

## ADSORPTION PROPERTIES OF NATURALLY OCCURRING ERIONITE AND ITS CATIONIC-EXCHANGED FORMS

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### ABSTRACT

The mineral erionite, a naturally occurring zeolite, has a surface area of 203 M.<sup>2</sup>/g and adsorbs 0.26, 0.29 and 0.15 mmoles/g of n-pentane, n-hexane and n-heptane, respectively, at 98.4° C. and 300 mm. Its capacity for branched isomers and benzene is essentially zero.

Thus, its effective pore diameter lies between 4.5 and 5.4 Å. This is in agreement with its crystal structure which indicates elliptical pore openings having a major and minor axis of 4.7–5.2 Å and 3.5 Å, respectively. Exchange of 15% of the cationic equivalents with potassium results in a material having capacity only for water. Calcium exchange nearly doubles the adsorptive capacity for n-pentane.

### INTRODUCTION

The structure of the mineral erionite, a naturally occurring zeolite, has been well defined by x-ray crystallography (Barrer *et al.*, 1959; Deffeyes, 1959; Regnier, 1960; Staples and Gard, 1959). The basic unit cell is hexagonal with  $a = 13.2\text{--}13.27$  Å and  $c = 15.05\text{--}15.12$  Å. The silica-alumina framework of this mineral contains cavities which are approximately cylindrical with a free diameter of 6.3 Å and a length of 15.1 Å. In each of these cavities there are six elliptical openings formed by eight-membered oxygen rings. Each opening has a major and minor axis of 4.7–5.2 Å and 3.5 Å, respectively. As such, the mineral should exhibit the properties of a molecular sieve whereby it occludes or adsorbs only those molecules with a critical dimension less than that of the elliptical openings. This behavior would be somewhat analogous to that of synthetic calcium-zeolite A (5A molecular sieve) which has roughly circular openings with an effective diameter of near 5 Å. This material adsorbs, for example, straight chain hydrocarbons but does not adsorb the branched isomers (Breck *et al.*, 1956).

Erionite was originally discovered in 1898 by Eakle in a deposit in Durkee, Oregon. Since that time, it has been identified in deposits from Wyoming, Nevada and South Dakota (Deffeyes, 1959); Idaho (Reed, 1937); and the Faroe Islands (Hey, 1959). Breck *et al.* (1956) mention the synthesis of erionite; however, no details are given.

Since synthetic erionite is not available, a sample of naturally occurring erionite was obtained from deposits located near Rome, Oregon. In this report, results are presented on the adsorption of various C<sub>5</sub> to C<sub>7</sub> hydrocarbons on this sample of erionite and its ion-exchanged forms for comparison with the known behavior of synthetic zeolite A.

## EXPERIMENTAL

*Ion-exchange* The various ion-exchanged forms of erionite were prepared by treating 50 g of erionite with a solution containing 75 g of the cationic chloride in 200 cm<sup>3</sup> of distilled water. The resulting slurry was stirred for two hours at 65° C. After settling, the supernatant liquid was decanted and a fresh solution of the chloride added and the treatment repeated. After a final third treatment, the solid was washed with distilled water until the filtrate was chloride-free. The sample was subsequently dried at 110° C. for four hours. Emission spectroscopy and other chemical techniques were used to analyze both the original erionite and the ion-exchanged products.

*Adsorption measurements* The isotherms for the liquid hydrocarbons were measured in a specially constructed glass apparatus. Details of the unit are in process of publication. Basically, the unit consists of an adsorption chamber which is maintained at a constant temperature of 98° C. by a n-heptane vapor jacket. Each of the erionite samples was initially calcined in a furnace at 540° C. for 16 hours. A weighed portion was transferred with a minimum exposure to air to a small bucket which was suspended inside the adsorption chamber. The sample was evacuated at 98° C. for 16 hours at which time the ultimate vacuum was generally 10<sup>-4</sup> mm. After isolating the chamber from the vacuum pumping system with mercury, aliquots of the hydrocarbon were successively injected by means of a specially constructed pipette through a mercury-covered glass frit. Resulting pressures were measured with a mercury manometer. From the known volume, pressure and temperature of the adsorption chamber, the amount adsorbed at each pressure was computed.

*Materials* The sample of erionite was obtained from a Rome, Oregon, deposit through the courtesy of the Kennedy Minerals Co., Inc. The hydrocarbons employed in the adsorption studies were research grade materials available from the Phillips Petroleum Company. Helium and nitrogen were obtained from the Matheson Company and were further purified by passing through either liquid nitrogen or dry ice cold traps and a column of 4A molecular sieve.

## RESULTS

*Characterization of naturally occurring erionite* The x-ray diffraction pattern of the Rome, Oregon sample used in our studies is shown in Table I and compared with previously published values of Deffeyes (1959) on a sample from Jersey Valley, Nevada. In general, there is excellent agreement in the pattern except for some minor differences in relative intensi-

TABLE I. COMPARISON OF  $x$ -RAY DIFFRACTION DATA (Cu K  $\alpha$ ) OF ERIONITE SAMPLE FROM ROME, OREGON WITH LITERATURE VALUES

d, Å	Relative Intensity, I	
	Rome, Oregon Sample	Literature
11.43	100	100
7.54	7	3
6.60	53	60
6.32	5	4
5.73	14	28
5.35	16	15
4.56	11	8
4.32	52	90
4.16	22	30
3.81	29	60
3.75	50	45
3.58	17	12
3.30	22	40
3.28	15	8
3.17	12	25
3.15	14	25
3.10	4	12
2.294	7	8
2.290		
2.858	40	75
2.843	39	25
2.808	33	40
2.673	12	14
2.493	14	22
2.477	12	12
2.287	2	4
2.200	8	12
2.112	6	7
2.078	3	4
1.981	4	4
1.956	2	1
1.880	5	2
1.831	6	10
1.772	7	5
1.699	4	5
1.650	14	30
1.585	8	10
1.514	4	3
1.464	3	8
1.462		
1.429	2	4
1.270	3	12

TABLE II. ANALYSES OF ERIONITE SAMPLES

	Wt. %		
	This Work	Other Work	
		Eakle	Staples and Gard
H <sub>2</sub> O <sup>1</sup>	10.57	17.30	17.58
Na <sub>2</sub> O	1.90	2.47	1.45
K <sub>2</sub> O	7.17	3.51	3.40
MgO	0.80	0.66	1.11
CaO	1.54	3.50	2.92
Al <sub>2</sub> O <sub>3</sub>	13.59	16.08	15.60
SiO <sub>2</sub>	60.81	57.16	57.40
Fe <sub>2</sub> O <sub>3</sub>	3.63	—	—

<sup>1</sup> Determined by measuring weight loss after heating at 800° C. for 16 hours.

ties. No lines other than those attributable to erionite were observed in our sample.

Although the diffraction pattern was nearly identical to that in the literature, there were some differences in composition. The analyses of various erionite samples are shown in Table II. The sample used for this investigation had a considerably lower water content and also contained 3.63% Fe<sub>2</sub>O<sub>3</sub>. In regard to the alkaline earth content, the sample for this work had a higher content of K<sub>2</sub>O and a lower amount of CaO than the other samples.

For zeolitic materials such as erionite, the number of moles of aluminum should be balanced by the total number of equivalents of the alkali and alkaline earth elements. On this basis, there is evidence for some impurity in the sample other than Fe<sub>2</sub>O<sub>3</sub>. The number of equivalents of these elements is about 15% higher than the moles of aluminum. This is believed to be larger than that which can be attributed to errors in the analyses.

For further characterization, the material was examined by electron microscopy. Figure 1 shows a carbon replica of the external surface of the Rome, Oregon, erionite sample. A direct electron micrograph is shown in Fig. 2. The characteristic fibrous structure of erionite is clearly seen.

The nitrogen isotherm at -195.8° C. is shown by Curve I in Fig. 3. The surface areas calculated from this isotherm both by the BET and Langmuir methods are listed in Table III. The value of 203 M.<sup>2</sup>/g is probably the more reliable since the pore structure of the erionite limits the nitrogen adsorption to a monomolecular layer. For this case, the BET equation reduces to the Langmuir equation (Emmett, 1954).

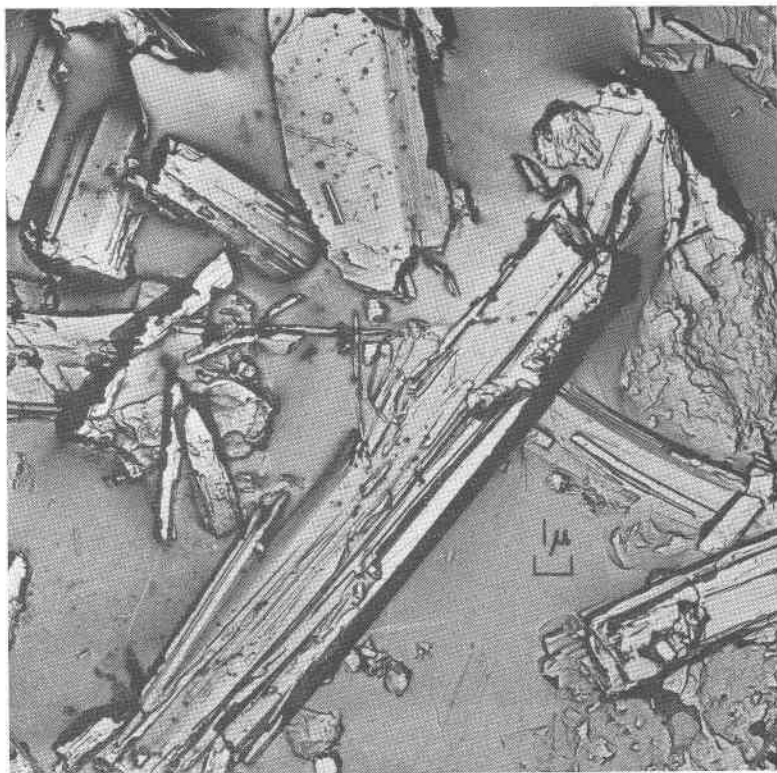


FIG. 1. Electron micrograph of carbon replica of external surface of erionite (5,000X)

*Ion-exchange* Results of the ion-exchange of erionite with various alkali and alkaline earth ions are listed in Table IV. The naturally occurring sample of erionite contained more chloride than its ion-exchanged products which had been washed with distilled water to reduce the chloride

TABLE III. SURFACE AREAS OF ERIONITE SAMPLE FROM ROME, OREGON AND ITS K- AND Ca-FORMS

Absorbent	Surface Area, M. <sup>2</sup> /g	
	BET	Langmuir
Form of Erionite		
Natural	155	203
KCl Treated	7.1	9.2
CaCl <sub>2</sub> Treated	143	171
5A Molecular Sieve	—	802 <sup>b</sup>

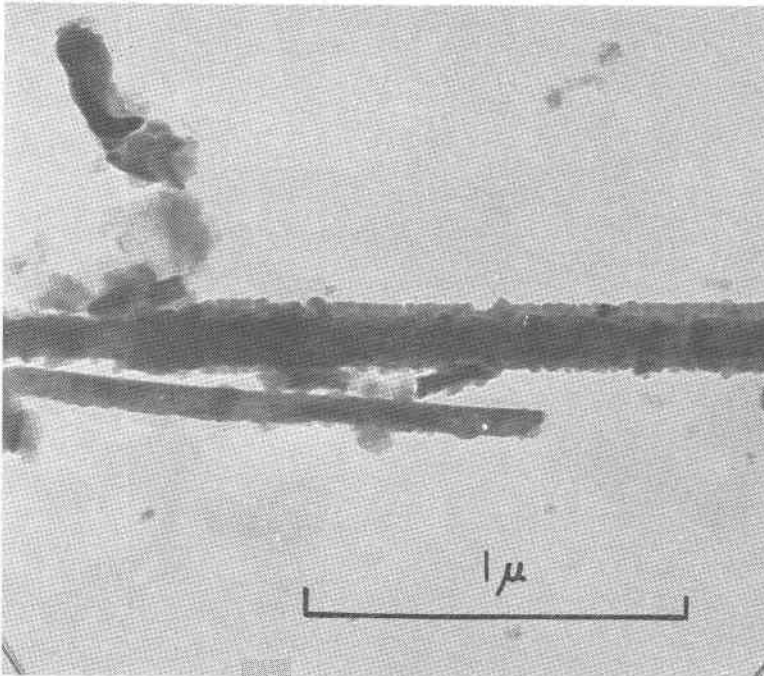


FIG. 2. Direct electron micrograph of erionite (50,000X)

content to essentially zero. Table IV lists the per cent of the total alkali and alkaline earth equivalents accounted for by the various elements. Only 10–15% of the original equivalents of erionite were subject to exchange. In certain cases, this small amount of exchange markedly affected the adsorptive properties. The calcium and potassium forms were of particular interest and their nitrogen adsorption isotherms are shown in

TABLE IV. RESULTS OF ION-EXCHANGE OF ROME, OREGON SAMPLE OF ERIONITE

Form of Erionite	Wt. % Cl	% of Total Equivalents					
		Li	Na	K	Mg	Ca	Sr
Natural	0.31	—	20	50	12	18	—
LiCl Treated	0.01	14	14	42	12	18	—
NaCl Treated	0	—	30	47	11	12	—
KCl Treated	0.03	—	16	65	9	10	—
MgCl <sub>2</sub> Treated	0	—	15	47	24	14	—
CaCl <sub>2</sub> Treated	0	—	11	47	12	30	—
SrCl <sub>2</sub> Treated	0	—	11	47	11	16	15

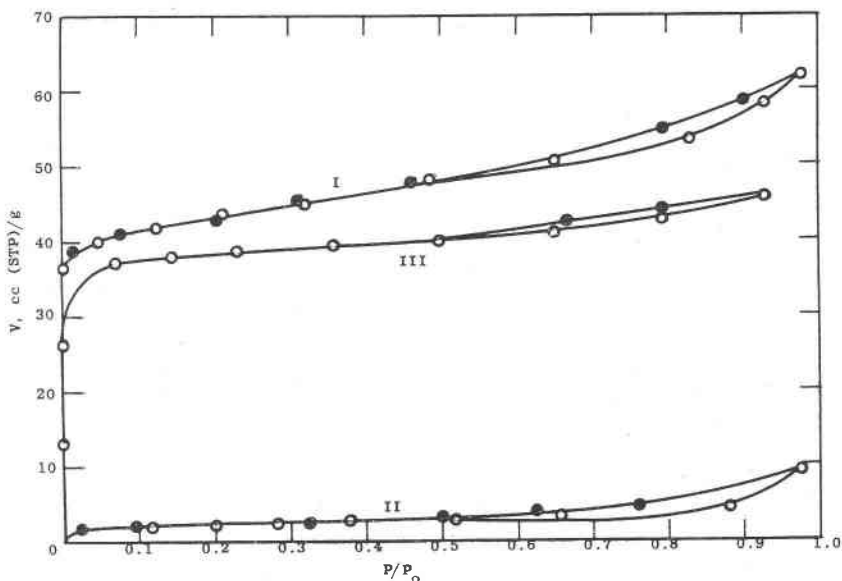


Fig. 3. Nitrogen adsorption isotherms at  $-195.8^{\circ}\text{C}$ . on natural erionite and its K- and Ca-exchanged forms. Curves I, II and III represent the isotherms on natural, K- and Ca-exchanged erionite, respectively.

Fig. 3. The resulting surface areas are listed in Table III. The potassium-exchanged material had only 5% of the surface area of the original erionite.

*Adsorption properties* The adsorption isotherms of various  $\text{C}_5$  to  $\text{C}_7$  hydrocarbons at  $98.4^{\circ}\text{C}$ . on naturally occurring erionite are plotted in Fig. 4. The amounts adsorbed in mmoles/g at 300 mm. pressure are listed in Table V. Natural erionite adsorbs 0.26 and 0.29 mmoles/g of n-pentane and n-hexane, respectively. The capacity for n-heptane is only about half this amount in spite of the fact that all three molecules have the same minimum cross-sectional diameter of 4.5 Å. On a molar basis, synthetic 5A molecular sieve adsorbs equal quantities of these three hydrocarbons. Molecules such as 2-methylpentane, 2,2-dimethylbutane and benzene having larger cross-sectional diameters of 5.4, 5.8 and 6.0 Å, respectively, are not adsorbed to an appreciable extent on any of the adsorbents. The lithium, sodium and strontium-exchanged materials have essentially the same adsorptive properties as the original erionite.

None of the hydrocarbons was adsorbed on the potassium-exchanged erionite. This is in line with its low surface area of  $9.2\text{ M}^2/\text{g}$ . The material, however, retained an adsorptive capacity for water. At  $98.4^{\circ}\text{C}$ . and 300 mm pressure, 3.0 mmoles of water were adsorbed per gram.

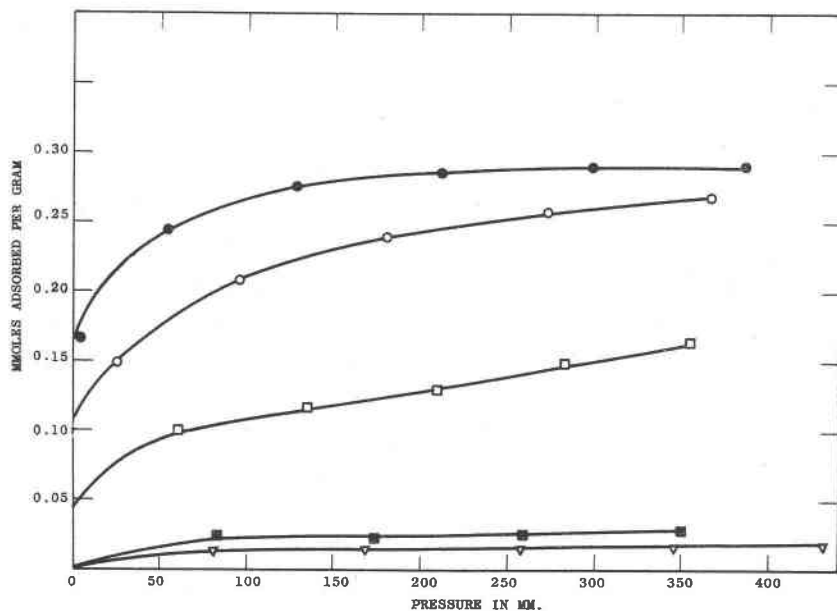


FIG. 4. Adsorption isotherms on natural erionite at 98.4° C. The symbols have the following significance: ■, benzene; ▽, 2-methylpentane; ○, n-pentane; ●, n-hexane; and □, n-heptane.

TABLE V. HYDROCARBON ADSORPTION ON ERIONITE, ITS ION-EXCHANGED FORMS AND 5A MOLECULAR SIEVE

Absorbent	Amount Adsorbed at 98.4° C. and 300 mm, mmoles/g					
	n-Pentane	n-Hexane	n-Heptane	2-Methyl-Pentane	2,2-Di-methyl-Butane	Benzene
Form of Erionite						
Natural	0.26	0.29	0.15	<0.02	0	<0.03
LiCl Treated	0.26	0.32	—	0	0	<0.02
NaCl Treated	0.17	0.24	—	0	—	—
KCl Treated	—	0	—	0	—	—
MgCl <sub>2</sub> Treated	0.41	0.25	—	0	0	0
CaCl <sub>2</sub> Treated	0.48	0.38	0.11	<0.03	0	<0.02
SrCl <sub>2</sub> Treated	0.29	0.34	—	0	0	<0.02
5A Molecular Sieve	1.20	1.20	1.07	0	0	0



The exchange with the divalent ions, magnesium and calcium, nearly doubled the adsorptive capacity for n-pentane and increased that for n-hexane. Adsorption isotherms on calcium-exchanged erionite are shown in Fig. 5. Evidently, this exchange serves to open up previously inaccessible adsorption cavities in the erionite structure.

#### DISCUSSION

The silica-alumina framework in erionite is such that adsorption cavities are formed which can be closely approximated by cylinders having a length of 15.1 Å and a diameter of 6.3 Å. The total volume of cavities per gram of erionite (dry basis) is 0.21 cm<sup>3</sup>/g as computed from the structure

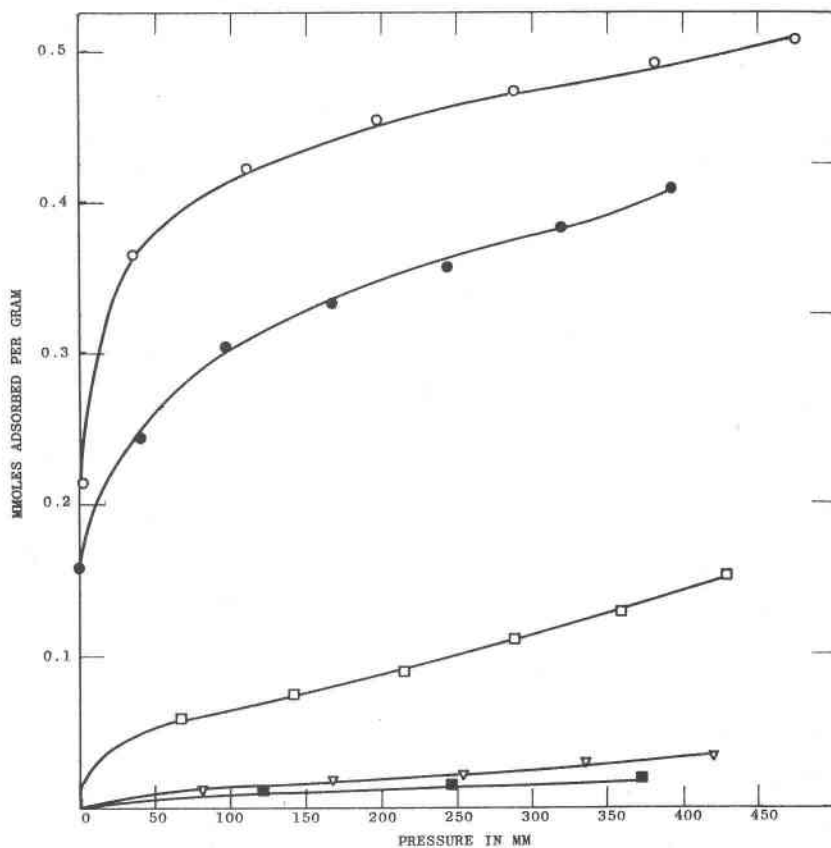


FIG. 5. Adsorption isotherms on CaCl<sub>2</sub>-treated erionite at 98.4° C. The symbols have the following significance: ■, benzene; ▽, 2-methylpentane; ○, n-pentane; ●, n-hexane; and □, n-heptane

and composition of the material. Experimentally, the pore volume can be measured by nitrogen adsorption at  $-195.8^{\circ}\text{C}$ . By constructing scaled models of the cavity and nitrogen molecules, we concluded that only five molecules of nitrogen could be adsorbed in each cavity. On this basis, the amount of liquid nitrogen necessary to fill all the cavities in a gram of erionite was calculated to be  $0.14\text{ cm}^3/\text{g}$ . From the nitrogen isotherm in Fig. 3, the actual amount of liquid nitrogen adsorbed at high values of  $P/P_0$  is seen to be  $0.093\text{ cm}^3/\text{g}$ . This is of the same order of magnitude as the calculated value. Some of the voids, however, may be obstructed by potassium ions.

Since natural erionite adsorbs the straight chain hydrocarbons and excludes the branched chain isomers, the effective size of the openings into the adsorption cavities must lie between  $4.5$  and  $5.4\text{ \AA}$ . This agrees well with the crystal structure as determined by  $x$ -ray diffraction which shows that the openings are essentially elliptical with a major and minor axis of  $4.7$ – $5.2\text{ \AA}$  and  $3.5\text{ \AA}$ , respectively. At the same conditions of pressure and temperature, natural erionite has a capacity for  $n$ -pentane and  $n$ -hexane amounting to  $22$ – $24\%$  of that observed on  $5\text{A}$  molecular sieve.

In regard to the straight chain hydrocarbon adsorption, erionite adsorbs considerably less  $n$ -heptane than either  $n$ -pentane or  $n$ -hexane. This behavior is not observed with  $5\text{A}$  molecular sieve which adsorbs the same amount of each of these normal paraffins. This can presumably be attributed to the cylindrical shape of the adsorption cavities in erionite. In  $5\text{A}$  molecular sieve, the cavities are essentially spheres having a diameter of  $11.35\text{ \AA}$ . The volume of a single cavity is  $766\text{ \AA}^3$ . In erionite, the corresponding value is  $406\text{ \AA}^3$ . Because of their smaller volume and cylindrical shape, the cavities in erionite apparently restrict the adsorption of  $n$ -heptane and higher straight chain hydrocarbons.

Exchange of  $15\%$  of the original cation equivalents in erionite with potassium results in a material having no adsorptive capacity for  $\text{C}_5$  to  $\text{C}_7$  hydrocarbons and very little capacity for nitrogen. Water, however, is still adsorbed. The large potassium ions presumably block off nearly all the adsorption cavities. The effective pore diameter of the potassium exchanged erionite must be close to  $2.8\text{ \AA}$ . With calcium exchange, however, more of the adsorption cavities are made available to  $n$ -pentane and  $n$ -hexane resulting in nearly a doubling of the adsorptive capacity for  $n$ -pentane. This behavior is somewhat analogous to that produced by potassium and calcium exchange of zeolite  $\text{A}$  molecular sieve (Breck *et al.*, 1956).

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