yields and melting points of *N,N'*-diaryldiamides of *o*-phthalic acid which have been successfully prepared via the method under consideration are summarized in Table I.

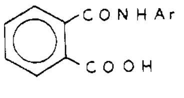
Table I. *N,N'*-Diaryldiamides of o-Phthalic Acid

Compound	Aryl Group	M.P., ° C.	Yield, %
1a	*o*-$CH_3C_6H_4$	209.0–209.5	78
1b	*p*-$CH_3C_6H_4$	181.0–182.0	65
1c	*m*-$CH_3C_6H_4$	200.5–201.2	31
1d	*o*-$CH_3OC_6H_4$	174.5–175.5	28
1e	*p*-$CH_3OC_6H_4$	197.5–199.0	18
1f	*m*-$CH_3OC_6H_4$	169.5–171.0	84
1g	*o*-ClC_6H_4	189.5–191.0	38
1h	*p*-ClC_6H_4	213.0–214.0	28
1i	*m*-ClC_6H_4	213.5–215.0	31
1j	C_6H_5	230.0–231.0[a]	65

[a] Lit., 231–32° C. (*8*).

Certain solid-state infrared absorption peaks of these compounds are summarized in Table II; because of the complexity of the spectra, definite assignments in other regions were not made. However, all spectra are consistent with structural assignments (*2*).

In some cases, another product, the monoamide, 2, was isolated from the reaction mixtures. Yields and melting points of these compounds are summarized in Table III.



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The rather poor agreement in values of melting points of these monoamides with previously reported melting points led us to question the structural assignments. However, the acidic nature of these materials, their elemental analyses, and their infrared spectra (Table IV) support the assigned identities. As with the diamides, the complexity of the spectra obtained precluded further assignments of absorption maxima.

That small amounts of water in the reaction mixtures could have resulted in formation of these materials is