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ACKNOWLEDGMENTS

Moisture Sorption Kinetics for Water-Soluble Substances II: Experimental Verification of Heat Transport Control

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Abstract □ The rates of water sorption as a function of relative humidity for water-soluble substances exhibiting deliquescence have been measured in an atmosphere of pure water vapor. The substances studied included a series of alkali halides, choline halides, and sugars. The results were compared with a theoretical model, previously described, which relates the rate of water uptake to the transport of heat produced during the process away from the surface. Taking into account the heat of water vapor condensation, heat of solution, and heat of hydration, when hydration occurs, the model allows excellent *a priori* prediction of water uptake rates as a function of relative humidity.

Keyphrases □ Sorption—kinetics, alkali halides, choline halides, and sugars in a water vapor atmosphere, application of theoretical model □ Kinetics—moisture sorption, alkali halides, choline halides, and sugars in a water vapor atmosphere, application of theoretical model □ Deliquescence—sorption kinetics, alkali halides, choline halides, and sugars in a water vapor atmosphere, application of theoretical model

A quantitative treatment for the kinetics of water vapor sorption onto water-soluble solids which exhibit deliquescence has been developed in the preceding paper (1). The treatment was confined to situations where the rate is determined solely by the kinetics of heat transfer away from the surface to the atmosphere surrounding the solid. It was assumed that the resultant film of aqueous solution is saturated with respect to the dissolved solid throughout the process.

The model essentially says that heat generated upon condensation of water vapor, and any other heat change occurring during sorption, maintains the liquid–vapor interface at a temperature, T_s, elevated above that of the bulk atmosphere, externally maintained at T_c. The water vapor pressure over the saturated film, therefore, rises with temperature until the pressure difference between surface and atmosphere becomes infinitesimal, and remains so during steady-state uptake. The ability of the system to transfer heat away from the surface is assumed to limit the sorption rate. This sorption rate, W_h', was shown to depend on the relative humidity of the atmosphere, RH_i, and that in equilibrium with the saturated aqueous film around the solid, RH_o, as described by the equation:

$$W_h' = \left[\frac{60 M_w \cdot 4\pi kab}{\Delta H(b-a)} \left(\frac{RT_c^2}{\Delta H_v - RT_c \ln \dfrac{RH_i}{RH_o}} \right) \right.$$
$$\left. + \frac{60 M_w \cdot 4\pi a^2 \sigma e}{\Delta H} \times \left(\frac{4RT_c^5}{\Delta H_v - 4RT_c \ln \dfrac{RH_i}{RH_o}} \right) \right] \cdot \ln \frac{RH_i}{RH_o} \quad (Eq.\ 1)$$

where the various symbols represent parameters defined in the preceding paper (1).

Since all of these parameters are either available in the literature or experimentally determinable, it is possible to use Eq. 1 to predict the value of W_h' for various values of RH_i and for solids of varying RH_o. In this paper we present experimental studies of water sorption kinetics under vacuum conditions, where diffusion of water vapor is not a consideration and where heat transport control would be expected to predominate.

EXPERIMENTAL

Materials—Potassium chloride[1], potassium bromide[2], potassium iodide[3], sodium chloride[4], anhydrous sodium bromide[1], choline chloride[5], choline bromide[5], choline iodide[5], tetrabutylammonium bromide[6], sucrose[7], fructose[5], D-glucose monohydrate[1], and anhydrous D-glucose[3] were all reagent grade and were used as received. The dihydrate of sodium bromide was prepared by dissolving a maximum amount of the anhydrous form in boiling distilled water, filtering the hot solution, and cooling to room temperature. The crystals were collected and dried on filter paper. Loss on drying indicated that the crystals contained 100.6% of the theoretical water content. All samples of the dihydrate were stored over their own saturated solution since it would effloresce at any relative humidity <57.7%. Manipulation of the more hygroscopic compounds, such as choline chloride, was performed within a plastic inflatible glove bag[8] in which a relative humidity of <15% could be maintained under nitrogen. Such compounds were stored in partially evacuated desiccators over anhydrous calcium sulfate[9].

Equipment and Procedures—The apparatus, consisting of an electrobalance associated with a vacuum system, and the general procedures used to measure sorption kinetics have been described in considerable detail elsewhere (2). In the studies reported here, silicone diffusion pump oil[10] was used as the oil manometer fluid because of its low vapor pressure $(2.3 \times 10^{-6}$ torr) and suitable viscosity (42 cps) at 25°. A chromel–alumel thermocouple, calibrated to 0.1° in vacuum against an external reference thermocouple kept at 25.0 ± 0.05°, was installed within the sample chamber and positioned in the vicinity of the solid sample surface. A vacuum of 10^{-2} torr was maintained and various relative humidities were provided from chambers containing different saturated inorganic salt solutions (2). Temperature of the sample chamber atmosphere was maintained at 25 ± 0.05° by a thermostated water jacket.

All studies were carried out using solid samples compressed into disks since the well-defined geometry could be expressed in terms of the hollow-sphere geometry used in the development of the theoretical model (1). These disks were prepared by compressing 300 mg of powder on a hydraulic press at 66 kN over a 1-min interval between two 1.91 cm flat-faced punches. The disks were generally cut in half with a razor blade to provide two samples per disk. The alkali halides were oven dried at temperatures >150° and ground to a fine powder before compression. The choline halides and sugars were not subjected to elevated temperatures, but were powdered by grinding under sub-RH_o conditions at 25°–27°.

Solubility and Heat of Solution—The molal solubilities at 25° for all compounds studied are listed in Table I. Because of their extremely high solubilities, values for the three choline halides, not previously reported, were determined in this study by a visual method. Known quantities of distilled water and choline halide were added in various proportions of 2-ml glass ampules which were then sealed with plastic film and equilibrated at constant temperature. After equilibration, the molal solubility was estimated by bracketing the point of saturation.

The heats of solution for the various compounds are also listed in Table I. All values were taken from the references cited or were determined as part of this study from the temperature coefficient of solubility and the

[1] J. T. Baker Chemical Co.
[2] Allied Chemical.
[3] Mallinckrodt Chemical Works.
[4] Fisher Scientific Co.
[5] Sigma Chemical Co.
[6] Aldrich Chemical Co.
[7] Mann Research Labs.
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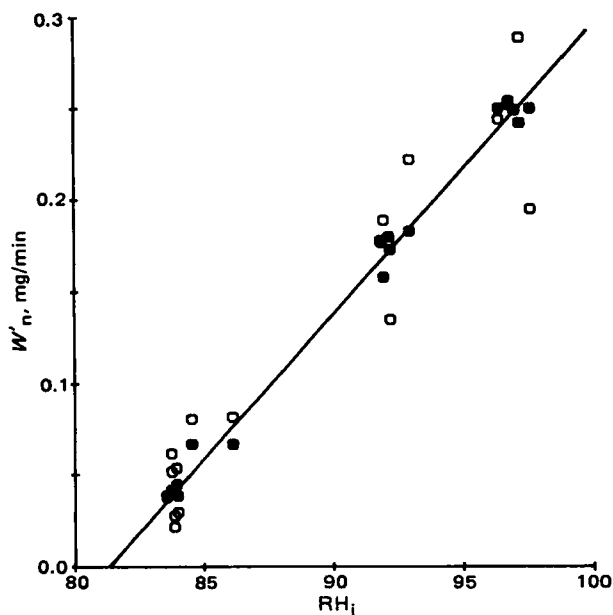[9] Drierite, Indicating; W. A. Hammond Drierite Co.
[10] DC704; Dow Corning.

Table I—Aqueous Solubility and Heats of Solution for Various Deliquescent Solids at 25°

Compound	C_{sat}, m (Ref. No.)	ΔH_{soln}, kcal/mole
Potassium chloride	4.81 (4)	4.115 (5)
Potassium bromide	5.65 (4)	4.750 (5)
Potassium iodide	8.86 (4)	4.860 (5)
Sodium chloride	6.14 (4)	0.928 (5)
Sodium bromide		
Anhydrous	—	0.58 (5)
Dihydrate	9.12 (4)	4.57 (5)
Choline iodide	14.0^a	9.900^a
Choline bromide	25.9^a	4.800^a
Choline chloride	32.2^a	3.260 (3)
Tetrabutylammonium bromide	26.4 (6)	−2.050 (7)
Sucrose	6.18 (5)	1.319 (5)
Glucose		
Monohydrate	5.5 (8)	5.272^b
Anhydrous	5.0 (8)	2.620^b
Fructose	18.5 (9)	2.222^b

^{a} Determined from solubility in this study. ^{b} Determined calorimetrically in the laboratory of Professor S. Lindenbaum, University of Kansas.

application of the van't Hoff equation or by solution calorimetry. A value of 3.26 kcal/mole from the literature for choline chloride (3) is in reasonably close agreement with an estimate of 2.6 kcal/mole from solubility considering the difficulty of handling the extremely hygroscopic choline chloride samples, its high solubility, and the method used to determine solubility. The general direction and magnitude of change in going from choline chloride to choline bromide is very similar to that seen for the chloride and bromide salts of a related quaternary ammonium ion reported in the literature (3).

RESULTS

Rate of Moisture Sorption—The rate of moisture sorption was estimated from the slope of the earliest portion of the water uptake versus time curve exhibiting extended linearity under stable RH_i conditions (2). In all cases, the time required to reach steady state was consistent with theoretical estimates (1). For the alkali halides (except sodium bromide), choline chloride, and sucrose, linear uptake of the disks was observed over very long time intervals (i.e., hours) and appeared independent of percent weight gained until sufficient moisture had been sorbed so as to cause distortion of the disk and drop formation on the bottom surface of the disk. For these materials, multiple data points could be collected for the same sample by subjecting it to successive increments (or decrements) in RH_i. For the other compounds a fresh sample was used for each RH_i.

Normalization of Disk Surface Area—Most disk samples were halved for testing as indicated in Experimental. Because the semicircular disks were not exact halves owing to slight crumbling or asymmetric cutting, there existed differences in surface areas between sample disks. Since the facial surface area-to-weight ratio of a partial disk is theoretically equal to the known facial surface area-to-weight ratio of the whole disk, the facial surface area of the sample could be normalized to that of a perfect semicircular disk by comparing its weight with one half that of the whole disk from which it was prepared. Edge effects on the resulting normalization factor are negligible. Since the uptake rate is approximately proportional to disk surface area over the small changes in area corrected for in this normalization, the weight ratio factor could then be directly applied to the observed sorption rate data. Thus the normalized rate, W_n', for a half disk, is calculated by:

$$W_n' = W_{obs}' \cdot \frac{0.5 (W_0, \text{whole disk})}{(W_0, \text{half disk})} \qquad \text{(Eq. 2)}$$

In Fig. 1 rates of sorption, W', are plotted versus relative humidity before and after normalization for potassium bromide disks intentionally cut to ⅓ and ⅔ sizes. In all cases normalization puts points closer to a straight line[11] going through RH_o for potassium bromide.

Effect of Varying Compression Pressure—Disks of potassium bromide (300 mg) compressed at 66, 44, 22, and 6.6 kN force were compared for their sorption characteristics. The disks were halved for testing.

[11] While theoretically incorrect (1), the linear plot is a reasonable approximation for the W' function at the high RH_i and small ΔRH_i values that pertain to potassium bromide and, thus, serves adequately to illustrate the success of normalization.

Figure 1—*Effect of normalization on treating observed W' data for potassium bromide disks of varying size. Key: (O) observed W'; (●) W$_n$'.*

On the basis of weight, disk dimensions, and the density of pure potassium bromide, porosity of the disks ranged from ~4% (at 66 kN) to 25% (at 6.6 kN). Each sample was subjected to successive RH$_i$ levels. The results are given in Fig. 2. It is clear from this plot that sorption rate did not depend significantly on disk porosity. It could, therefore, be inferred that lack of density uniformity in the disk is of no consequence to sorption, other than its potential effect on the normalization factor. The apparent reason porosity plays no role in sorption is that a film of (saturated) solution builds immediately during initial uptake, providing a smooth surface for continued sorption regardless of the internal porous structure of the disk.

Effect of Varying Disk Size—Heat transport-controlled sorption governed by Eq. 1 has a complex dependence on the effective disk (inner sphere) radius a. For a whole disk of real diameter 1.905 cm and average thickness 0.6 mm, $A = 4\pi a^2 = 2\pi(1.905/2)^2 + \pi(1.905)(0.06) = 6.06$ cm^2, or $a = 0.69$ cm. As the disk is cut, the value of radius a does not fall by simple proportion. Accordingly, W' should not be expected to fall pro-

Table II—Predicted Sorption Rate Dependence on Disk Size

Disk Size	a^a cm	W_h' (Eq. 4)	W_h'/W_h' at ½ disk
Whole	0.694	1.53 C'	1.72
⅔	0.567	1.10 C'	1.24
½	0.491	0.89 C'	1.00
⅓	0.401	0.66 C'	0.74

^{a} Calculated neglecting edge effects for partial disks.

portionally with decreasing disk size. From the expression given for W_h' by Eq. 1, one can write that:

$$W_h' = C' \cdot \frac{ab}{(b-a)} + F' \cdot a^2 \qquad \text{(Eq. 3)}$$

where C' and F' are conduction and radiation coefficients defined to reflect the dependence of W_h' on the characteristic disk dimension, a, pertaining to the hollow-sphere geometry of the system. If conduction and radiation contribute equally to heat transfer (1), then C' = F', and:

$$W_h' = C' \left(\frac{a}{1 - a/b} + a^2 \right) \qquad \text{(Eq. 4)}$$

The theoretical dependence of W_h' on disk W size is calculated according to Eq. 4, the results of which are summarized in Table II. A value of b = 2.05 cm was used for these calculations and for all subsequent calculations using Eq. 1 and related equations where b appears.

The sorption rates plotted for partial disks of potassium bromide in Fig. 1 to illustrate the normalization method are plotted again in Fig. 3, this time normalized to their appropriate facial surface area fraction, e.g., ⅓, ⅔. Linear curves[11] for uptake by a whole disk, ⅔ disk, and ⅓ disk are drawn in Fig. 3 with appropriate theoretical slopes relative to the half disk, according to Table II. Excellent agreement is obtained between these curves and the observed (normalized) sorption rates, substantiating the appropriateness of the heat transport model expressed by Eq. 1, in general, and the relation between W' and disk size expressed by Eq. 4, specifically.

Effect of Varying the Initial Weight, W_0—Unless the heat capacity of the sample plays a significant role in the control of the sorption process, varying W_0 for a given disk size should have little or no effect on uptake rates. Again, W' should be expected to depend more on overall disk surface area than volume or weight of solid. Sorption by whole disks and half disks of potassium bromide of differing W_0 is compared in Fig. 4. The half-disk data have been normalized as usual according to Eq. 2. From the results in this plot[11], it can be concluded that W' is indeed relatively independent of W_0. Based on all of the preceding results, the sample preparation chosen for characterizing the sorption characteristics of
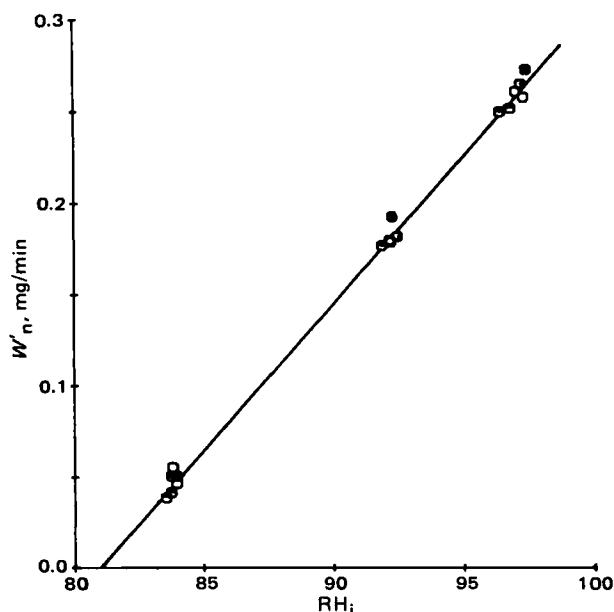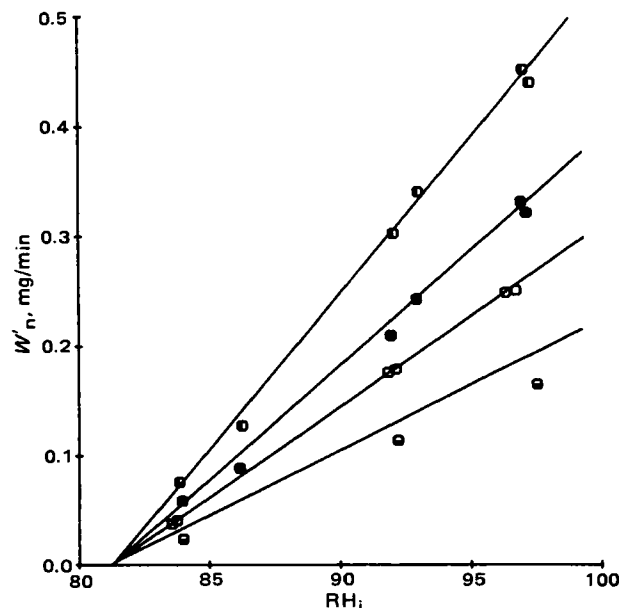

Figure 2—*Effect of compression pressure on sorption rates for potassium bromide disks. Compression pressure: (◑) 6.6 kN; (●) 22 kN; (O) 44 kN; (◒) 66 kN.*

Figure 3—*Dependence of sorption rate for potassium bromide disks on disk size; data normalized to appropriate partial disk surface area. Key: (◓) ⅓ disk; (O) ½ disk; (●) ⅔ disk; (◐) whole disk.*
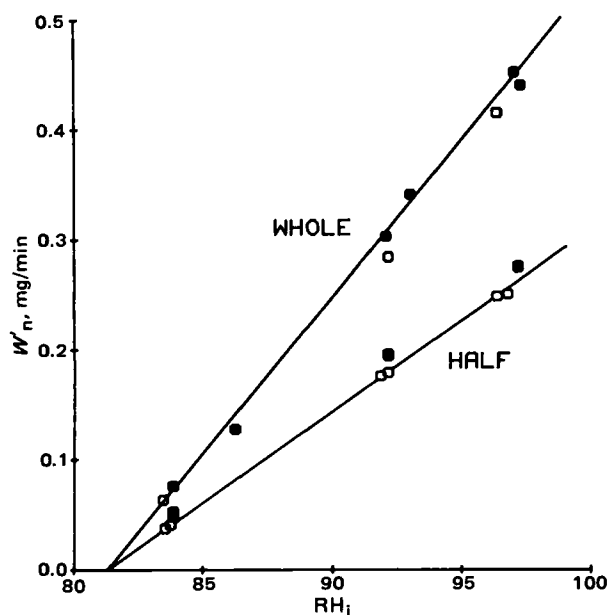
Figure 4—*Dependence of sorption rate for potassium bromide disks on disk W_0 for given approximate size. Key: (O) $W_0 \sim 150$ mg; (●) $W_0 \sim 300$ mg.*

various compounds in vacuum was that of a halved disk of $W_{00} = 150$ mg placed directly on the open wire stirrup.

Temperatures Changes at the Surface—Simultaneous measurement of temperature in the vicinity of the solid surface using the thermocouple allowed the estimation of ΔT, the temperature difference between the atmosphere (25°) and the point near the surface where the thermocouple was positioned. Since a substantial gradient in temperature is predicted to exist at the surface by the heat transport model, direct measurement of such gradients would provide some additional support for such a model. Consequently, the bimetallic junction of the thermocouple installed in the sample chamber was adjusted to hang over the sample disk within 0.5 mm of the top surface. Measurements of temperature taken at varying heights above the sample, >0.5 mm, allowed some definition of the temperature gradients created during the process of water sorption. Although exact fit to theory was not expected because the thermocouple could not be positioned exactly at the disk surface
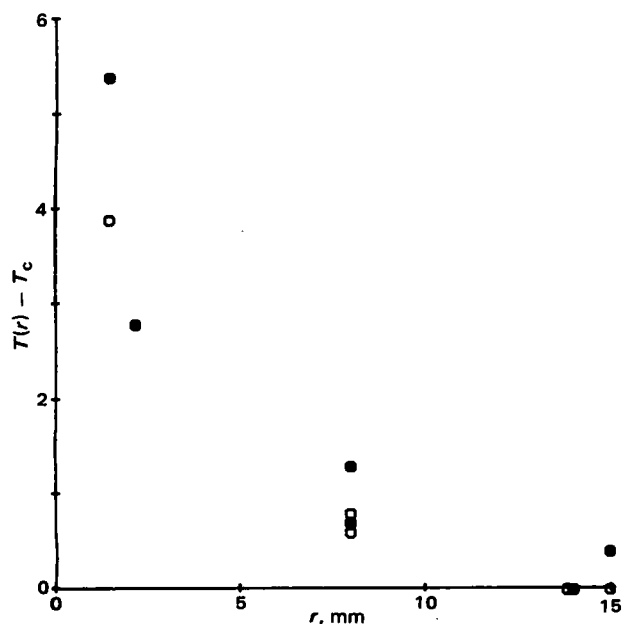
Table III—Values of ΔH and RH_0 Used in Calculating Rates of Water Sorption from Eq. 1

Compound	ΔH kcal/mole	RH_0
Potassium chloride	−10.140	84.3
Potassium bromide	−10.020	80.7
Potassium iodide	−9.725	68.3
Sodium chloride	−10.400	75.3
Sodium bromide		
Anhydrous	−10.520	57.7
Dihydrate	−9.414	57.7
Choline iodide	−8.003	72.5
Choline bromide	−8.260	40.6
Choline chloride	−8.609	23.0
Tetrabutylammonium bromide	−11.475	61.0
Sucrose	−10.350	84.3
Glucose		
Monohydrate	−9.974	81.3
Anhydrous	−10.260	81.3
Fructose	−9.759	64.0

where the temperature gradient is steepest in its decline, it was possible to show that ΔT exists, and that it falls off at increasing distance from the surface. This is seen in Fig. 5 for choline bromide at two rates of sorption, *i.e.*, two values of RH_i. Figure 6 also shows the distance-dependent temperature difference for choline bromide and potassium iodide and also shows that an increase in uptake rate at any position of the thermocouple is generally associated with an increasing temperature difference. Similar observations were made with the other compounds studied.

Prediction of Water Uptake Rates—To test Eq. 1 quantitatively, steady-state uptake rates were determined at various values of RH_0. Table III lists the values of RH_0 and ΔH used to obtain theoretical plots from Eq. 1. Other constants were as described in the preceding paper (1). The value of ΔH, unless otherwise specified, was calculated using the heat of condensation of water vapor (ΔH_c, which is −10.5 kcal/mole), the heat of solution (ΔH_{soln}), and the aqueous molal solubility (C_{sat}) as follows:

$$\Delta H = \Delta H_c + (C_{sat} \cdot \Delta H_{soln})/55.5 \qquad \text{(Eq. 5)}$$

where C_{sat} has units of moles of solute/1000 g of water, and ΔH_{soln} is in kilocalories per mole. The number 55.5 converts values into appropriate units. In the case of anhydrous potassium bromide and anhydrous glucose, the value of RH_0 used was that of the hydrated form and ΔH was estimated by including the heat of hydration along with the heat of
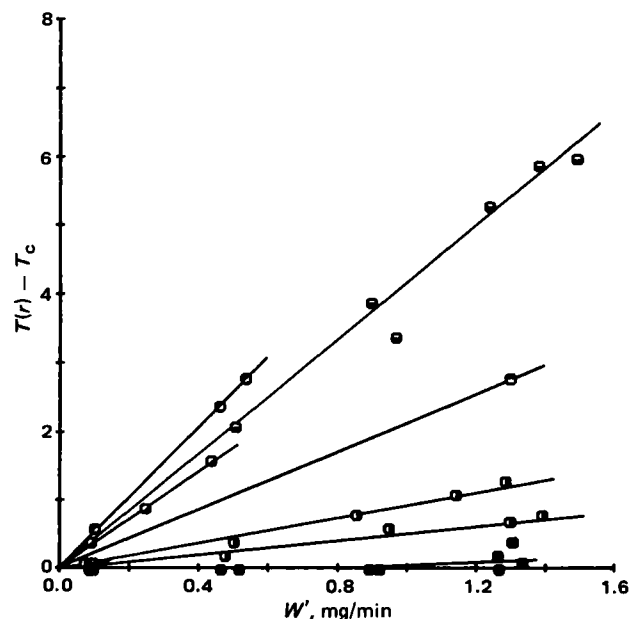

Figure 5—*Dependence of observed ΔT on distance, r (in mm), from sample disk during sorption by choline bromide at a given W'. Key: (●) $W' \sim 1.3$ mg/min $(RH_i \sim 75)$; (O) $W' \sim 0.9$ mg/min $(RH_i \sim 64)$.*

Figure 6—*Dependence of observed ΔT on sorption rate at varying distances r (in mm) from sample disk. The lines serve only to distinguish data from a given sorption run. Choline bromide: (●) $r \sim 15$; (◑) $r \sim 8$; (◒) $r \sim 2$; (◓) $r \sim 1$. Potassium iodide: (◐) $r \sim 1$; (◉) $r \sim 0.5$.*
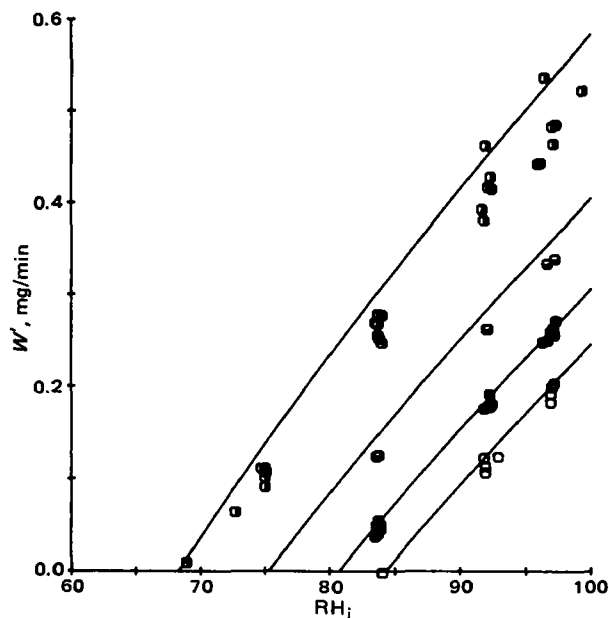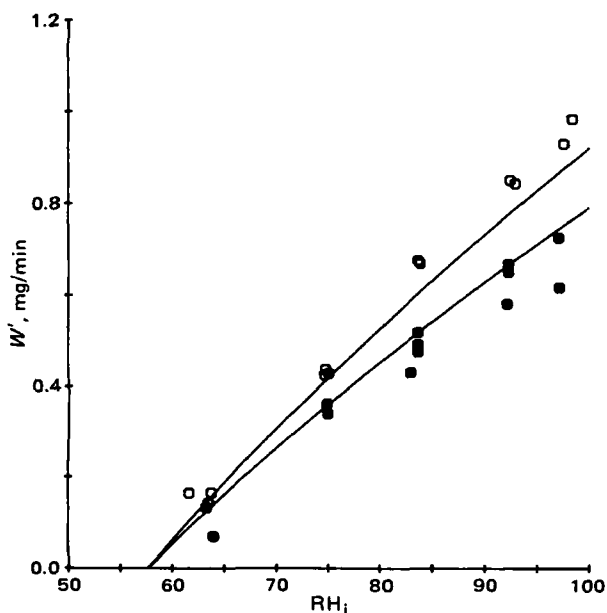
Figure 7—*Sorption rates for disks of alkali halides as a function of RH_i. The lines are the theoretical sorption curves plotted for W' according to Eq. 1. Key (◐) potassium iodide; (◒) sodium chloride; (●) potassium bromide; (O) potassium chloride.*

Figure 9—*Sorption rates for disks of quaternary ammonium halides as a function of RH_i. The lines are the theoretical sorption curves plotted for W' according to Eq. 1. Key: (◒) choline chloride; (●) choline bromide; (◐); choline iodide; (O) tetrabutylammonium bromide.*
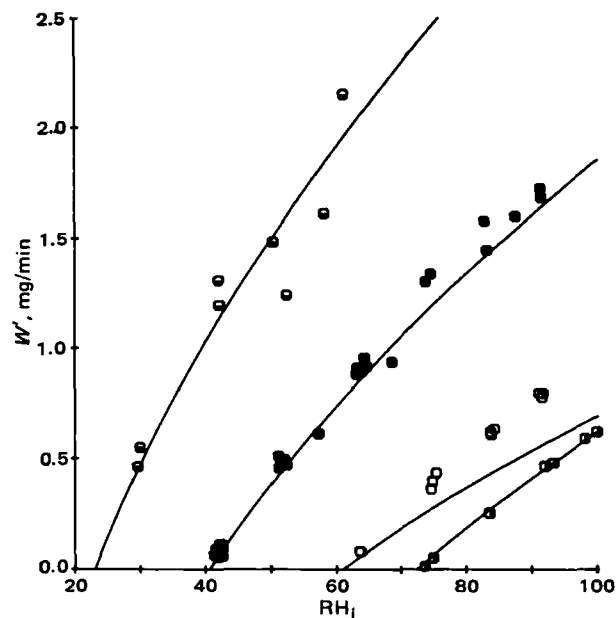
condensation and heat of solution, using Eq. 5. Figures 7–10 present theoretical graphs with experimental data for the heat transport-controlled W' (W_h') versus RH_i.

DISCUSSION

The results of experimental studies on water uptake rates of deliquescent substances in an atmosphere of pure water vapor, with the exception of tetrabutylammonium bromide and anhydrous glucose, provide excellent confirmation of the heat transport model described in the preceding paper (1). Thus, it appears possible to predict rates of uptake in a vacuum for most solids a priori, knowing their RH_0, solubility in water, and heat of solution, all experimentally determinable parameters. If crystalline hydrates can form, as in the case of sodium bromide, anhydrous glucose, and perhaps tetrabutylammonium bromide, the con-
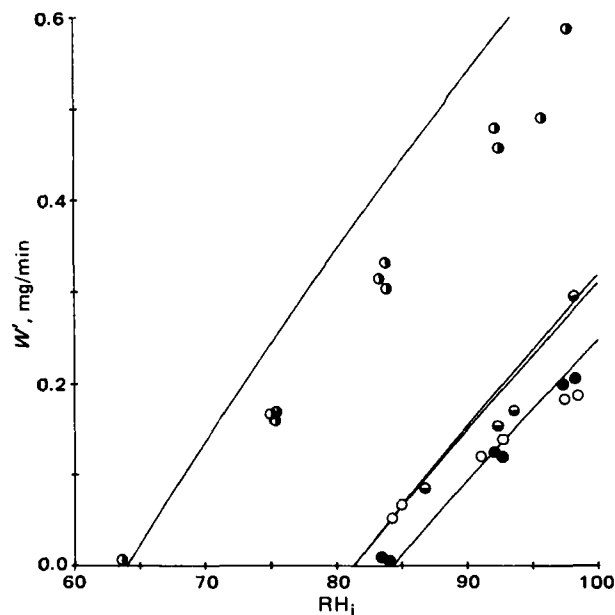
tribution of heat changes, attributable to hydration, however, must also be considered.

Fit of the model to solids varying very greatly in rates of water uptake, having also a broad range of solubilities and values of RH_0 and ΔH_{soln}, supports the important assumption that mass transport in the aqueous film surrounding the solid does not become rate limiting in determining the concentration of material dissolved in the film. In this regard, it is interesting to note that for systems having saturated solutions with viscosities 15–200 times that of water, agreement between theory and experiment for sorption rates was excellent. Analysis of the results using anhydrous sodium bromide and its dihydrate suggests the following picture. Below the value of RH_0 for the hydrate, water vapor can be taken up by the anhydrous form to form the hydrate. When RH_0 for the hydrate is exceeded, the hydrate layer dissolves in the liquid film to begin the

Figure 8—*Sorption rates for disks of the anhydrous (●) and dihydrate (O) forms of sodium bromide as a function of RH_i. The lines are the theoretical sorption curves plotted for W' according to Eq. 1.*

Figure 10—*Sorption rates for disks of sugars as a function of RH_i. The lines are the theoretical sorption curves plotted for W' according to Eq. 1, where higher and lower curves intercepting $RH_i = 81.3$ represent W' for the monhydrate and anhydrous forms of glucose, respectively. Key: (◒) fructose; (●) glucose · H_2O; (●) glucose; (O) sucrose.*

process of deliquescence. This exposes more anhydrous crystal surface which quickly forms the hydrate. The heat released by hydrate formation increases the overall heat released, and this slows down the rate of water uptake relative to that observed with the hydrated crystal (see Fig. 8). The key to this picture is the rapid formation of the crystalline hydrate at the solid–liquid interface relative to the rate of heat transport and water uptake.

The significant lack of fit to the theoretical plot >84% RH_i for anhydrous glucose (Fig. 10) as opposed to the excellent fit for the monohydrate form of glucose, suggests strongly that the simple picture of rapid crystalline hydrate formation is not applicable. Rather, it appears that at higher RH_i values other kinetic processes, yet to be determined, are assuming greater significance. That the situation can be more complicated in some cases is seen with tetrabutylammonium bromide (Fig. 9) where the values predicted using only the heat of condensation of water and the reported heat of solution (7) are very different than those experimentally observed. In the case of tetrabutylammonium halide, the large cation has the tendency to exist in unusual states of hydration both in aqueous solution and in the crystalline form. In solution, tetrabutylammonium ions exhibit significant amounts of water structuring, leading to what has been termed "caging" of water around the cationic group (10, 11); this degree of structuring will decrease with increasing temperature. This strong tendency for hydration is also reflected in the formation by tetrabutylammonium salts of well-defined crystalline hydrates, having hydration numbers of 32 (12, 13). These hydrates are assumed to be of the clathrate type, similar in character to gas hydrates. Here, the cation acts as a guest in a host cavity created by water molecules and the anion. Evidence for polymorphism in these crystalline systems has also been reported (14).

Considering what takes place during the deliquescent process, any number of processes of structure formation or breaking in this system can contribute to ΔT and the net heat which must be transported away from the surface. If crystalline hydrate formation, as described for sodium bromide and glucose, predominates, we might expect a much slower rate than is actually observed. However, if water structuring in solution was being broken down, for example, as the temperature in the film increased, the net heat released would be much less than predicted from the heat of solution and this would lead to faster rates. In such a complex process involving higher degrees of ordering, there is also the possibility that simple equilibrium conditions are not reached and that incomplete hydration or slow rates of change during rapid water uptake affect the final rate of heat released and hence water uptake. It is interesting to note in this regard that the data obtained with tetrabutylammonium bromide can be fitted excellently if we assume a ΔH_{soln} of ~4.0 kcal/mole, which is close to the values of ΔH_{soln} for choline chloride and choline bromide, both of which have molal solubilities close to that of tetrabutylammonium bromide. This suggests the possibility that the part of the equilibrium heat of solution attributable to the unusual hydration properties of this ion is not making a contribution to the overall kinetic process. This certainly points out the importance of knowing as much as possible about the molecular nature of such complex water vapor–solid interactions when attempting to interpret the overall mechanisms of hygroscopicity. Fortunately, the behavior of many water-soluble species of pharmaceutical interest, exemplified by all of the other compounds studied, are much less complicated than tetrabutylammonium bromide.

CONCLUSIONS

A theoretical model for heat transport-controlled water uptake by deliquescent solids has been experimentally tested in an environment of pure water vapor (vacuum) where resistance to mass transport in the vapor phase would not be expected to be a factor. Studies with alkali halide salts, sugars, and choline salts provide excellent agreement with theory. As long as all heat-producing or -consuming processes are taken into account, knowing only solubility, various heat changes, and RH_o, it is possible to predict a priori the rate of water uptake for deliquescent substances as a function of RH_i, the chamber relative humidity.

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