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Water vapor sorption by potash fertilizers studied by a kinetic method

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Abstract

Equilibrium vapor pressures, kinetics, and enthalpy changes for the reaction of water vapor with commercial potash (KCl) fertilizers have been studied by a rapid, kinetic method. The results show that water vapor sorption is controlled by two reactions, one occurring at about 60% relative humidity, the other at about 85% relative humidity. The results are used to predict stable conditions for storage and handling of these fertilizers.

Keywords: Calorimetry; Fertilizer; Kinetics; Potash; Water vapor

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1. Introduction

Understanding the thermodynamics and kinetics of water vapor sorption by inorganic fertilizers is critical in establishing proper storage conditions. If stored under high humidity conditions, the fertilizers may cake because of interparticle cementing, or break down under shear or impact stress to yield fines and dust. These changes are undesirable because they cause problems in handling and applying the fertilizer. Rapid methods for determination of the humidities critical for handling and storage of fertilizers would be useful for establishing the causes of problems and for quality control.

A new instrument for the rapid determination of the thermodynamics and kinetics of water vapor sorption has recently become commercially available [1]. This instrument uses an isothermal heat conduction calorimeter to measure the rate of water vapor

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uptake by a sample as a function of water vapor pressure over the sample. Previous studies [2,3] with a prototype of this instrument dealt only with pure materials. In this study this method is applied to commercial-grade potash fertilizers (KCl typically $>95\%$, but containing significant amounts of sodium, magnesium, calcium, and sulfate salts), to determine the applicability of these methods in the rapid determination of the acceptable ranges of temperature and humidity for stable storage and handling. This method also provides information not easily obtained by other methods concerning the reaction mechanism of water vapor with materials [3]. Thus, in addition to testing the method on a mixture, we are interested in discovering what can be learned about the reaction of potash fertilizers with water vapor by this method. Particle composition, size, and structure all play important roles in determining the properties of water vapor sorption by these fertilizers. In this study, fertilizers with different amounts of magnesium and different particle sizes were studied.

2. Materials and methods

The four commercially available potash fertilizers used in this study were supplied by the Potash Corporation of Saskatchewan Inc. (PCS). The samples studied came from two mine sites; Lanigan (low magnesium) and Rocanville (high magnesium). The samples are labeled "plus 14-mesh Lanigan Granular" (LG) "plus 14-mesh Rocanville Granular" (RG), "minus 14-mesh Lanigan Standard" (LS), and "minus 14-mesh Rocanville Standard" (RS). Evaporated (100–105°C) process brines from both the Lanigan and Rocanville mines, also supplied by PCS and labeled LB and RB, respectively, were also studied. Sample descriptions are summarized in Table 1. The samples, including the brine evaporites, were used as received. Samples were stored at room temperature in sealed bottles. The bottles were opened to the laboratory atmosphere only during transfer and weighing of aliquots into the calorimeter ampules.

The method used for studying water vapor sorption is described in detail elsewhere [2]. Briefly, the sample is held isothermally in the 1 ml ampule of a Hart Scientific model 7707 differential scanning calorimeter and exposed to a nitrogen gas stream containing a continuously increasing water vapor pressure. The water vapor pressure is

Table 1
Characteristics of potash and evaporated brine samples

			Mass %			
Sample	Label	Particle size, mesh	Mg	Ca	Na	SO_4^{2-}
Lanigan Granular	(LG)	+14	0.05	0.05	1.4	0.1
Lanigan Standard	(LS)	−14	0.01	0.05	1.5	0.1
Rocanville Granular	(RG)	+14	0.12	0.02	1.4	0.04
Rocanville Standard	(RS)	−14	0.3	0.02	1.4	1.0
Lanigan Brine	(LB)	–	–	–	–	–
Rocanville Brine	(RB)	–	–	–	–	–

calculated from the temperature of an aluminum block containing the water used to saturate the gas stream. The rate of water vapor sorption by the sample is proportional to the heat rate measured by the calorimeter. Sample temperatures were measured to ±0.001°C and are accurate to ±0.2 K. Measurements were made at sample temperatures of 24.7, 34.7, 44.7, and 54.7°C. Heat rate and water temperature were recorded in a computer file every 60 s. The water temperature was scanned from about 10°C up to the sample temperature at scan rates from 2 to 7°C h^{-1}. During an experiment, the samples are thus exposed to water vapor pressures gradually increasing from about 1 kPa up to the saturation vapor pressure of water at the sample temperature.

Equation (1) was used to convert water temperature to water vapor pressure.

$$\ln(p_{H_2O}/\mathrm{kPa}) = 16.500 - [3855.8/(T/\mathrm{K})] - [214690/(T^2/\mathrm{K}^2)] \quad (1)$$

Water vapor pressure data were obtained from Ref. [4].

Abrupt changes in slope occur in a plot of heat rate ϕ versus p_{H_2O} when p_{H_2O} equals the equilibrium vapor pressures, $p^c_{H_2O}$, of phases, i.e. hydrates and saturated solutions, formed by reaction with the water vapor. Thus, $p^c_{H_2O}$ values are obtained from the intersection points of linear extrapolations of branches of the curve with different slopes. The rate of heat production from water vapor sorption ϕ is given by

$$\phi = \Delta HbA(p_{H_2O} - p^c_{H_2O}) \quad (2)$$

where ΔH is the enthalpy change for the sorption reaction, b is a rate constant and A is the area of the sample exposed to water vapor [2]. Taking the derivative of Eq. (2) with respect to p_{H_2O} gives

$$\mathrm{d}\phi/\mathrm{d}p_{H_2O} = \Delta HbA = k \quad (3)$$

where k is a material- and lot-dependent rate constant, the value of which is readily obtained from the slope of a plot of ϕ versus p_{H_2O}. Since ΔH and A are nearly independent of temperature, an Arrhenius plot of k can be used to obtain the activation energy for sorption of water vapor. ΔH can be obtained from a van't Hoff plot of the $p^c_{H_2O}$ values at different temperatures.

Multiple measurements were made on each sample at each temperature. The measurements were averaged at each temperature to construct Arrhenius and van't Hoff plots.

3. Results

Fig. 1 shows a plot of a representative data set for each of the samples at 24.7°C. The curves shown in Fig. 1 are essentially a plot of rate of water vapor uptake versus the water vapor pressure in contact with the sample. The curves show that the RB and LB samples both sorb water vapor at a significant rate at all accessible vapor pressures, with the RB sample sorbing water vapor at a much higher rate than the LB sample. The curve for the LB sample shows the appearance of a new phase at about 2.3 kPa. The curves for the RB sample give no indication of a phase change anywhere in the range of water vapor pressure studied. The data in Fig. 1 show that a new phase appears in all four of the fertilizer samples (RG, LG, RS and LS) at approximately the same water vapor pressure, i.e. 1.9 kPa or a relative humidity of about 60%. This first reaction involves much less water in the Lanigan samples than in the Rocanville samples.

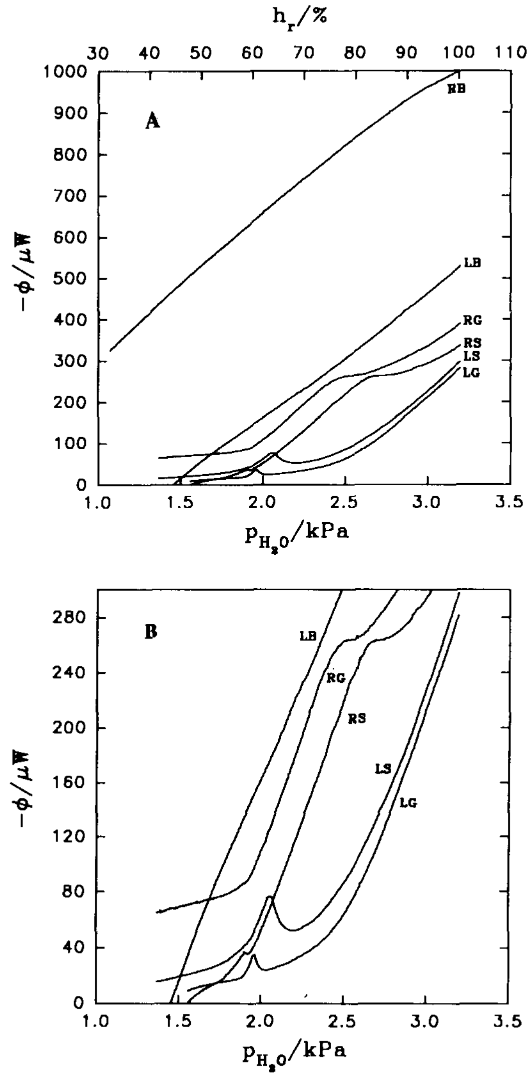

Fig. 1. Measured heat rate versus water vapor pressure and relative humidity at 24.7°C. RB is Rocanville evaporated process brine, LB is Lanigan evaporated process brine, RG is +14-mesh Rocanville Granular fertilizer, RS is −14-mesh Rocanville Standard fertilizer, LS is −14-mesh Lanigan Standard fertilizer, and LG is +14-mesh Lanigan Granular fertilizer. Curves show raw data; baseline data with empty ampules [2] have not been subtracted from these curves. Fig. 1B is simply an expansion of Fig. 1A.

Reaction with the Lanigan fertilizers is complete and the heat rate begins to decrease back toward baseline when p_{H_2O} reaches about 2.0 kPa. The first water vapor sorption reaction with the Rocanville samples continues to substantially higher p_{H_2O}, i.e. up to about 2.7 kPa. In addition to the major change in slope, the curve for the RS sample has a small, but reproducible bump at about 1.9 kPa indicating the presence of a small amount of another reaction at this vapor pressure. However, the small bump is absent in curves at higher temperatures. A second phase appears in all four fertilizer samples at 2.4–2.9 kPa.

The curves obtained at temperatures of 34.7, 44.7, and 54.7°C are similar to those shown in Fig. 1 for all six samples, except for LB at 54.7°C. At this temperature LB shows two phase changes, one occurring at 22% relative humidity which is complete at 34% relative humidity, and one at about 60% relative humidity which is the same as that observed at lower temperatures. Thus, the LB curve at 54.7°C has the same general shape as the RG and RS curves shown in Fig. 1. The reaction of LB at 22% relative humidity probably occurs at too low a p_{H_2O} to be observed at lower temperatures. The curves obtained at all temperatures are independent of scan rate.

All of the data are summarized in Table 2. The critical relative humidity, h_r^c, values given in Table 2 are the ratios of the equilibrium vapor pressure over the hydrate or saturated solution phase to the equilibrium vapor pressure of pure water at the sample temperature, i.e. experimental $p_{H_2O}^c$ values from this study divided by $p_{H_2O}^0$. The slopes, $d\phi/dp_{H_2O}$, given in Table 2 indicate the dependence of the rate of water vapor sorption on the excess water vapor pressure, i.e. on $(p_{H_2O} - p_{H_2O}^c)$. In each case, A refers to the reaction occurring at the lower water vapor pressure and B to the reaction occurring at the higher water vapor pressure. In the case of the LB sample, the critical relative humidity for reaction A was obtained only at 54.7°C.

Examination of the data in Table 2 shows there are no significant differences among the four fertilizer samples in the h_r^c values. This means that the equilibrium constants for reaction of these samples with water vapor are independent of particle size and of sample composition. The rate constants for water vapor sorption are also independent of particle size. The $d\phi/dp_{H_2O}$ values for the second reaction at humidities greater than about 75% are the same for all four fertilizer samples. The only significant difference among the data sets for the four fertilizer samples (RG, RS, LG, and LS) in Table 2 occurs for the $d\phi/dp_{H_2O}$ values for the reaction occurring at humidities around 60%. The $d\phi/dp_{H_2O}$ values for the LG and LS samples are about half as large as the values for the RG and RS samples. The $d\phi/dp_{H_2O}$ values for the LB sample at 24.7, 34.7 and 44.7°C are the slopes taken before and after the one change in slope observed. The RB sample sorbs water vapor at too high a rate at all accessible vapor pressures to obtain reliable kinetic data by this method. The $d\phi/dp_{H_2O}$ values appear to be independent of temperature; thus the activation energy is approximately zero for reaction of all the samples with water vapor.

Fig. 2 is a van't Hoff plot of the $p_{H_2O}^c$ values for each of the reactions tabulated in Table 2 and for pure water. The van't Hoff plots show that the same reactions occur at all temperatures and can be used to linearly interpolate and extrapolate $p_{H_2O}^c$ values at other temperatures. Table 3 gives the van't Hoff ΔH values calculated from Fig. 2 for the water vapor sorption reactions of each sample. The ΔH values range from 35 to 41

Table 2
Data for water vapor sorption by Rocanville and Lanigan potash fertilizers and Lanigan evaporated process brine[a]

Sample temp./ °C	h_r^c/% (Reaction A)	$(d\phi/dp_{H_2O})$ /μW kPa^{-1} (Reaction A)	h_r^c/% (Reaction B)	$(d\phi/dp_{H_2O})$ /μW kPa^{-1} (Reaction B)
Plus 14-Mesh Rocanville Granular (RG)				
24.7	62.7 ± 0.8(3)[a]	333 ± 13(3)	88.9 ± 1.1(2)	291 ± 17(2)
34.7	58.3 ± 0.2(3)	327 ± 16(3)	94.5 ± 2.4(2)	254 ± 11(2)
44.7	56.7 ± 0.5(5)	301 ± 18(5)	86.9 ± 0.5(3)	257 ± 35(3)
54.7	53.9 ± 1.0(3)	320 ± 5(3)	73.5 ± 5.1(3)	225 ± 40(3)
Minus 14-Mesh Rocanville Standard (RS)				
24.7	63.0 ± 0.4(4)	321 ± 24(4)	95.2(1)	274(1)
34.7	60.2 ± 0.6(3)	320 ± 11(3)	95.0 ± 2.9(3)	185 ± 12(3)
44.7	57.3 ± 0.4(3)	330 ± 16(3)	88.7 ± 1.8(3)	248 ± 8(3)
54.7	53.7 ± 1.0(2)	349 ± 29(4)	80.6 ± 1.5(2)	245 ± 5(2)
Plus 14-Mesh Lanigan Granular (LG)				
24.7	62.6 ± 0.8(4)	260 ± 5(4)	83.3 ± 1.6(4)	305 ± 33(4)
34.7	57.6 ± 1.4(4)	213 ± 32(4)	76.8 ± 1.2(4)	278 ± 33(4)
44.7	55.5 ± 0.8(6)	167 ± 32(6)	74.8 ± 1.0(5)	294 ± 56(5)
54.7	53.6 ± 1.2(3)	215 ± 27(3)	71.9 ± 1.0(3)	368 ± 24(3)
Minus 14-Mesh Lanigan Standard (LS)				
24.7	56.8 ± 2.6(3)	164 ± 66(3)	81.6 ± 0.2(3)	261 ± 71(3)
34.7	57.4 ± 1.7(4)	218 ± 41(4)	78.4 ± 0.9(4)	279 ± 26(4)
44.7	53.0 ± 2.4(3)	154 ± 47(3)	76.1 ± 0.2(2)	338 ± 38(2)
54.7	51.1 ± 0.9(5)	145 ± 29(5)	70.3 ± 1.0(5)	322 ± 20(5)
Lanigan Evaporated Process Brine (LB)				
24.7		180 ± 83(2)	81.7 ± 0.3(2)	296 ± 25(3)
34.7		145 ± 42(3)	72.8 ± 3.6(3)	316 ± 17(3)
44.7		137 ± 22(3)	70.1 ± 3.4(3)	389 ± 59(3)
54.7	22.1 ± 0.2(4)	331 ± 17(4)	59.9 ± 1.0(3)	329 ± 32(4)

[a] Uncertainties are given as the standard deviation of the mean of the number of data points given in parentheses.

kJ mol^{-1}. The heat of solution or hydrate formation of the materials controlling the equilibrium vapor pressures ($p_{H_2O}^c$) measured at both low and high humidity in all the samples is about $+6 \pm 3$ kJ mol^{-1}, i.e. -44 kJ mol^{-1} from condensation of water plus $+6 \pm 3$ kJ mol^{-1} equals the -38 ± 3 kJ mol^{-1} measured.

The h_r^c values in Table 2 decrease with increasing temperature. This decrease is a result of the ΔH value for reaction with liquid water. If ΔH for the hydration reaction with liquid water is endothermic, h_r^c will decrease with increasing temperature, and if ΔH for the hydration is exothermic, h_r^c will increase with increasing temperature [2].

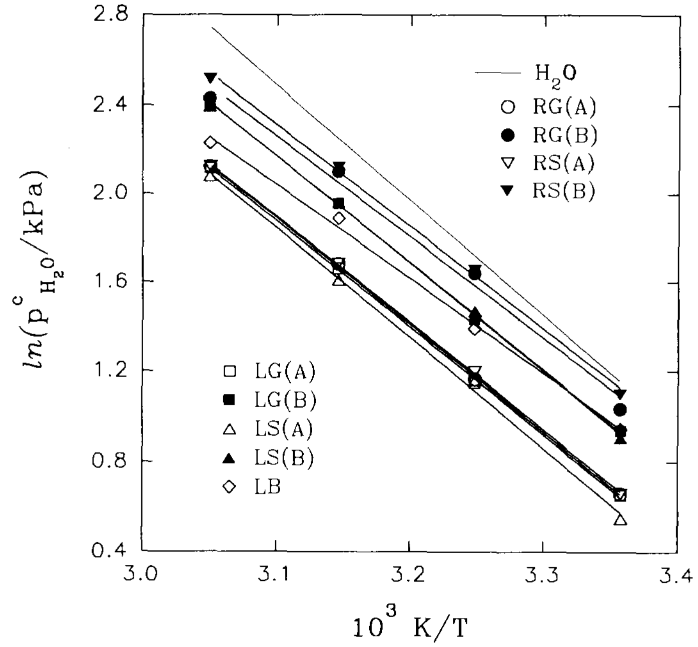

Fig. 2. Van't Hoff plots of equilibrium water vapor pressures. Labels are the same as in Fig. 1. Open symbols are for the first reaction and solid symbols for the second reaction with water vapor. ΔH values calculated from the slopes are given in Table 3.

Table 3
Van't Hoff ΔH values for water vapor sorption by potash fertilizers and Lanigan evaporated process brine

Sample	$-\Delta H$ (Reaction A)/kJ mol^{-1}	$-\Delta H$ (Reaction B)/kJ mol^{-1}
Plus 14-Mesh Rocanville Granular (RG)	39.8 ± 0.5[a]	37.9 ± 2.8
Minus 14-Mesh Rocanville Standard (RS)	39.6 ± 0.5	38.3 ± 1.3
Plus 14-Mesh Lanigan Granular (LG)	39.8 ± 0.5	40.1 ± 0.6
Minus 14-Mesh Lanigan Standard (LS)	40.9 ± 1.4	40.3 ± 0.8
Lanigan Evaporated Process Brine (LB)		35.4 ± 1.3

[a] Uncertainties are calculated from the standard error in the slope of the van't Hoff plots, see Fig. 2.

4. Discussion

The reaction occurring at about 85% relative humidity is deliquescence of a mixture of NaCl and KCl. Both the equilibrium vapor pressure over saturated solutions of these salts [5-7] and the heats of solution [8] are in agreement with this assignment. The reaction occurring around 60% relative humidity is probably formation of a saturated solution of mixed magnesium, potassium, and sodium salts, with magnesium controlling the rate and amount of reaction. This assignment is based on literature values of equilibrium vapor pressures over representative salts (mixed (Na,K)Cl, $MgCl_2$, $CaCl_2$, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Mg(C_2H_3O_2)_2$) [5–7,9] and the relative concentrations of magnesium and other contaminant ions on the surface of the Rocanville and Lanigan fertilizers. The Rocanville samples contain several times more magnesium than the Lanigan samples. The evaporated process brines also reflect this difference in their reactions with water vapor, see Fig. 1. Because process brine is dried on the surface of the fertilizer particles during manufacture, both the Rocanville and Lanigan samples have a thin layer of salts from the brine on the surface. The layer on the Rocanville samples is higher in magnesium than the layer on the Lanigan samples. The data in Fig. 1 show that there is about 70 times more heat liberated, and hence about 70 times more material accessible, for the first reaction in the RG and RS samples than in the LG and LS samples. The reaction with an equilibrium vapor pressure of 3.5 kPa (22% h_r^c) observed only at 54.7°C in the Lanigan brine sample is probably a reaction of another magnesium salt.

The practical applications of these data are prediction and understanding of caking phenomena of these fertilizers. Although moisture uptake is known to occur in these fertilizers at humidities as low as 35%, the data presented here show that no significant change in the properties of the material should occur from reaction with water vapor if the humidity is kept below 55%. If the humidity exceeds about 60%, i.e. the water vapor pressure exceeds the equilibrium vapor pressure of the first reaction, the film of salts on the surface of the particles will deliquesce and become liquid. If the humidity then drops below the critical relative humidity, the salts will recrystallize and cement the particles together. If the humidity remains between about 60 and 85%, the particles may change their flow properties, i.e. cohesion may increase and the product will probably become sticky, but no caking will occur. Only on humidity cycling will the particles cake. Diurnal temperature changes often cause cycling of the humidity within this range. The same caking process will occur if the humidity cycles around the critical relative humidity ($\approx 85\%$) of the second reaction, but caking will be even more severe because of involvement of the bulk material in addition to the surface film.

On a practical basis, caking is not more evident with Rocanville than with Lanigan fertilizers. The higher magnesium concentration on the surface of Rocanville fertilizers does not exacerbate caking probably because magnesium depresses the solubility of sodium and potassium salts. Thus, the concentration of total dissolved salts is probably about the same in the surface water film on both types of fertilizer.

In conclusion, the methods presented here can be used to quickly determine the critical humidities for storage of fertilizers and to characterize the kinetics and thermodynamics of water vapor uptake in commercial materials. Some of the results obtained by the method used in this study would be difficult or impossible to obtain by equilibrium methods.

Acknowledgement

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References

[1] Hart Scientific, Inc., P.O. Box 435, Pleasant Grove, UT 84062.

[2] L.D. Hansen, J.W. Crawford, D.R. Keiser and R.W. Wood, Calorimetric method for rapid determination of critical water vapor pressure and kinetics of water sorption on hygroscopic compounds, Int. J. Pharmaceutics, (1995), in press.

[3] L.D. Hansen, M.T. Pyne and R.W. Wood, Water vapor sorption by cephalosporins and penicillins, Int. J. Pharmaceutics, (1995), in press.

[4] R.C. Weast (Ed.), Vapor pressure of water below 100°C, Handbook of Chemistry and Physics, CRC Press, Cleveland, OH, 1974, p. D-159.

[5] D. Kitic, M.L. Pollio, G.J. Favetto and J. Chirife, J. Food Sci., 53 (1988) 578.

[6] A. Nyqvist, Int. J. Pharm. Tech. Manufact., 4 (1983) 47.

[7] L.B. Rockland, Anal. Chem., 32 (1960) 1375.

[8] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney and R.L. Nuttall, J. Phys. Chem. Ref. Data, 11 (1982) Suppl. 2.

[9] D.R. Lide (Ed.), Constant humidity, Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 1991, p. 15–21.