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Gas chromatographic thermodynamics on hydration processes of magnesium chloride with low water①

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Abstract: The dehydration and hydration processes of magnesium chloride hydrates were studied by means of frontal chromatography analysis, calorimetry, thermogravimetry and chemical analysis. The mathematical imitation for the adsorption isotherms of $MgCl_2·4H_2O$ and $MgCl_2·2H_2O$ at different temperatures indicates that Boltzmann Function is the ideal equation to describe those adsorption isotherms. Its adsorption heat is − 13.06 kJ/mol and − 16.11 kJ/mol, respectively. The adsorption equilibrium constants are also given. From the data obtained, there is a thermodynamical possibility to use partial dehydrated magnesium chloride hydrates as an absorbance to clean water vapor contained in bischophite dehydration equipment and let the protection gas HCl recycle in the fluid bed reaction system.

Key words: magnesium chloride with low water; hydration heat; adsorption heat; differential scanning calorimetry; frontal chromatography

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1 INTRODUCTION

Magnesium chloride is a basic material for chemical industry, and it has wide applications in metallurgy, architectural material and textile industry. It is also a material for fire-resistant products, cryogen and compound fertilizer productions[1]. The fully dehydrated magnesium chloride is a good material for electrolytic metal magnesium production. Because magnesium chloride has a strong adsorptive ability, it is also used as a drying agent. Many successful works have been done on the dehydration of bischophite[2-10]. But in fact, the dehydration processes of magnesium chloride hydrates are inseparably connected to the hydration process. The latter one will influence the dehydration process. Very few scientific research on its hydration process has been reported so far[11].

The aims of this paper are to obtain basic data for hydration process of magnesium chloride with low water and check the thermodynamic possibility of using partial dehydrated magnesium chloride to clean the vapor in the dehydration tail gas and let protection gas recycle.

2 EXPERIMENTAL

The experimental materials are $MgCl_2 · 5.97 H_2O$, $MgCl_2·3.98H_2O$ and $MgCl_2·1.95H_2O$ with a grain size of 30 − 80 mesh, which are obtained from $MgCl_2 · 5.97H_2O$ (analytical pure material heated about 4 h at 40 ℃) after dehydration in the fluid system[2]. The compositions of samples are shown in Table 1.

Table 1 Compositions of samples (mass fraction, %)

Sample	$MgCl_2$	MgO	H_2O
$MgCl_2·5.96H_2O$	46.96	0	53.04
$MgCl_2·3.98H_2O$	57.01	0	42.99
$MgCl_2·1.95H_2O$	72.07	1.37	26.56

In order to decide the experimental temperature, thermogravimetric analysis for $MgCl_2·5.97H_2O$ at different temperature increasing rates was carried out. The results are shown in Fig. 1.

According to thermogravimetric analysis, under the experimental conditions the dehydration temperature of those processes, from 6 moles water to 4, from 4 moles water to 2, and from 2 moles of water to 1, is 121.7 − 131.7 ℃, 169.2 − 191.6 ℃ and 201.1 − 225.0 ℃, respectively.

In order to let the reactions go towards hydration direction, the highest temperature of those processes should be lower than 121.7, 169.2 and 201.1 ℃, respectively. But relatively high aqueous vapor partial

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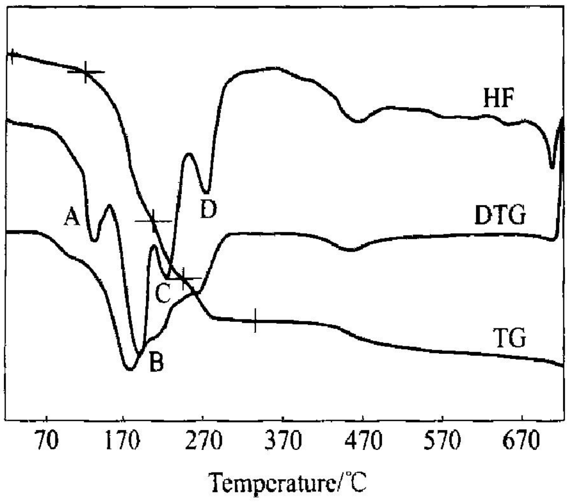

Fig. 1 DTA and TG curves of dehydration process of $MgCl \cdot 6H_2O$ at temperature increase rate of 10 ℃/min

Mode of equipment: SETARAM TG-DTA92, made in France;
Test samples: 11.83 - 17.29 mg $MgCl_2 \cdot 5.96H_2O$;
Reference sample: calcined Al_2O_3;
Holders for test and reference sample: quartz crucible;
Temperature range: room temperature - 750 ℃;
Temperature increase rate: 5, 10 and 15 ℃/min;
Carrying gas: pure N_2

pressure is needed at high experimental temperature. Considering that maximum water vapor partial pressure can be supplied at room temperature, we choose the adsorptive temperature for $MgCl_2 \cdot 4H_2O$ and $MgCl_2 \cdot 2H_2O$ as 40 - 60 ℃ and 70 - 90 ℃.

The experimental equipment diagram for measurement of hydration isotherms is shown in Fig. 2.

Highly pure nitrogen, from pressure pan, goes into gas chromatography and then flows out from it. Before N_2 goes into gas chromatography once again, it has three different channels to go through.

Channel Ⅰ. N_2 goes through cut-off valve T_2 and gas chromatography. Because no aqueous vapor is carried by N_2 in this channel, it is only used before the equipment goes steady.

Channel Ⅱ. After going through cut-off valve T_3 and spiral pipe 6, nitrogen gas will go through vaporizer 7, which is put in a carefully temperature controlled water bath, and carries aqueous vapor from it. Then nitrogen gas goes through cold trap 1 and magnesium chloride column 2. Magnesium chloride with low water adsorbs aqueous vapor contained in the nitrogen gas. The surplus aqueous vapor will go into chromatographic column and be analyzed at the column temperature.

Channel Ⅲ Nitrogen gas goes through flow controller T_1, flow indicator F, cold trap 1, magnesium chloride column and chromatography column. This channel is used for adjusting the molar ratio of nitrogen gas and aqueous vapor, so as to measure the amount of water vapor adsorbed by magnesium chloride hydrates under different partial pressure of aqueous vapor.

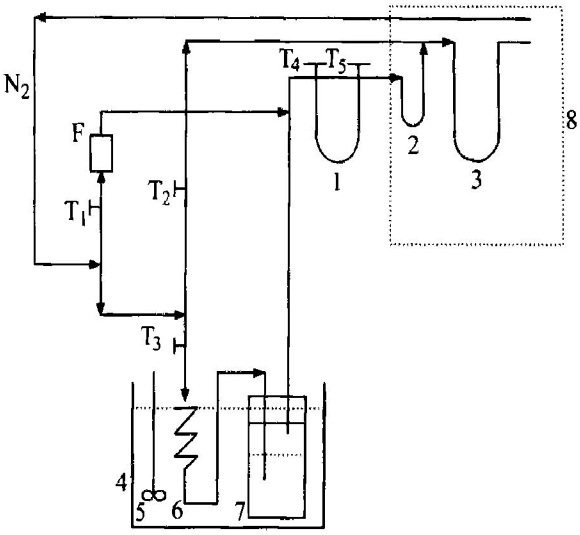

Fig. 2 Experimental diagram for measurement of adsorption isotherms of magnesium chloride hydrates by means of frontal gas chromatography analysis

1 —Cold trap; 2 — Magnesium column;
3 —Chromatography column; 4 —Water bath;
5 —Agitator; 6 —Spiral pipe; 7 —Vaporizer;
8 —Gas Chromatography; T_1 —Flow controller;
T_{2-5} —Cut-off valve; F —Flow indicator

The gas chromatography used in this experiment is GC-9AM, made in Japan Hitach Company, along with a data processor, C-R4A. Analytical column: GDX301, *d* 3.0 mm × 1.0 m; reference column: GDX301, *d* 3.2 mm × 3.6 m; water bath temperature: 20.2 - 24.0 ℃; chromatographic column temperature: 40 - 90 ℃; temperature of injector: 85 ℃; temperature of TCD: 100 ℃; total pressure: 490 kPa; pressure of first chamber: 120 kPa; pressure of second chamber: 110 kPa; flow rate of first chamber: 90 mL/mim; flow rate of second chamber: 45 mL/mim; current of detector: 80 mA. The magnesium chloride column, with a height of about 2 cm, was filled under minus pressure in a dry glove box.

3 RESULTS AND DISCUSSION

3.1 Measurement of input aqueous vapor and calibration curve

Cold trap is used to condense aqueous vapor carried by input nitrogen gas. The collected water within a certain period of time was weighed to determine the amount of input aqueous vapor. The soap film gas meter is used for measuring gas flux.

From calibration curve, as shown in Fig. 3, it is seen that the height of chromatography peak is proportional to the concentration of water vapor. But the

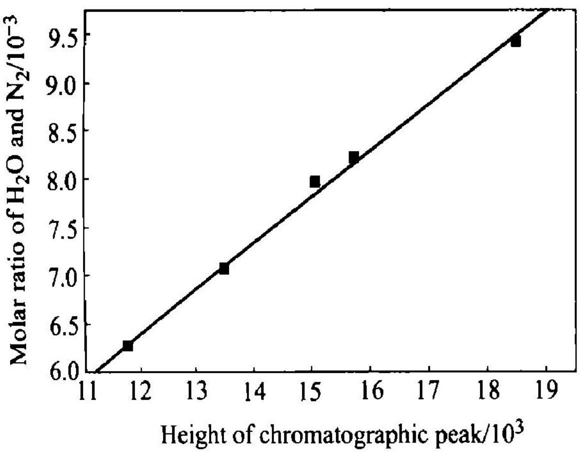

Fig. 3 Calibration curve

line does not go through the coordinate origin and there is a positive intercept. Because there is a temperature drop near the cold trap due to the cold liquid nitrogen, the cold trap just likes a "pump", which will make the flow flux increase. On the other hand, due to water condensation in the cold trap, a concentration grade would form and lead to an increase of flow flux. Based on the above analysis, the calibration line should be moved and let it go through coordinate origin.

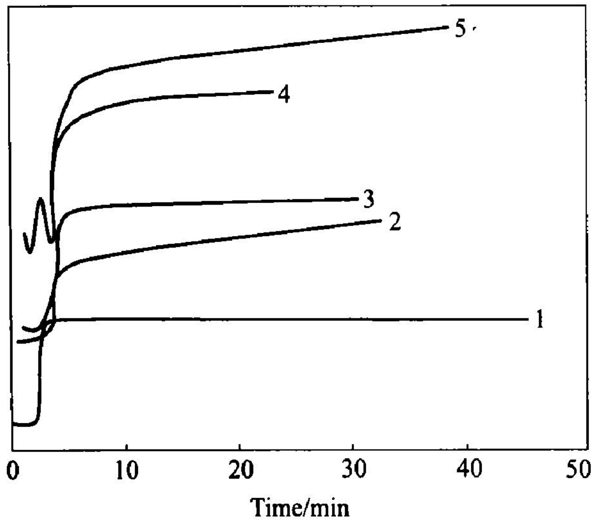

Fig. 4 Gas chromatography curves for $MgCl_2 \cdot 3.98H_2O$ hydration at 60 ℃

Curve 1: $p(H_2O) = 1.12$, t(water bath) = 20.2 ℃;
Curve 2: $p(H_2O) = 1.53$, t(water bath) = 24.05 ℃;
Curve 3: $p(H_2O) = 1.46$, t(water bath) = 24.0 ℃;
Curve 4: $p(H_2O) = 1.29$, t(water bath) = 20.03 ℃;
Curve 5: $p(H_2O) = 1.83$, t(water bath) = 24.0 ℃

The equation of the calibration line is given as follows:

$$C = K \times h = 8.642 \times 10^{-11} \times h \qquad (1)$$

where C is concentration of aqueous vapor in N_2, mol·mL^{-1}; h is the height of chromatography peak, μV; K is a constant of thermal conductivity cell, mol·μV^{-1}·mL^{-1}, it is considered an unchangeable constant within experimental temperature range[12].

3.2 Adsorption isotherms

The hydration processes for magnesium chloride hydrates are expressed as:

$$MgCl_2 \cdot RH_2O\ (s) + 2H_2O\ (g) \Leftrightarrow MgCl_2 \cdot (R+2)\ H_2O\ (s) \qquad (R = 2, 4) \qquad (2)$$

In order to let a hydration process take place, relatively high and stable aqueous vapor is needed and the frontal chromatography analysis was selected for this system.

There is a relationship between the absorbance and the area of chromatographic curves[13].

$$\Gamma = \frac{KF'_C}{u_1 m} \cdot A_C \qquad (3)$$

where Γ is the absorbance of adsorbent over unit mass adsorbate; A_C is the area of chromatography curve; K is the constant of TCD (Thermal Conductivity Detector); m is the mass of adsorbate; F'_C is the calibrated fluid rate of carrier gas; u_1 is a moving speed of data recording paper.

$$F'_C = j \cdot \frac{p_0 - p_W}{p_0} \cdot \frac{T_C}{T_R} \cdot F_C \qquad (4)$$

In Eqn. (4)[14], p_0 and p_w are saturated aqueous vapor pressure at experimental temperature and under atmospheric pressure, respectively; j is a coefficient; F_C is the fluid rate of carrying gas; T_C and T_R are chromatographic column temperature and room temperature, respectively.

The chromatographic adsorption peaks under 60 ℃ for $MgCl_2 \cdot 3.98H_2O$ are shown in Fig. 4. The amount of water adsorbed by magnesium chloride hydrates may be obtained from Eqns. (3) and (4). The blank assay should be subtracted from it.

From chromatographic adsorption peaks, data for adsorption isotherms are obtained and listed in Table 2, and plotted in Fig. 5 and Fig. 6 correspondingly.

3.3 Adsorption isotherm equation

The Langmuir equation and B. E. T Equation are not suitable for this system. But Boltzmann equation (5) fits these isotherms quite well and it is a good adsorption isotherm equation for this system.

$$\Gamma = \frac{\alpha}{1 + \exp\left(\frac{p - \beta}{\gamma}\right)} + \theta \qquad (5)$$

where Γ is the absorbance, mol/kg; α, β, γ and θ are simulative parameters, as shown in Table 3 and Table 4. It is seen from Fig. 5 and Fig. 6 that the isotherm data agree with Boltzman equation, only with the exception of data at 40 ℃. The simulation errors for adsorption isotherms are smaller than 0.07, only with the exception of isotherm at 40 ℃, 0.393.

Table 2 Data of adsorption isotherms for $MgCl_2 \cdot RH_2O$ [$\Gamma/(mol \cdot kg^{-1})$]

Sample No.	$p(H_2O)$/kPa	$MgCl_2 \cdot 1.95H_2O$			$MgCl_2 \cdot 3.98H_2O$				
		90 ℃	80 ℃	70 ℃	60 ℃	55 ℃	50 ℃	45 ℃	40 ℃
1	1.12	3.49	11.86	13.36	0	0.89	1.94	2.73	3.59
2	1.29	8.74	13.23	15.51	2.03	2.74	3.72	4.75	5.37
3	1.46	12.83	14.08	17.73	2.29	4.15	5.02	5.66	6.29
4	1.53	13.21	14.49	18.31	2.61	4.49	5.73	6.20	7.63
5	1.83	14.00	14.68	19.15	2.82	4.91	6.10	6.27	8.27

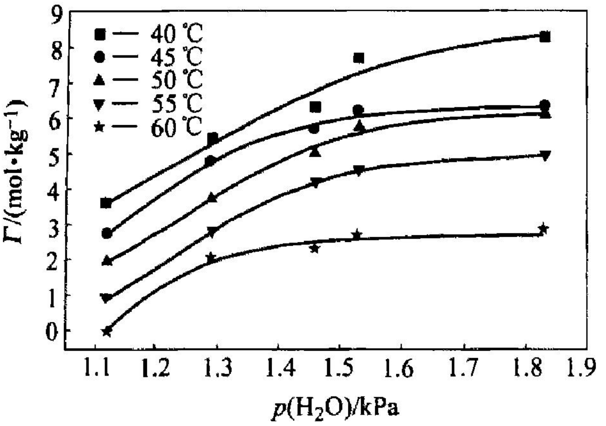

Fig. 5 Adsorption isotherm of $MgCl_2$. $3.98H_2O$ to aqueous vapor

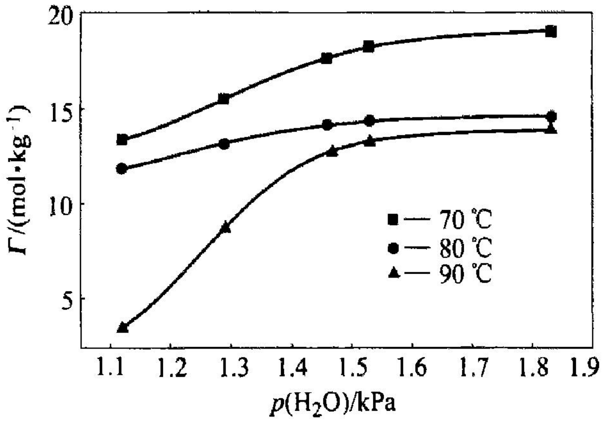

Fig. 6 Adsorption isotherm of $MgCl_2$. $1.95H_2O$ to aqueous vapor

Table 3 Parameter of hydration isotherms for $MgCl_2 \cdot 3.98H_2O$

Parameter	Isotherm				
	B	C	D	E	F
α	- 27.29	- 5.679	- 5.799	- 6.628	- 7045 6
β	1.260	1.143	1.256	1.235	0.828 8
γ	0.188 9	0.129 6	0.132 8	0.124 1	0.131 5
θ	8.667	6.344	6.210	4.960	2.727

Table 4 Parameter of hydration isotherms for $MgCl_2 \cdot 1.95H_2O$

Parameter	Isotherm		
	B	C	E
α	- 7.258	- 4.347	- 12.95
β	1.297	1.209	1.254
γ	0.121 9	0.132 3	0.092 34
θ	19.24	14.74	13.98

3.4 Adsorption heats

The adsorption heat may be defined by Calusis — Clapeyron Equation:

$$Q = RT^2\left|\frac{\partial \ln(p/p_0)}{\partial T}\right|_q = -R\left|\frac{\partial \ln(p/p_0)}{\partial(1/T)}\right|_q \tag{6}$$

Select Γ as 3.63, 4.47 and 13.50, 13.31 mol/kg from Fig. 5 and Fig. 6 respectively, we obtain the corresponding equilibrium partial pressure of aqueous vapor, p. There is a linear relationship between ln (p/p_0) and $1/T$ (see Fig. 7 and Fig. 8). The adsorption heat equals minus R times the slope of the line.

From Fig. 7 and Fig. 8, the adsorption heats of magnesium chloride hydrates were obtained and listed in Table 5.

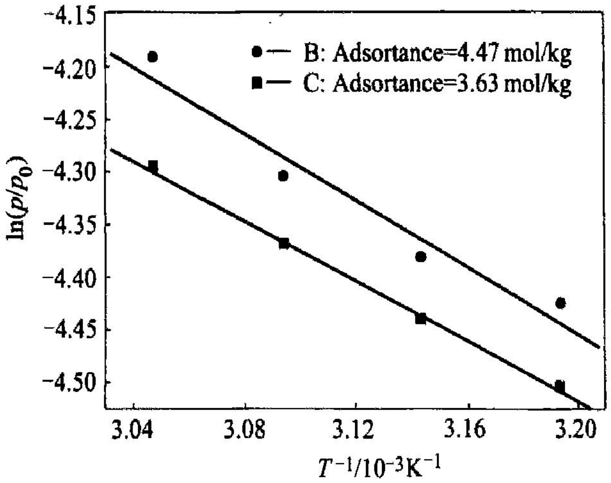

Fig. 7 Diagram of $\ln(p/p_0)$ to $1/T$ for isotherms of $MgCl_2 \cdot 3.98H_2O$

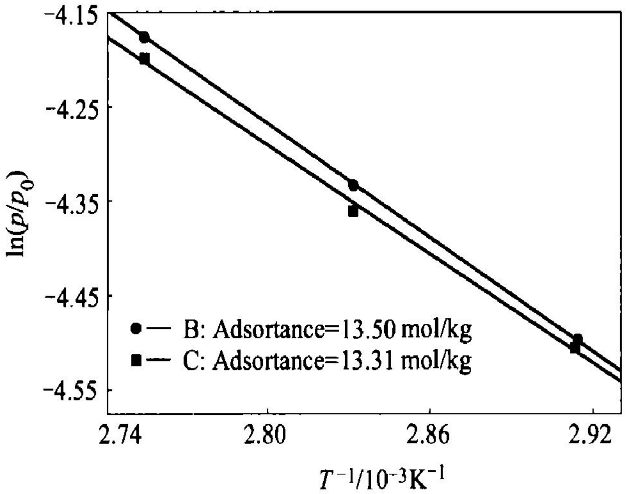

Fig. 8 Diagram of $\ln(p/p_0)$ to $1/T$ for isotherms of $MgCl_2 \cdot 1.95H_2O$

Table 5 Adsorption heats of magnesium chloride hydrates to aqueous vapor

Adsorbent	Absorbance $\Gamma/(\mathrm{mol(kg^{-1}})$	Absorption Heat $Q/(\mathrm{KJ \cdot mol^{-1}})$
$MgCl_2 \cdot 3.98H_2O$	3.63	- 13.06
	4.47	- 14.17
$MgCl_2 \cdot 1.95H_2O$	13.31	- 15.59
	13.50	- 16.61

3.5 Adsorption equilibrium constant

Adsorption equilibrium constant is defined as[15]:

$$K_a = \frac{n^s/m}{n^g/n_c} \tag{7}$$

where n^s is molar quantity of aqueous vapor adsorbed by magnesium chloride hydrates when the system reaches adsorption equilibrium; m is the mass of magnesium chloride hydrates. Meantime; n^g is the molar quantity of aqueous vapor contained in n_c moles of carring gas. So, in equation (7), n^s/m equals absorbance Γ; n^g/n_c is a molar ratio of aqueous vapor and nitrogen , which goes through gas chromatography.

It is found from Table 6 that the adsorption equilibrium constant for $MgCl_2 \cdot 3.98H_2O$ is less than those for $MgCl_2 \cdot 1.95H_2O$. As the temperature increases, the adsorption equilibrium constant is decreased. The highest adsorption constant for $MgCl_2 \cdot 1.95H_2O$ at 70 ℃ is 2 338 mol/kg and it would be higher if the experimental temperature is lower than 70 ℃.

Moscowtz[3] used partial dehydrated(P. D) magnesium chloride hydrates mixture as an adsorbent to absorb water vapor contained in tail gas of fluid bed system for bischophite dehydration. In this way, protection gas, HCl(g), mixed in tail gas, can be circulated and it will not be harmful to our environment. But Moscowtz did this work on a small scale experiment.

Dehydration of $MgCl_2 \cdot 6H_2O$ may take place in two stage fluid bed system. After treatment in the first fluid bed, about 4 mol of water is removed from $MgCl_2 \cdot 6H_2O$. Meantime $MgCl_2 \cdot 2H_2O$ is yielded, which includes about 17.7% of water waiting for further treatment in the next fluid bed. The highest absorbance of $MgCl_2 \cdot 2H_2O$ is 34.5% at 70 ℃ under the experimental conditions. It would be much higher at lower temperatures. So, using P. D magnesium chloride as an adsorbent to treat aqueous vapor contained in the tail gas of second fluid bed and let HCl circulate is possible in a thermodynamics view.

Usually, adsorption equilibrium constant is obtained by static method, but the system mentioned in this paper is not a static one. So, the reliability of adsorption equilibrium constants obtained in this work needs further confirmation.

3.6 Influence of grain size

In order to investigate the influence of sample grain size on hydration process, we select two samples of $MgCl_2 \cdot 1.95H_2O$ with the grain size of 30 ~ 80 mesh and small than 80 mesh to check their absorbance under the same experimental conditions as before. The chromatography column temperature is 70 ℃.

It is found from Table 7 that the absorbance decreases with the decrease of sample grain size, and the average adsorption equilibrium time extends from 63 min to 97 min, which contradicts with the general concept. In this case, the authors guess that when the sample grain size is decreased, the hydration tendency of $MgCl_2 \cdot 1.95H_2O$ is a dominant process compared to the dehydration. From this result, the authors guess that the hydration process of $MgCl_2 \cdot 2H_2O$ is not a solid state inner diffusion controlled process, but probably its dehydration process is.

Table 6 Adsorption equilibrium constants of aqueous vapor adsorbed on magnesium chloride hydrates ($\mathrm{mol \cdot kg^{-1}}$)

$MgCl_2 \cdot 3.98H_2O$					$MgCl_2 \cdot 1.95H_2O$		
40 ℃	45 ℃	50 ℃	55 ℃	60 ℃	70 ℃	80 ℃	90 ℃
1 010	766	744	599	334	2 338	1 792	1 709

Table 7 Influence of grain size on absorbance of $MgCl_2 \cdot 1.95H_2O$ at 70 ℃

Comparison parameters	Grain between 30 and 80 mesh					Grain small than 80 mesh				
	1	2	3	4	5	1	2	3	4	5
Equilibrium time/min^{-1}	80	85	50	55	45	120	115	85	60	10
Absorbence Γ_w/%	24.08	27.91	31.94	32.96	34.46	23.74	24.05	27.19	30.54	32.18

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