

# WATER-VAPOR SORPTION ON KAOLINITE : HYSTERESIS

*by*

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## ABSTRACT

Detailed water-vapor sorption measurements were made on Li, Na, K, Cs and Mg kaolinite at 25°C. When desorption is started from  $P/P_0$  near saturation, all ionic modifications show reversible hysteresis. The size and  $P/P_0$  range of the hysteresis loop varies with the nature of the exchangeable ion and sample history.

No hysteresis occurs on Li and K kaolinite when desorption is started at  $P/P_0 < 0.8$  which along with other data indicates that Li and K exchangeable ions are not truly hydrated below  $P/P_0 = 0.8$ . The hysteresis for all ionic modifications is traced to hydration of the exchangeable ions. The apparent anomalous position of Li and K ionic hydration is attributed to control of hydration of exchangeable ions by the difference between the hydration energy of the ion minus the specific adsorption energy of the ion for the clay. This difference must be positive before true ionic hydration occurs.

A molecular model for sorption is postulated in which sorption is assumed to take place at specific sorption sites upon the clay surface. The energy of sorption at different sites is believed to be different and also to be a function of the hydration state of the exchangeable ion. By the use of the proposed model and the detailed sorption data, hydration of the different exchangeable ions as a function of the relative vapor pressure can be obtained. The sorption model also predicts phase changes in the sorbed film at certain relative pressures. These calculated phase changes agree very well with phase changes indicated from Jura-Harkins' plots of the experimental data.

## INTRODUCTION

An isotherm is said to exhibit hysteresis when the desorption curve is different from the adsorption curve. The desorption branch of the hysteresis loop always has more vapor sorbed at a given pressure than does the adsorption branch. Brunauer (1945) recognizes two types of hysteresis: "hysteresis may be reversible or irreversible; it is reversible if on repetition of the experiment the adsorption isotherm is completely reproduced, irreversible if a second experiment gives a different curve."

Hysteresis has not been observed previously for water-vapor sorption on kaolinite. In fact a consideration of hysteresis has been rarely mentioned. Orchiston (1954) reported no hysteresis on kaolinite; however, no details are given about sample preparation or outgassing technique, and for the kaolinite isotherm the ordinate axis (amount of water adsorbed) is so compressed that appreciable hysteresis would not be noticed. Keenan, Mooney and Wood (1951) found no hysteresis for kaolinite but their data show just one desorption point between  $P/P_0 = 0.85$  and 0.18 and this one point lies above the adsorption isotherm.

Martin (1957) found that reversible hysteresis occurred on Li kaolinite and suggested that hydration of the exchangeable ions was an important factor determining the size and pressure stability range of the hysteresis loop. A detailed consideration of hysteresis was omitted from the earlier work (Martin, 1957) because some preliminary data on Cs and Na kaolinites appeared to be contradictory to what one would expect if ion hydration were responsible for the hysteresis loop. Namely, Cs kaolinite behaved similarly to Li kaolinite in that the hysteresis loop persisted from  $P/P_0 \approx 0.85$  to  $P/P_0 < 0.02$  while for Na kaolinite the loop closed at about  $P/P_0 = 0.07$  and the initial adsorption on kaolinite saturated with any of these three alkali ions was the same up to  $P/P_0 \approx 0.07$ .

These preliminary results have been extended in an attempt to explain the hysteresis phenomena that occur upon water-vapor sorption on various homoionic kaolinites. Detailed adsorption and desorption isotherms have been obtained for homoionic Li, Na, K, Cs and Mg kaolinite. In addition to the isotherms, considerable loop scanning data are included which contribute significantly to the discussion of hysteresis phenomena and of hydration of exchangeable ions.

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## MATERIALS AND PROCEDURE

Natural gradation kaolinite from Bath S. C. was used.<sup>1</sup> This particular batch of kaolinite has a cation exchange capacity of 2.7 meq/100 g and a surface area of 13.0 m<sup>2</sup>/g.

Sodium and lithium ionic modifications were prepared by extracting 1 g of clay ten times with 200 ml portions of the appropriate 1 N salt solution whose pH had been adjusted to 3.0 with HCl; time of contact for each extraction was from 8 to 24 hr. This extraction has been found to reduce the aluminum in solution to a low and constant value. The amount of exchangeable hydrogen is believed to be negligible because for the sodium ionic modification the exchangeable sodium and cation exchange capacity agree to within 5 percent of each other. Other ionic modifications, Cs, K and Mg, were prepared by taking a sample which had been extracted with NaCl to reduce the aluminum in solution and then extracting five times with 200 ml portions of neutral 1 N chloride salt solution to effect the desired ion exchange; time of contact for each extraction was 20–30 min. The resultant homoionic clay was repeatedly extracted with ethanol until the supernatant liquid gave a negative test for chloride ions. The clay paste was dried 5–10 min in an air oven at 100°C and crushed to pass a sieve with 0.25 mm openings; this modest drying reduced the water content to between 0.5 and 1.0 percent.

<sup>1</sup> The clay, trade name "Peerless kaolinite," was purchased from R. T. Vanderbilt Co., New York City.

A sample left 1 hr in the oven gave very different sorption behavior, indicating the importance of careful experimental procedures in sample preparation.

Sorption isotherms were determined as described previously (Martin, 1957). In the present investigation the isotherm temperature is 25.5°C. After placing the partially dried clay into the sorption chamber the sample is outgassed for 48 hr under a vacuum of  $10^{-5}$  mm Hg and at a temperature of 70°C. The sample weight obtained following this drying procedure is taken as the reference clay weight for subsequent calculation of the weight of water adsorbed per gram of clay,  $X$ , in mg  $H_2O/g$  clay. The adsorption isotherm obtained from this thoroughly degassed clay is designated—adsorb from  $X = 0$ . Two other isotherm conditions that need to be defined are: (1) desorb from  $X > 50$ , nonequilibrium, arbitrarily chosen weight of water adsorbed, such that considerable variation about this point is of no consequence to the sorption data for  $P/P_0 < 0.9$ . This condition  $X > 50$  is reached by introducing sufficient water vapor into the sorption chamber that bulk condensation of liquid water occurs on the sides of the chamber. After 4–8 hr the sample will have adsorbed sufficient water that  $X > 50$ . Even when the time period is extended so that the sample adsorbs water to  $X \approx 250$ , there is no visible water in the clay sample and the desorption isotherm is not altered. Adsorption from  $X = 2-3$  is the adsorption following desorption from  $X > 50$  where the desorption is stopped with  $X$  somewhere between 2 and 3, and adsorption is started immediately.

## RESULTS

Data in Tables 1–5 are displayed graphically in Figs. 1–3. Part of the data for Na kaolinite, Fig. 2, have been plotted on an expanded scale to show that there is good justification for drawing the isotherms with discontinuities rather than as smooth curves.

The isotherms for all five ionic modifications of kaolinite show reversible hysteresis between adsorption from  $X = 0$  and desorption from  $X > 50$ . Figure 2 illustrates the stability of this hysteresis because the adsorption from  $X = 0$  and desorption from  $X > 50$  isotherms on Na kaolinite contain data from seven complete cycles. A cycle includes thorough outgassing of the sample at 70°C, taking adsorption points starting from  $X = 0$ , adsorption to  $X > 50$ , and taking desorption points. Loop scanning, which is a technique for studying hysteresis, involves adsorbing to a certain  $P/P_0$  and then desorbing until the desorption isotherm from this particular  $P/P_0$  joins the general desorption isotherm from  $X > 50$  for the kaolinite under investigation.

Figures 1–3 show that the loop scanings for the different homoionic kaolinites are very different. There is no hysteresis for either Li or K clay (see Fig. 1) when the initial adsorption is started from  $X = 0$  and desorption begun for any value of  $X < 11.9$  for potassium clay or  $X < 10.7$  for lithium clay; further, all these data give a single isotherm. Curve A, Fig. 1, will also

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TABLE 1.—SORPTION DATA FOR LITHIUM KAOLINITE AT 25.5°C

$P/P_0$	$X^*$ mg/g	$P/P_0$	$X^*$ mg/g	$P/P_0$	$X^*$ mg/g
Adsorb from $X = 0$		Desorb from $X > 50$		Adsorb from $X > 2.5 < 3.8$	
0.003 <sub>4</sub>	1.15	0.950	28.7	0.068 <sub>2</sub>	2.91
0.026 <sub>3</sub>	1.95	0.877	18.9	0.089 <sub>3</sub>	2.32
0.061	2.57	0.833	15.6	0.122	3.51
0.112	2.90	0.828	15.2	0.157	3.75
0.221	3.75	0.801	13.7	0.164	3.93
0.306	4.24	0.748	11.7	0.195	4.04
0.371	4.85	0.680	10.0	0.211	4.08
0.402	5.20	0.662	9.85	0.220	4.17
0.473	5.66	0.595	8.24	0.238	4.24
0.527	6.26	0.588	8.29	0.259	4.45
0.583	6.82	0.538	7.68	0.288	4.63
0.606	7.22	0.502	7.07	0.300	4.81
0.695	8.36	0.478	6.60	0.304	4.83
0.708	8.50	0.453	6.39	0.360	5.28
0.766	9.78	0.415	6.11	0.392	5.56
0.793	10.7	0.328	5.26	0.439	5.92
0.819	12.0	0.317	5.34	0.509	6.52
0.835	12.7	0.309	5.20	0.589	7.44
0.880	16.7	0.264	4.78	0.680	8.75
0.917	20.9	0.222	4.39	0.770	10.9
Desorb from $X = 10.7$ ; when ads. started from $X = 0$		0.212	4.30	0.842	14.3
		0.176	3.92	0.877	16.6
		0.146	3.79	0.945	25.3
		0.129	3.68		
0.727	9.01			Desorb from $X = 4.82$ , $P/P_0 = 0.302$	
0.599	7.14	0.110	3.50		
0.413	5.26	0.079 <sub>6</sub>	3.22	0.263	4.48
0.281	4.16	0.074 <sub>7</sub>	3.16	0.244	4.28
		0.048	2.72	0.222	4.18
0.194	3.50			0.172	3.96
0.081	2.75	0.032 <sub>6</sub>	2.53		
0.047	2.34	0.020 <sub>4</sub>	2.26	0.133	3.63
		0.006 <sub>8</sub>	1.79	0.100	3.41
		0.003 <sub>5</sub>	1.57	0.061	2.86
NOTE: Desorb from $P/P_0$		Desorb from $X = 25.3$ ,		Desorb from $X = 6.52$ ,	
0.61 and 0.72 similar		$P/P_0 = 0.945$		$P/P_0 = 0.509$	
to from $P/P_0 = 0.51$ in		0.900	19.3		
that the desorb curve goes		0.842	15.1	0.399	5.84
right over to meet desorb		0.772	12.4	0.298	5.09
curve from $X > 50$ . From		0.694	10.2	0.198	4.14
$P/P_0 = 0.84$ joins at $P/$				0.149	3.76
$P_0 = 0.67$		0.561	7.85		
		0.510	7.33		
		0.446	6.48		
		0.359	5.62		
		0.233	4.45		
		0.059	2.90		
		0.023	2.24		
		0.002	1.47		

\* $X$  = mg H<sub>2</sub>O sorbed/g clay.

TABLE 2.—SORPTION DATA FOR POTASSIUM KAOLINITE AT 25.5°C

$P/P_0$	$X^*$ mg/g	$P/P_0$	$X^*$ mg/g	$P/P_0$	$X^*$ mg/g
Adsorb from $X = 0$ †		Desorb from $X < 11.9$ ‡		Desorb from $X > 51$ §	
0.014 <sub>5</sub>	1.35	0.741	9.31	0.880	17.6
0.017 <sub>1</sub>	1.54	0.634	7.67	0.783	11.65
0.045 <sub>5</sub>	2.15	0.470	5.95	0.679	8.74
0.069 <sub>5</sub>	2.51	0.398	5.13	0.669	8.65
0.090 <sub>5</sub>	2.70	0.322	4.58	0.518	6.63
0.129	3.01	0.265	4.08	0.494	6.32
0.166	3.29	0.259	4.07	0.382	5.45
0.180	3.45	0.175	3.46	0.310	4.67
0.200	3.58	0.172	3.41	0.268	4.34
0.211	3.63	0.102	2.79	0.179	3.67
0.267	4.09	0.039	2.13	0.147	3.17
0.296	4.33			0.086	2.67
0.356	4.84			0.033	1.97
0.384	5.05			0.018 <sub>4</sub>	1.47
0.425	5.39				
0.452	5.55				
0.503	5.99				
0.531	6.32				
0.627	7.54				
0.670	8.10				
0.733	9.23				
0.815	11.9				

\*  $X =$  mg H<sub>2</sub>O sorbed/g clay. † Data from 4 adsorptions.

‡ Data from 3 desorptions. § Data from 2 desorptions.

fit sorption data when adsorption is started from  $X = 0$ , for Na clay up to  $P/P_0 = 0.075$  and for Cs clay up to  $P/P_0 = 0.30$ . These data indicate that for  $P/P_0 < 0.075$  exchangeable ions Li, Na, K and Cs have the same effect upon the water-vapor adsorption on kaolinite. That this does not hold regardless of the exchangeable ion is shown by data for Mg kaolinite (Fig. 3). For Na kaolinite (Fig. 2), if desorption is begun for  $X < 5.1$  and  $P/P_0 < 0.34$  no hysteresis is observed; however, if desorption is begun on curve A for  $X > 6.2$  and  $P/P_0 > 0.45$  a marked hysteresis loop occurs. With Mg kaolinite, Fig. 3, even though desorption is begun at  $P/P_0 = 0.2$  after adsorb from  $X = 0$ , a decided hysteresis loop appears.

The nature of the hysteresis loop is very different for the various ionic modifications. The extreme variations in hysteresis loops are shown by Li and K which gave identical adsorption isotherms. Desorption isotherms from  $X > 50$  are the same for K and Cs clay down to  $P/P_0 = 0.80$  and are the

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TABLE 3.—SORPTION DATA FOR SODIUM KAOLINITE AT 25.5°C

$P/P_0$	$X^*$ mg/g	$P/P_0$	$X^*$ mg/g	$P/P_0$	$X^*$ mg/g
Adsorb from $X = 0$		Desorb from $X > 50$		Adsorb from $X = 2.1$ to $2.8$	
0.003 <sub>7</sub>	1.10	0.923	24.1	0.046	2.30
0.005 <sub>5</sub>	1.14	0.888	19.6	0.091	3.04
0.026 <sub>8</sub>	1.98	0.840	16.45	0.121	3.52
0.068	2.61	0.815	15.2	0.130	3.70
0.087	2.83	0.775	13.5	0.196	4.40
0.092	2.84	0.754	13.05	0.198	4.40
0.119	3.19	0.717	11.85	0.205	4.35
0.150	3.47	0.681	10.8	0.216	4.48
0.172	3.74	0.659	10.25	0.246	4.84
0.235	4.29	0.594	8.91	0.269	5.20
0.261	4.51	0.558	8.22	0.334	5.44
0.290	4.68	0.551	8.14	0.375	5.72
0.316	4.94	0.525	7.85	0.439	6.43
0.338	5.06	0.508	7.65	0.456	6.49
0.395	5.62	0.472	7.24	0.475	6.75
0.402	5.68	0.409	6.58	0.510	7.10
0.416	5.96	0.399	6.38	0.567	7.83
0.443	6.20	0.389	6.23	0.612	8.77
0.496	6.88	0.375	6.20	0.653	9.25
0.509	7.10	0.365	6.02	0.669	9.70
0.524	7.30	0.286	5.25	0.719	10.9
0.536	7.44	0.277	5.30	0.776	12.4
0.641	9.24	0.264	5.10	0.837	14.75
0.738	11.35	0.261	5.06	0.895	18.5
0.772	12.2	0.230	4.77	0.925	22.7
Desorb from $X = 3.74$		0.218	4.78	Desorb from $X = 5.20$	
0.101	3.00	0.208	4.53	0.214	4.65
0.039	2.17	0.190	4.40	0.155	4.00
		0.155	4.05		
Desorb from $X = 5.06$		0.153	4.00	Desorb from $X = 6.75$	
0.229	4.27			0.409	6.38
0.152	3.64	0.135	3.81	0.330	5.65
0.083	2.84	0.129	3.74	0.271	5.03
0.024	1.85	0.098	3.25	0.176	4.29
		0.081	2.89	0.121	3.52
Desorb from $X = 6.20$		0.078	2.97	0.067	2.75
0.395	5.84				
0.283	5.17	0.076	2.93	Desorb from $X = 8.77$	
0.183	4.23	0.066	2.64	0.539	7.59
0.124	3.60	0.050	2.44	0.462	6.82
0.031	2.13	0.048	2.39	0.375	6.19
		0.037	2.26	0.307	5.46
		0.034	2.20	0.255	4.95
		0.030	2.08	0.168	4.18
		0.029	2.04	0.121	3.53
		0.024	1.98	0.049	2.47
		0.017 <sub>7</sub>	1.87	Desorb from $X = 10.9$	
		0.014	1.65	0.640	9.17
		0.008	1.36	0.560	7.81
		0.003	1.10		

\* $X = \text{mg H}_2\text{O sorbed/g clay.}$

TABLE 4.—SORPTION DATA FOR CESIUM KAOLINITE AT 24.7°C

$P/P_0$	$X^*$ mg/g	$P/P_0$	$X^*$ mg/g	$P/P_0$	$X^*$ mg/g
Adsorb from $X = 0$		Desorb from $X = 1.9†$		Desorb from $X > 50$	
0.016	1.50	0.087	3.03	0.884	17.2
0.036	1.96	0.203	4.17	0.827	13.3
0.060	2.35	0.310	5.12	0.684	9.61
0.065	2.35	0.492	7.06	0.587	8.08
0.097	2.75	0.603	8.31	0.498	7.16
0.128	3.00	0.692	9.50	0.432	6.33
0.236	4.02	0.826	12.7	0.346	5.54
0.250	4.10			0.270	4.76
0.323	4.77			0.205	4.24
0.352	4.94			0.128	3.43
0.383	5.24			0.121	3.28
0.524	6.85			0.076	2.86
0.546	7.10			0.023	1.94
0.618	7.84			0.021	1.87
0.626	8.03				
0.750	10.25				
0.787	11.1				
0.808	11.5				
0.849	13.4				
0.894	16.2				
0.895	16.0				
0.933	20.0				
0.952	22.1				

\*  $X = \text{mg H}_2\text{O sorbed/g clay}$ . † Adsorb after desorption from  $X > 50$ .

same for Li and Na clay down to  $P/P_0 = 0.85$ . Inspection of Figs. 1-3 reveals that adsorption from  $X = 2-3$  is quite different for the different ionic modifications.

## DISCUSSION

### *Hysteresis*

The hysteresis revealed in Figs. 1-3 may arise from any one of several factors or a combination of these factors. Factors that could give rise to hysteresis on kaolinite are (a) a change in particle arrangement as water is adsorbed, (b) a temporary cementation or molecular friction between particles, (c) capillary condensation and (d) hydration of exchangeable ions. The complete reproducibility of the hysteresis through seven cycles fairly well eliminates a change in particle arrangement as a significant factor. Further, the sorption isotherms on Li kaolinite are the same whether the sample is placed in the sorption cup as a dry, loose powder having a void

TABLE 5.—SORPTION DATA FOR MAGNESIUM KAOLINITE AT 25.5°C

$P/P_0$	$X^*$ mg/g	$P/P_0$	$X^*$ mg/g	$P/P_0$	$X^*$ mg/g
Adsorb from $X = 0$		Adsorb from $X > 3.6†$		Desorb from $X > 50§$	
0.004	1.75	0.083	4.48	0.853	18.5
0.010	2.16	0.133	5.05	0.745	13.5
0.014	2.33	0.185	5.75	0.628	10.7
0.025	2.69	0.236	6.32	0.612	10.45
0.028	2.79	0.290	6.80	0.598	10.1
0.046	3.23	0.379	7.65	0.480	8.62
0.063	3.60	0.451	8.28	0.475	8.65
0.094	4.10	0.490	8.60	0.437	8.22
0.127	4.45	0.585	9.75	0.370	7.59
0.137	4.48	0.604	10.0	0.309	7.03
0.192	5.07	0.699	11.7	0.263	6.64
0.196	5.16			0.247	6.43
0.248	5.53	Desorb from $X = 5.16‡$		0.179	5.79
0.305	6.15	0.116	4.59	0.154	5.31
0.340	6.50	0.064	3.87	0.107	4.80
		0.012	2.64		
0.363	6.75			0.085	4.53
0.450	7.80	Desorb from $X = 6.75‡$		0.046	3.64
0.552	8.86	0.277	6.43	0.021	3.05
0.688	11.1	0.184	5.75	0.009	2.41
		0.101	4.63	0.000	0.95

\*  $X$  = mg  $H_2O$  sorbed/g clay.

† Adsorb after desorption from  $X > 50$ .

‡ Desorb after adsorption started from  $X = 0$ .

§ Includes data for desorption from  $X = 11.7$ ,  $P/P_0 = 0.699$ .

ratio of approximately 5 or placed in the sorption cup as a moist, heavily compacted cake having a void ratio about 1.0; therefore, a change in particle arrangement is ruled out as a factor contributing to hysteresis in the present study. A permanent sticking together of kaolinite particles has been demonstrated to occur under conditions of high vacuo and zero water content (Martin, 1957); however, clay aged for a sufficient time to show reduced water adsorption also shows the same hysteresis phenomenon, and soaking the vacuo-aged clay in liquid water did not change the adsorption isotherm. One concludes that hysteresis does not result from a temporary sticking together of kaolinite particles.

Capillary condensation must not begin below  $P/P_0 = 0.8$  because there is no hysteresis for isotherm A in Fig. 1 and Bangham (1944) has shown that capillary condensation always gives hysteresis. When adsorption is started at  $X > 2.0$  following desorption from  $X > 50$  there is no hysteresis on Cs clay below  $P/P_0 = 0.65$ , a further indication that below  $P/P_0 \approx 0.7$  there is no capillary condensation. From the Kelvin equation and the size of a water molecule one calculates that capillary condensation can occur only at  $P/P_0$



$> 0.17$  because at this vapor pressure the calculated pore size is less than twice the diameter of a water molecule. Since hysteresis occurs on all ionic modifications except potassium at  $P/P_0 < 0.17$ , capillary condensation alone cannot account for the observed phenomena. The fact that the adsorption and desorption isotherms for the different ions are different even in the  $P/P_0$  range 0.8–0.9 indicates that capillary condensation is probably not very

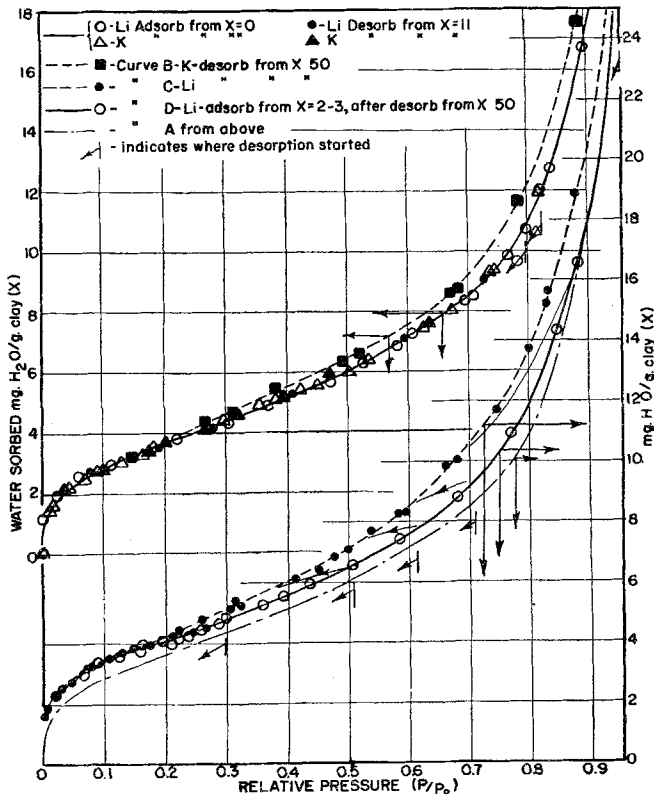


FIGURE 1.—Sorption isotherms for Li and K kaolinite at 25.5°C.

important below  $P/P_0 = 0.8$ . One is forced to the conclusion that the major factor contributing to hysteresis is ion hydration.

If ion hydration is the factor controlling hysteresis, the relative hysteresis should be in the same order as the relative hydration energies of the cations involved; however, such is not the case. In fact, at  $P/P_0 < 0.075$  adsorption from  $X = 0$  is the same for Li, Na, K and Cs. It seems unlikely that ions with as different hydration energies as Li and Cs would be hydrated to the same amount at very low vapor pressures; therefore, it is postulated that there is no ion hydration upon adsorption from  $X = 0$  at  $P/P_0 < 0.075$ .

This assumption is quite reasonable when one recalls that the ions involved are not free ions but exchangeable ions associated with a clay surface, and when water vapor is added to the clay there are two opposing forces acting upon the ion: one is the tendency for hydration, the other is the electrostatic bond between the ion and the clay surface. At very low  $P/P_0$  the exchangeable ion-clay bond is stronger than the hydration tendency for all the alkali metal ions. The small Li ion has a shorter bond length which permits the Li ion to be strongly bonded to clay surface and thereby resist hydration. In

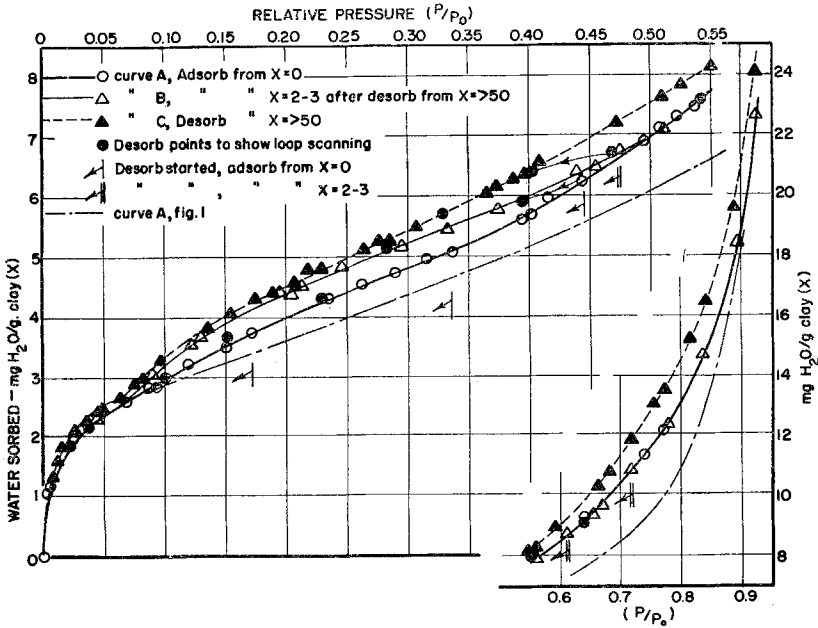


FIGURE 2.—Sorption isotherms for Na kaolinite at 25.5°C.

view of the fact that Li and K isotherms are identical up to  $P/P_0 = 0.8$  and show no hysteresis, it is postulated that there is no true hydration of Li or K below  $P/P_0 = 0.8$  when adsorption is started from  $X = 0$ . Thus the isotherm Curve A, Fig. 1, represents water sorption on the kaolinite surface *per se*.

### Relative Ion Hydration

Accepting the postulate that Curve A, Fig. 1, does represent water sorption on the clay surface *per se*, then water sorbed in excess of that shown by Curve A, Fig. 1, must be due to variations in the hydration of the exchangeable ions associated with the clay. Since this water is assigned to the exchangeable ions it will be convenient to express the excess water as the number of

water molecules per exchangeable ion rather than as so many mg  $H_2O/g$  clay. This relative ion hydration,  $n$ , is defined as the number of water molecules sorbed per ion at any chosen  $P/P_0$  in excess of the water sorbed on Li or K kaolinite when adsorption is started from  $X = 0$ . Water sorption of  $0.5 \text{ mg } H_2O/g$  clay corresponds to  $n = 1$ . Inspection of the isotherms in Figs. 1-3 indicates that  $n$  will be an integer for a considerable range of  $P/P_0$ , and that changes from one integer to the next generally occur rather abruptly.

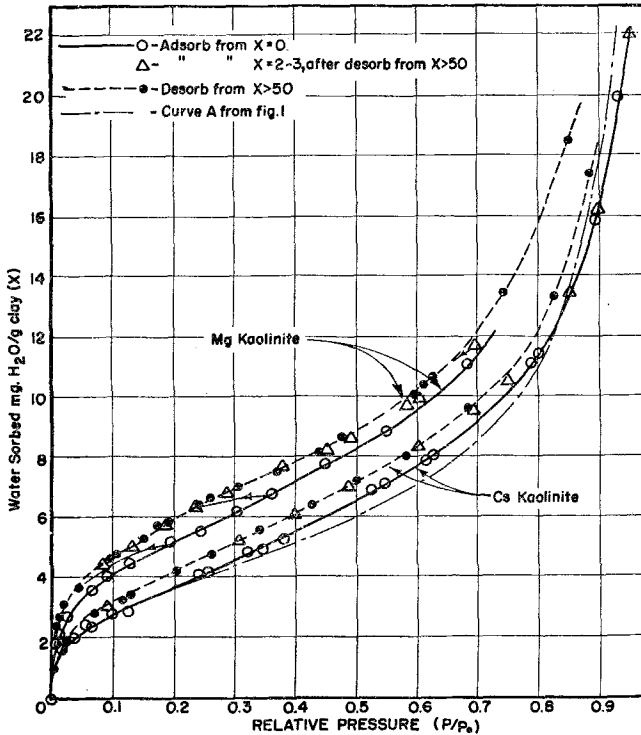


FIGURE 3.—Sorption isotherms for Mg and Cs kaolinite at 25.5°C.

In order to attach physical significance to these arbitrary hydration numbers, they must be considered in conjunction with the water adsorbed on the clay surface; therefore, a mechanism is presented by which water adsorption proceeds upon a clay surface. The mechanism is based upon variations in adsorption energy at different postulated specific adsorption sites. Before the adsorption mechanism is discussed the nature of the kaolinite clay surface will be considered briefly.

*Surface Roughness*

From the general dimensions of kaolinite particles which are assumed to be smooth surfaces one finds that the edge area comprises 20-35 percent of

the total surface area. There are a number of situations where smooth-surfaced kaolinite particles make rational interpretation of experimental data rather difficult, and one of these occurs when one compares the surface area determined from sorption measurements with the surface area obtained from geometric considerations.

The surface area determined from sorption data of a carefully sized kaolinite (1–2  $\mu$  equivalent spherical diameter) was  $9.7 \pm 0.2$  m<sup>2</sup>/g. Particle dimensions, and subsequently the geometric area, can be calculated from the hydrodynamics of fall for an oblate spheroid of an assumed diameter ( $D$ ) to thickness ( $L$ ) ratio. For 1  $\mu$  equivalent spherical diameter and a  $D/L = 10$  the geometric area is 4 m<sup>2</sup>/g, which is less than half the measured surface area. If the particles are thinner the specific surface increases; however, a  $D/L \approx 40$  is required to give a geometric area equal to the measured area. Further, electron microscopy and other data indicate that  $D/L$  is probably actually somewhat less than 10.

A certain amount of surface roughness can be assigned to kaolinite particles, based upon crystal structure and crystal chemical considerations. From the crystal structure of kaolinite it seems safe to consider the hydroxyl surface as smooth and, since a water molecule can not fully enter the hexagonal holes in the oxygen surface, the oxygen surface is essentially smooth. Therefore, any surface roughness must be at the particle edges. Without unduly straining the crystal, the edges could be notched to  $5 \pm 2$  percent of the diameter and a minimum width of serrations possibly  $160 \pm 20$  Å. Application of these roughness factors, with the assumption that the serrations are regular, to the edges of particles of 1.5  $\mu$  equivalent spherical diameter and a  $D/L = 10$  yields a geometric surface area of 9.7 m<sup>2</sup>/g which coincides with the measured surface area.

These computations are highly speculative; nevertheless recent electron microscopy (Bates and Comer, 1955; Woodward, 1955) confirms that several features of these speculations have been experimentally verified. Namely, the oxygen and hydroxyl surfaces are smooth and the edges of kaolinite particles are generally serrated. The width of the serrations varies, but 150–200 Å appears reasonable from the electron micrographs.

In discussion of the mechanism of adsorption these serrated edges become important because the edge area now contributes about 5 percent to the total area. The above calculations have been highly idealized; however, it is felt that they are sufficiently realistic that the edge area can be neglected in the following mechanism for water adsorption.

#### *Sorption Mechanism*

The sorption of water by clay is assumed to take place, in the early stages, at specific active sites on the clay surface. One obvious potential active site is the exchangeable ion. On the oxygen surface the most probable location of other sites would be the holes in the surface of the crystal, for two reasons: (a) the oxygen surface is unsaturated, and (b) these spots provide sites as far

as possible from the exchangeable ion so that the stray surface forces would be at a maximum. On the hydroxyl surface active adsorption sites are: (a) exchangeable ions and (b) spots as far as possible from the ion so that stray surface forces are at a maximum. The number of spots on the hydroxyl surface is arbitrarily chosen as three per sorption unit cell so that except for the holes in the oxygen surface the two kaolinite surfaces can be treated simultaneously.

Distributions of these sorption sites, exchangeable ion positions and associated vacant sites are computed from the cation exchange capacity and the measured surface area. The area occupied per exchangeable ion is found

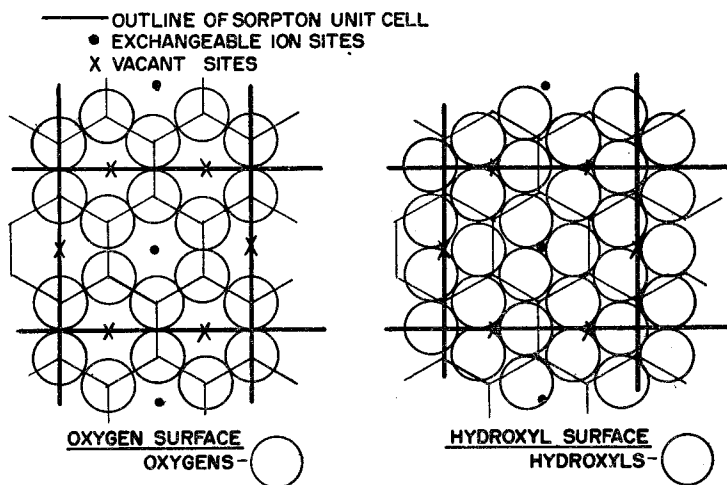


FIGURE 4.—Sorption unit cell on kaolinite surfaces.

to be  $80 \text{ \AA}^2/\text{ion}$  or  $9 \text{ \AA}$  between exchangeable ion sites. The  $80 \text{ \AA}^2/\text{ion}$  assumes a uniform distribution of charge over the kaolinite surface; since the exchangeable ions that occupy these sites may have a diameter of  $3 \text{ \AA}$  it should be obvious that gross deviations from a uniform charge distribution are unlikely. Further, in view of the fact that the source of the charge deficiency is isomorphous substitution in the crystal structure, any local concentration of charge would rupture the crystal. The area per two unit cells of crystal surface is  $91 \text{ \AA}^2 [(5.1 \times 2) \times 8.9]$ , which is fairly close to the area occupied by each exchangeable ion; therefore, a good first approximation is to assign one exchangeable ion to every two crystal unit cells. This distribution is shown in Fig. 4. On the hydroxyl surface the hexagons have been shifted slightly so that the center of the hexagon is over the proposed active sites, as on the oxygen surface.

For purposes of discussion, sorption is considered as a stepwise process. If it were possible to consider sorption at a single adsorption site the process

probably would be stepwise but in any real system there are millions of sorption sites; therefore, it should be kept in mind that in a real system there will always be considerable overlapping of the various stages which are presented here as separate steps in the sorption process.

Figures 5 and 6 present diagrammatically the first steps in the water sorption process on a kaolinite surface where there is no ion hydration. Beginning with a thoroughly degassed clay:

*Step 1.*—Adsorb one water molecule at vacant sites on oxygen surface.  $X = 0.75$  mg  $H_2O/g$  clay at completion of this step. The vacant sites on oxygen surface are considered to be the most active sorption sites initially because: (a) the oxygen surface is unsaturated; and (b) exchangeable ions tend to reduce stray surface forces at the exchangeable ion site. Step 1

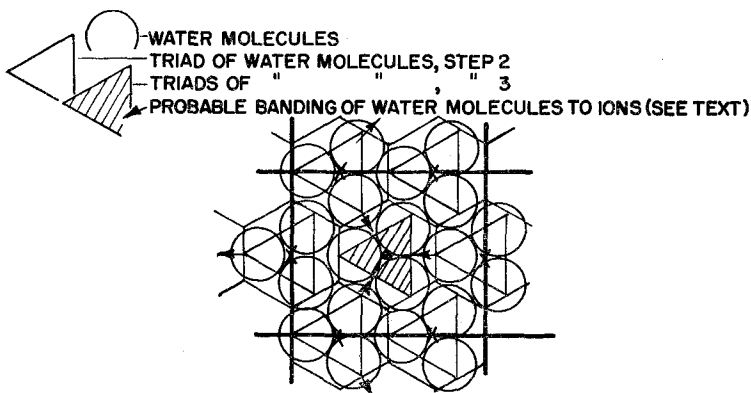


FIGURE 5.—Packing of water molecules on kaolinite surfaces.

implies that no water is adsorbed on the hydroxyl surface during this step; however, since much overlap is anticipated for Steps 1 and 2, no adsorption on the hydroxyl surface merely emphasizes the simplification implied when treating sorption as a stepwise process. Further, with the present experimental apparatus, accurate data cannot be obtained at extremely low  $P/P_0$  ( $< 0.003$ .)

*Step 2.*—Adsorb three water molecules at each exchangeable ion site. The water is adsorbed as a triad of molecules over the exchangeable ion.  $X = 2.25$  mg  $H_2O/g$  clay at completion of this step. The adsorption of this triad of water molecules may or may not be ion hydration. For Li, Na, K and Cs, which all have the same amount of water adsorbed beyond  $X = 2.25$ . Step 2 is not called ion hydration. That is, the ion remains more strongly bonded to the clay than to the water. The energy of sorption at sites for Steps 1 and 2 is probably considerably different than that for Step 3, so that one might expect a phase change in the adsorbed phase between Steps 2 and 3. Phase changes can be evaluated from the Jura-Harkins' theory (Jura and Harkins, 1946). According to this theory, a phase change is said to occur

when the plot of  $\ln P/P_0$  vs.  $1/X^2$  shows a change in slope.<sup>2</sup> The Jura-Harkins' plot for Li kaolinite in Fig. 7 indicates a phase change at  $P/P_0 = 0.049$  which corresponds to  $X = 2.28$  mg H<sub>2</sub>O/g clay. The  $X = 2.28$ , shows excellent agreement with  $X = 2.25$  mg/g which is the amount of water adsorbed at the completion of Step 2. The other breakpoint at  $P/P_0 = 0.39$  on this Jura-Harkins' plot will be discussed under Step 3.

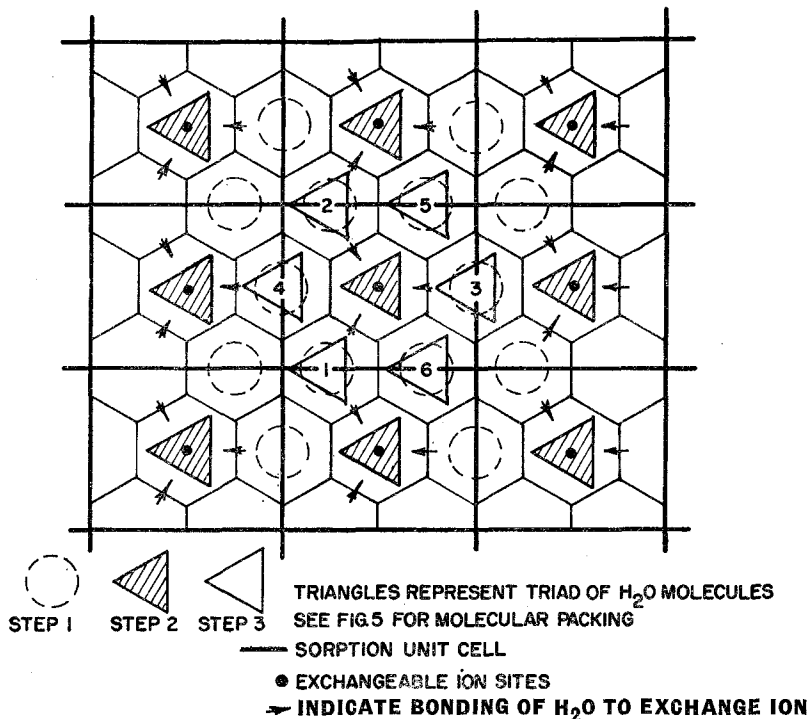


FIGURE 6.—Schematic representation of water sorption on the oxygen surface of kaolinite.

*Step 3.*—Adsorb a triad of water molecules at each vacant site. This step may have several stages. Where no ion hydration occurs all vacant sites are equivalent and at the completion of Step 3 there is a true film of water with  $X = 6.75$  mg/g. Desorption from this point should be completely reversible; i.e. there is no hysteresis. Data for Li and K kaolinite when adsorption is started from  $X = 0$  satisfy this condition. The idealized molecular arrangement at the end of Step 3 (shown in Fig. 6) assumes that a monolayer is complete before the second layer begins to form. This assumption has proved to be valid if the B.E.T.  $c$  constant is  $> 100$ , an indication of high energy of

<sup>1</sup> Jura and Harkins actually plot  $\pi$ , film pressure, vs.  $\sigma$ , inverse surface concentration of adsorbate; however, this merely serves to emphasize the break points. Since the breaks are clear on a  $P$ - $V$  plot there is no need to calculate  $\pi$  and  $\sigma$ .

adsorption for the first layer. Adsorption from  $X = 0$  on Li and K kaolinite gives a  $c$  constant of 33 from which it is estimated that the monolayer would be 75 percent complete before the second layer began to form. A change in adsorbed phase might be expected when the second layer begins to form at  $X = 5.07$  mg/g ( $0.75 \times 6.75$ ) or  $P/P_0 = 0.393$ . The agreement between the calculated phase change point and that experimentally observed in Fig. 7 is remarkable.

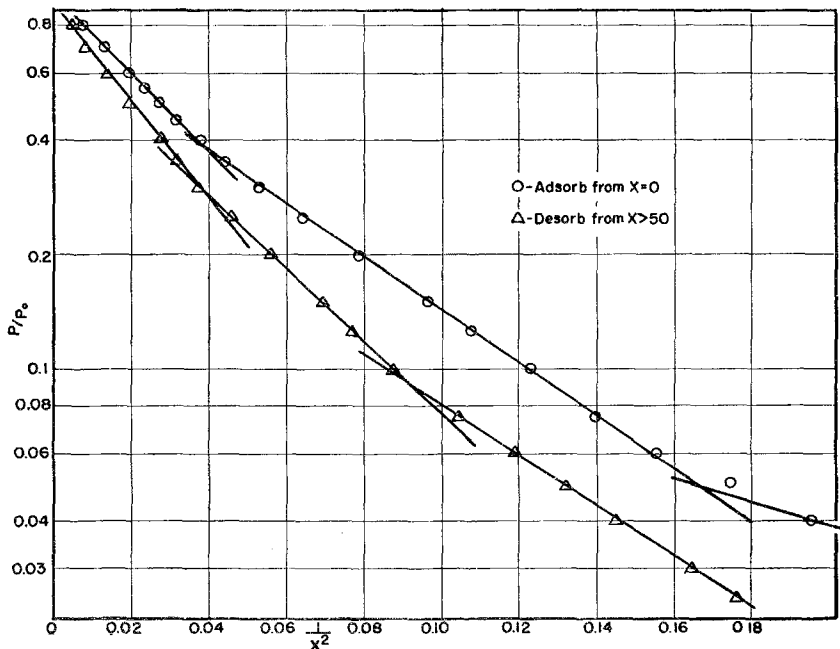


FIGURE 7.—Jura-Harkins' plot for Li kaolinite.

*Step 4.*—Adsorb a second layer of water molecules. Ideally,  $X = 12.75$  mg/g when the second layer is completed. As already mentioned, the second layer begins to form when the first layer is 75 percent complete; therefore, a third layer undoubtedly begins to form before the second layer is 75 percent complete or before  $X$  reaches 11.25. For Li kaolinite, desorption started from  $X = 10.7$  mg/g shows no hysteresis and therefore no ion hydration even though the second layer of adsorbed water molecules is nearing completion and a third layer already forming. Near the completion of Step 4, sufficient water has been adsorbed that the Gouy-Chapman double layer begins to develop. Further water sorption probably can be explained in terms of the Gouy-Chapman theory.

If the adsorption of water at vacant sites, or for that matter during Step 2, brings about a dissipation of stray forces which weaken the exchangeable



ion-clay bond, then the ion may be free to hydrate. The ion will hydrate when the ion-water bonds become stronger than the ion-clay bonds. As the ion hydrates, it will be drawn away from the clay surface so that now vacant sites 1 and 2, Fig. 6, are more active than the others because two molecules of the triad at vacant sites 1 or 2 tend to associate with the exchangeable ion in order to complete a hydration shell about the ion. Vacant sites 3 and 4 will be less active than 1 and 2 but more active than sites 5 and 6 where none of the  $H_2O$  molecules contribute toward completion of the hydration shell.

### *Hydration of Exchangeable Ions*

With the aid of the proposed mechanism for water adsorption and the relative ion hydration numbers,  $n$ , the hydration of the different exchangeable ions associated with the kaolinite surface can be discussed. One must keep in mind that hydration of exchangeable ions is always opposed by the attraction of the clay surface for the ion, so that what ion hydration occurs is in reality the energy difference between the hydration energy,  $U$ , and the specific ionic adsorption energy,  $A$ . The specific adsorption energy is a function of the partial vapor pressure so that  $U - A$  varies with changes in  $P/P_0$ . Any water associated with the exchangeable ion under the condition where  $U - A$  is negative must be held by van der Waals forces, so the process is reversible and no hysteresis occurs. When  $U - A$  is positive, specific ion hydration takes place and hysteresis develops. An exchangeable ion with very strong hydration tendencies would be most likely to show these substeps.

The Jura-Harkins' plot for Mg kaolinite adsorb from  $X = 0$  breaks at  $P/P_0 = 0.06, 0.21$  and  $0.47$  which correspond closely to the amount of water adsorbed when Step 2 is completed, vacant sites 1 and 2 are filled, and vacant sites 3 and 4 are filled respectively. Actually, at the completion of Step 2,  $n = 3$ ; that is, there are 3 more water molecules per exchangeable ion than for the no ion hydration condition. These three water molecules plus the triad of waters normally adsorbed during Step 2 yield a Mg ion hydrated to the extent of  $Mg \cdot 6H_2O$  at the termination of Step 2. When vacant sites 1 and 2 are filled, the total Mg ion hydration is 4 from  $n$ , plus 3 from Step 2, plus 2 from the water molecules nearest the ion at sites 1 and 2, giving  $Mg \cdot 9H_2O$ . Similar reasoning applied to the situation when vacant sites 3 and 4 are filled yields  $Mg \cdot 11H_2O$ , so that there are approximately two full hydration shells before the first layer of adsorbed water normally would be complete.

From the proposed sorption mechanism, it is anticipated that the energy difference between vacant sites 1 and 2, and vacant sites 3 and 4 is not so large as between vacant sites 3 and 4, and vacant sites 5 and 6. Therefore, an ion that does not have very large positive  $U - A$  would probably show a single phase change when vacant sites 3 and 4 are filled.

The Na ion displays fairly ready hydration but still much less than Mg, because by the time the Na ion starts to hydrate the Mg ion is hydrated to  $6H_2O$ . The Jura-Harkins' plot for Na kaolinite adsorb from  $X = 0$  has a sharp break at  $X = 6.5$  ( $P/P_0 = 0.46$ ) which coincides with the change from

$n = 1$  to  $n = 2$  and where vacant sites 1 through 4 are filled. Vacant sites 1 and 2 fill without a break in the Jura-Harkins' plot. Hydration of the Na ion at the point where the sharp break occurs is  $\text{Na} \cdot 8\text{H}_2\text{O}$ . The Na ion apparently does not hydrate beyond  $\text{Na} \cdot 8\text{H}_2\text{O}$  below  $P/P_0 = 0.73$  because desorption from this  $P/P_0$  is reversible down to the  $P/P_0$  where the ion first became hydrated to this degree.

Lithium kaolinite adsorb from  $X = 0$  satisfies the condition that water sorbed is more strongly bonded to the clay than to the ion ( $U - A$  is negative); however, for Li kaolinite desorb from  $X > 50$  at the  $P/P_0$  equivalent to the completion of Step 3, Li ion has moved out from the clay surface. Therefore, in addition to the water molecules strongly bonded with the Li ion as indicated by  $n = 2$ , the triad of water molecules over the Li ion (represented by Step 2 during adsorption) and the three water molecules indicated by arrows in Fig. 6 are all strongly bonded to the Li ion. The Li ion hydration is actually  $\text{Li} \cdot 8\text{H}_2\text{O}$  upon desorb from  $X > 50$  to  $P/P_0 = 0.5$ . Application of similar reasoning to the other ionic modifications indicates that upon desorb from  $X > 50$  to  $P/P_0 = 0.5$  the actual hydrations of the different ions are:  $\text{Na} \cdot 9\text{H}_2\text{O}$ ,  $\text{K} \cdot 7\text{H}_2\text{O}$ ,  $\text{Cs} \cdot 8\text{H}_2\text{O}$  and  $\text{Mg} \cdot 12\text{H}_2\text{O}$ .

Potassium kaolinite upon desorb from  $X > 50$  to  $P/P_0 = 0.2$  shows  $n = 0$ . This change from  $n = 1$  to  $n = 0$  takes place just at the point where vacant sites 1 and 2 are filled so that the K ion could still be hydrated to the extent of  $\text{K} \cdot 5\text{H}_2\text{O}$ . However, since subsequent adsorption without thorough degassing follows the isotherm for adsorb from  $X = 0$ , the evidence is that below  $P/P_0 = 0.2$  the K ion-clay bond is stronger than the ion-water bond even when approached from the higher water content side.

The influence of different ions upon water sorption is clearly illustrated by a comparison of desorb from  $X > 50$  for K and Cs kaolinites. Even though the hydration energy of Cs is less than that for K the value of  $n$  is greater for Cs than for K at any  $P/P_0 < 0.7$ . A further indication of the specific ion effect is noticed when the adsorb from  $X = 2-3$  isotherms for K and Cs are compared; the K curve is identical with the adsorb from  $X = 0$  isotherm while the Cs curve follows the desorb from  $X > 50$  isotherm up to  $P/P_0 = 0.65$ . This behavior is believed to indicate that at  $P/P_0 = 0.05$  on the desorption isotherm of Cs kaolinite the Cs ion is still hydrated to the extent of  $\text{Cs} \cdot 3\text{H}_2\text{O}$ ; that is, the triad of water molecules adsorbed over the exchangeable ion during Step 2 of adsorption, while the K ion is not hydrated at  $P/P_0 = 0.05$ . The reason for this apparent contradiction arises from the fact that while the hydration energy ( $U$ ) and specific adsorption energy ( $A$ ) are greater for K than for Cs, it is the difference ( $U - A$ ) that determines hydration of the exchangeable ion and the difference must be greater for Cs than for K. The differences in the adsorption isotherms for Cs and K are consistent with this interpretation.

The combination of hydration energy and specific ionic adsorption energy is believed to account for the Na and Li kaolinite isotherms. The Na ion is larger than Li so that Na will be less tightly bound to the clay surface than is the Li ion; again the difference ( $U - A$ ) is greater for Na than for Li so

that hydration of Na occurs before hydration of Li. Likewise, this difference ( $U - A$ ) is greater for Na than for K or Cs so hydration of Na ion begins before hydration of K or Cs. Once the exchangeable Li ion is hydrated, the specific adsorption energy reduction is much greater than for the other alkali ions; therefore, upon desorb from  $X > 50$  the Li ion stays hydrated to a very low  $P/P_0$ . At  $P/P_0 = 0.05$  on the desorption curve where  $n = 1$ , the hydration of Li is actually  $\text{Li} \cdot 4\text{H}_2\text{O}$  which explains why adsorb from  $X = 2-3$  follows up the desorption isotherm to  $P/P_0 = 0.3$ . On the desorption curve for Na kaolinite at  $P/P_0 = 0.05$   $n = 0$ ; therefore, ( $U - A$ ) for Na at this point is less than for Li. Although  $n = 0$  for Na kaolinite on desorption curve at  $P/P_0 = 0.05$ , there is still ion hydration to the extent of  $\text{Na} \cdot 3\text{H}_2\text{O}$  because adsorb from  $X = 2-3$  goes up the desorption curve, not the adsorb from  $X = 0$  curve as in K kaolinite where there is no ion hydration at  $P/P_0 = 0.05$ .

Sodium and cesium appear to be hydrated to the same extent,  $3\text{H}_2\text{O}$ , at  $P/P_0 = 0.05$  on the desorption curve; however, the Jura-Harkins' plots for both adsorption and desorption on Cs kaolinite are curved to such a degree that it is impossible to obtain a straight line segment except for a very small  $P/P_0$  range. This curvature means that the energy changes are extremely small and continuous for Cs kaolinite, whereas the Jura-Harkins' plots for Na kaolinite show very clear changes in slope corresponding to a marked change in ( $U - A$ ). The phase changes indicated by Jura-Harkins' plots can also be observed from the loop scanning behavior. Loop scanning for Li and Na kaolinite suggest that the Na ion forms fairly stable hydrates while the Li ion, once hydrated, continuously hydrates as  $P/P_0$  increases. In other words, the hydration tendency for exchangeable Li ions is greater than for exchangeable Na ions only below  $P/P_0 = 0.2$  on the desorption curve.

## CONCLUSIONS

Water-vapor sorption on kaolinite shows a pronounced hysteresis loop between the adsorption and desorption branches. The size of the hysteresis loop depends upon the exchangeable ion and the sorption history of the sample. Data indicate that hysteresis below  $P/P_0 = 0.8$  results entirely from hydration of the exchangeable ions. Lithium and potassium kaolinite have no hysteresis when desorption is started at or before  $P/P_0 = 0.8$ ; however, when desorption is started from near  $P/P_0 = 1.0$ , Li kaolinite has a large hysteresis loop that persists to  $P/P_0 < 0.02$ . The data clearly indicate the necessity for specification of sample history and relative vapor pressure ( $P/P_0$ ) when discussing hydration of exchangeable ions.

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