

陽이온 交換한 天然 제올라이트에 依한
有機黃化合物의 液相吸着 特性

金淙澤¹ · 許南湖

慶北大學校 工科大学 工業化學科

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Liquid Phase Adsorption Properties of Organo Sulfur
Compounds on Cation Exchanged Natural Zeolites

Jong-Taik Kim[†] and Nam-Ho Heo

Department of Industrial Chemistry, Kyungpook National University,

Taegu 635, Korea

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요 약. 陽이온 交換한 天然제올라이트에 依한 有機黃化合物의 液相吸着特性을 考察하였다. 平衡吸着량은 天然제올라이트의 交換한 陽이온과 吸着質인 有機黃化合物의 構造에 影響을 받고 있음을 알 수 있었다. 또한 平衡吸着량은 메르캅탄(mercaptane), 설파이드(sulfide), 디설파이드(disulfide), 치오펜(thiophene) 順으로 減小하였으며, 치오펜 誘導體의 경우는 π 電子가 많아짐에 따라 吸着량이 減小하였다. 吸着等溫線은 Langmuir의 吸着모델을 따랐으며 吸着劑의 이온種에 따른 吸着能은 交換한 이온의 polarizing power에 比例하였다. 吸着速度로부터 有機黃化合物의 吸着은 pore 內의 擴散이 律速段階임을 알 수 있었고, 水分과 같은 작은 吸着質은 micro pore에 吸着이 일어나는 反面, 有機黃化合物은 transitional-pore에 吸着이 일어났다.

ABSTRACT. The adsorption properties of organo sulfur compounds on cation exchanged natural zeolites from *n*-heptane were investigated. The equilibrium adsorbed amounts were dependent upon the exchanged cation and the nature of organo sulfur compounds such as length, volume, electronical structure. The increasing orders of equilibrium adsorbed amounts were thiophene derivatives, disulfide, sulfide mercaptane and thiophene, benzothiaphene, dibenzothiophene. And Co^{+2} -zeolite was the most prominent adsorbent. Rate determining step of the adsorption at initial stage was intraparticle diffusion into the transitional pores of zeolite. These adsorption rates were dependent upon the bulkiness of adsorbate. Finally, preadsorbed water didn't affect these adsorption until the cation exchanged natural zeolite contained 2.26×10^{-3} mol/g of water. It indicated that water preferentially occupied the micro pores of the cation exchanged natural zeolites.

INTRODUCTION

A number of studies for adsorption of organo sulfur compounds have been reported^{1~4} since E. B. Maxted and his coworkers⁵ reported the poisoning effects of sulfur compounds on catalyst

in 1937. The primary interest of sulfure compounds was that they contained unshared electron pairs. It has been proposed⁶ that the molecules like sulfur compounds that contain unshared electron pairs are chemisorbed on transition metals by forming coordination links.

However, it is not always that these evidences are enough to support this view.⁷

Lygin and his coworkers⁸ reported that the decreasing order of formation tendencies of hydrogen with surface hydroxyl groups on silica were sulfides, mercaptanes, disulfides and thiophenes. And, these hydrogen bonds were much weaker than those of corresponding oxygen compounds.

Recently, Rochester and Terrell⁹ studied the perturbation of hydroxyl groups on infrared spectra of organo sulfur compounds adsorbed on silica. Their results were approximately consistent with the Badger and Bauer relationship¹⁰ which predicted that OH band shifts for a given proton donor to a series of acceptors should be proportional to their enthalpies of hydrogen bonding. They also proved that the chemisorption of *n*-propyl mercaptane and dimethyl sulfide on siloxane group of silica took place in infrared absorptions at 3400 cm^{-1} and 2990, 2955, 2895, 2865 cm^{-1} and these results were attributed to the stretching vibrations of surface OH hydrogen bonded with vicinal sulfur or OMe group.

Quite a number of reports on the complexation of organo sulfur compounds were made. The bonds of these compounds with alkali metals were known generally weak, while the bonds with heavy metals, such as mercury and copper, were strong enough to result in C-S cleavage.¹¹ Complex bonding for aromatic sulfides were relatively weak due to the participation of unshared electrons of sulfur in $p\pi$ -conjugation with aromatic ring.¹²

The adsorption of gaseous organo sulfur compounds on zeolites and silica have been reported by Mars and Friedrich¹³⁻¹⁴ but none for the liquid phase. Friedrich¹⁵ studied adsorption of sulfur containing compounds on zeolite and showed that the adsorbed amounts were

dependent on the nature of sulfur compounds and the solvents. Mikhal'skaya¹⁶ reported stronger bondings and larger amounts of adsorption on NaY zeolite than on NaX zeolite.

In this study, the natural zeolite from Young-il Gun in Korea was saturated by several cations. The liquid phase adsorption properties of organo sulfur compounds, such as ethyl mercaptane, diethylsulfide, dimethyldisulfide, diethyldisulfide thiophene, benzothiophene and dibenzothiophene, were discussed in terms of equilibrium adsorbed amount, rate of adsorption, other adsorption parameters and effects of preadsorbed water. Effects of adsorbate structure and exchanged cations were also discussed.

EXPERIMENTAL

Materials. All organo sulfur compounds were purchased from commercial sources—Tokyo and Katayama industries Co.—and used without further purification. HCl, NaOH, KCl, CaCl_2 , CoCl_2 , and FeCl_3 used for the surface activation and ion exchange procedure were extra pure grade obtained from Tokyo and Wako Chemicals. 1st grade *n*-heptane from Kokusan and Junsei chemicals was distilled and followed by sodium distillation.

Preparation and analysis of adsorbents. Natural zeolite from Young-il Gun was grinded finely and sieved to yield 100 mesh size. They were treated successively by 0.5 *N* HCl and 0.5 *N* NaOH solution for 2 hours at 100 °C and washed with demineralized water until the chloride ions were not detected. Consequently, they were treated by solutions of 1 *N* KCl, 1 *N* CaCl_2 , 1 *N* CoCl_2 and 1 *N* FeCl_3 for 2 hours 100 °C in order to have each cation saturated and were washed with water and sieved after drying.

The chemical composition of natural zeolite

was analysed by means of wet method (KSL-3120). The X-ray diffractograms were obtained for the identification of minerals at 30 KV, 800 cps using Cu target and 1 nm slits (JEOL LTD., JDX-8 E, JAPAN). The elemental consistencies and the cation exchange capacities were determined by X-ray fluorescence (Rigaku Denki Kogyo Co., Ltd. Japan) at 40 KV, 40 mA, 10,000cps using EDDT crystal and Cr target under 25 ml/min argon-methane gas flow.

Adsorption and Adsorption Rate. 25ml of organo sulfur compounds-heptane solution and ca. 1.5g of adsorbent were poured into 50ml erlenmyer flask and stopped by the rubber and shaken in the thermostat water bath (Blue M. Co., USA) at 25°C with 100rpm for 24 hours. The solution was separated by centrifuge and its concentration was measured by the absorbance at λ_{max} . The blank test were carried out in order to make up the concentration due to the solvent evaporation. The concentration measurements taken after each of 10, 15, 30, 60, 120, 300 and 900 minute intervals, the rates of adsorption were obtained. Shimadzu UV & VIS spectrophotometer was used for the measurements.

Water Preadsorbed Adsorbents. Water pre-adsorption was made by Diamond and Kinter

method¹⁹ in order to study its effect on the sulfur compounds adsorption. The various equilibrium vapor pressure of water at room temperature were accomplished by the different H₂O/H₂SO₄ ratios such as 0.3, 0.5, 0.7, and 1.0. Furthermore, the adsorbents were heated at 200, 300, 400 and 500 °C to see the effects of trace amounts of adsorbed water on the adsorption.

RESULTS AND DISCUSSION

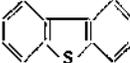
Adsorbate and adsorbent. Physical properties of organo sulfur compounds, used as adsorbate, were shown in Table 1.

Their λ_{max} value and absorption coefficients of each organo sulfur compounds in *n*-heptane were measured and calculated by Beer Lambert's law at the ultraviolet range.

The results analysis of the natural zeolite by wet method, X-ray fluorescence and diffraction were shown in Table 2. It was mordenite rich mineral and its cation exchange capacity was 130milli equivalent/100g-zeolite.

Equilibrium adsorbed amounts. Equilibrium loadings of each organo sulfur compounds on several cation exchanged natural zeolites calculated from the following equation are shown in Table 3.

Table 1. Physical properties of organo sulfur compounds

Organo sulfur comped.	Structure	MW	BP	λ_{max} (log ϵ)
Ethyl mercaptane(EM)	EtSH	62.13	35	225nm (2.20)
Diethylsulfide(DES)	Et ₂ S	90.19	92.1	229* (2.14)
Dimethyldisulfide(DMDS)	Me ₂ S ₂	94.19	109.7	256 (2.50)
Diethyldisulfide(DEDS)	Et ₂ S ₂	122.25	154.0	251.5 (2.60)
Thiophene(TP)		84.14	84.4	231 (3.87)
Benzothiophene(BTP)		134.20	221	288 (3.31)
Dibenzothiophene(DBTP)		184.27	97~98**	286 (3.50)

*Shoulder. **Melting point

Table 2. The chemical compositions of natural zeolite

pH	Igni- tion loss	SiO ₂	Al ₂ O ₃	CaCO ₃	Si/Al	Diagnosis
5.5	24.23	50.37	20.43	1.12	4.19	Mordenite

Table 3. Equilibrium loadings ($\mu\text{mol/g}$) of organo sulfur compounds on the cation saturated zeolites in the $1 \times 10^{-2} \text{ mol/l}$ *n*-heptane solution for 24 hours at 25°C

Sulfur compd.	Zeolite				
	K ⁺ - Zeol.	Ca ²⁺ - Zeol.	Co ²⁺ - Zeol.	Fe ³⁺ - Zeol.	N- Zeol. *
EM	51.0	49.2	140.4	122.5	193.5
DES	28.0	33.2	132.2	83.0	91.0
DMDS	32.6	34.4	107.5	68.7	116.2
DEDS	19.2	27.0	100.1	43.0	70.3
TP	7.0	12.4	51.0	16.5	69.5
BTP	2.8	3.1	13.2	11.4	13.9
DBTP	2.7	3.1	8.7	5.0	8.7

*N-Zeol. means Natural zeolite.

$$Q = L(C_0 - C_e) / W,$$

where Q , L , C_0 and C_e are equilibrium loading (mol/g), volume of solution for the adsorption system (l), weight of adsorbents (g), initial and equilibrium concentrations (mol/l), respectively.

Each equilibrium loading differed due to the cations were so obvious. It was concluded the effect of the surface cations on the adsorption was predominant factor. Therefore, it was also clear that the selectivities of the organo sulfur compounds on the cation exchanged natural zeolites were significant.

Adsorption isotherms of each organo sulfur compounds on several cation exchanged natural zeolites are presented in Fig. 1~5. From these isotherms, it was confirmed that the adsorbed amounts were dependent on the nature of adsorbed molecules, such as molecular weight, length, geometric and electronic structure. The decreasing order of adsorbed amounts was EM,

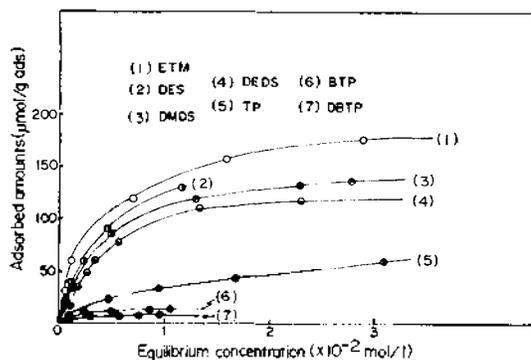


Fig. 1. Adsorption isotherms of organo sulfur compounds on Co²⁺-zeolite.

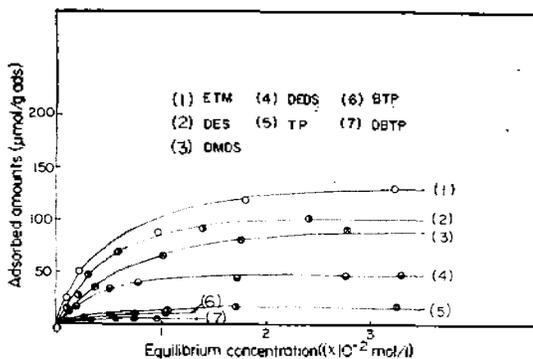


Fig. 2. Adsorption isotherms of organo sulfur compounds on Fe³⁺-zeolite.

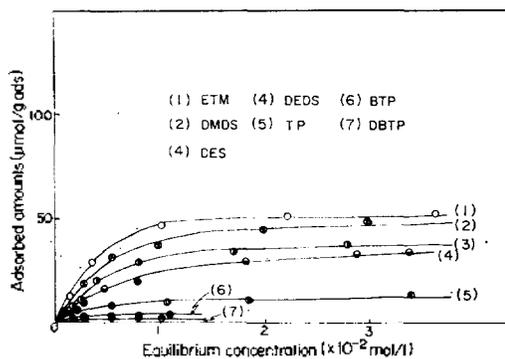


Fig. 3. Adsorption isotherms of organo sulfur compounds on Ca²⁺-zeolite.

DES, DMDS, DEDS, TP, BTP and DBTP for Co²⁺- and Fe³⁺-zeolites, while the decreasing order on the K⁺- and Ca²⁺-zeolites was EM, DMDS, DES, DEDS, TP, BTP and DBTP.

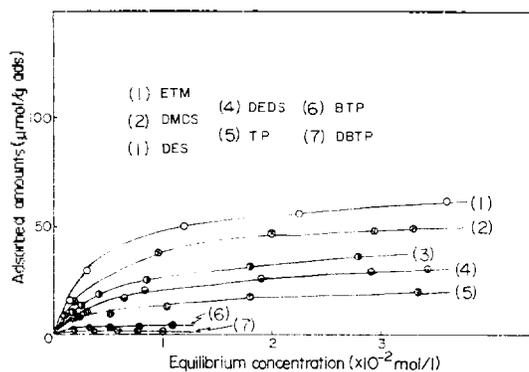


Fig. 4. Adsorption isotherms of organo sulfur compounds on K^+ -zeolite.

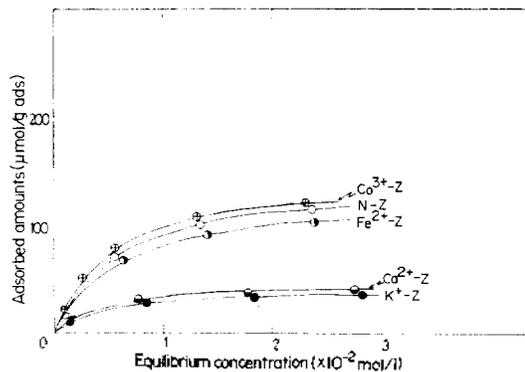


Fig. 7. Adsorption isotherms of diethylsulfide on cation exchanged natural zeolites.

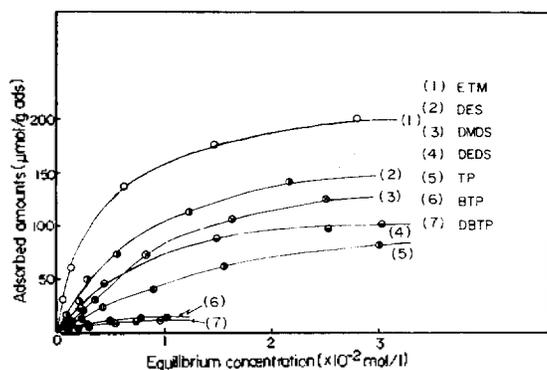


Fig. 5. Adsorption isotherms of organo sulfur compounds on natural zeolite.

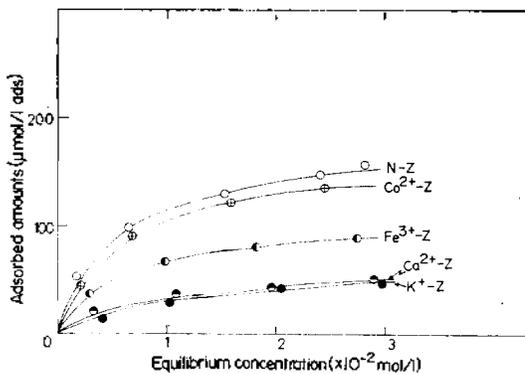


Fig. 8. Adsorption isotherms of dimethyldisulfide on cation exchanged natural zeolites.

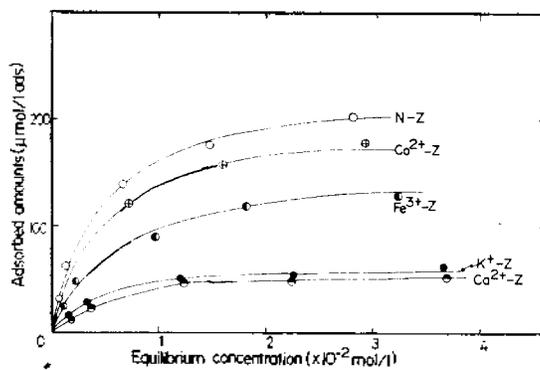


Fig. 6. Adsorption isotherms of ethylmercaptane on cation exchanged natural zeolites.

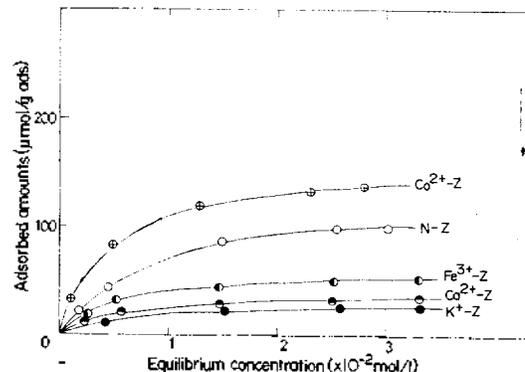


Fig. 9. Adsorption isotherms of diethyldisulfide on cation exchanged natural zeolites.

And, EM, the smallest molecule, exhibited itself the best adsorbate. This meant that the

size and dipole moment of the substrate were very important factors for the molecule to get

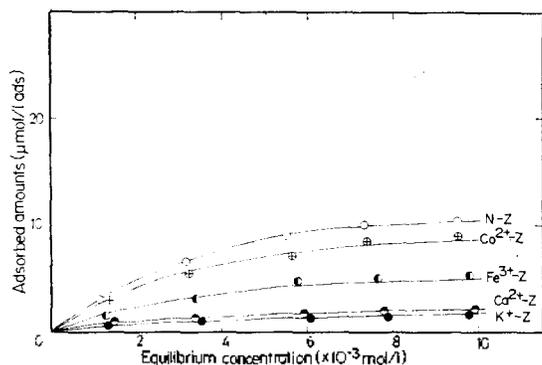


Fig. 10. Adsorption isotherms of thiophene on cation exchanged natural zeolite.

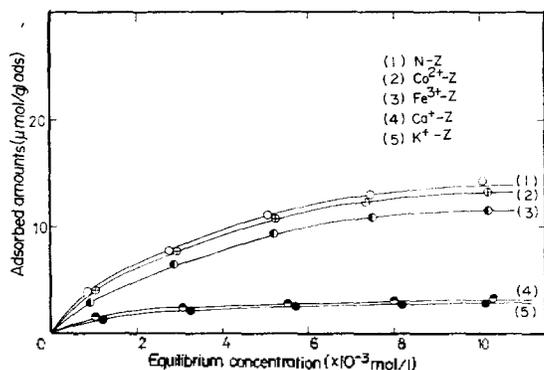


Fig. 11. Adsorption isotherms of benzothiophene on cation exchanged natural zeolites.

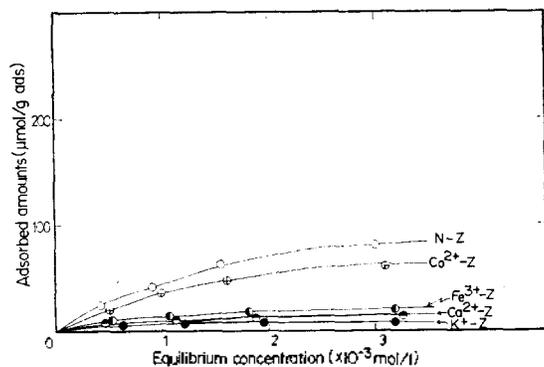


Fig. 12. Adsorption isotherms of dibenzothiophene on cation exchanged natural zeolites.

into the pores of minerals and be adsorbed selectively. In the case of symmetrical adsorption,

such as DES, DMDS, DEDS, the adsorbed amounts generally decreased with the increase in their length and bulkiness. For the Co^{2+} - and Fe^{3+} -zeolites, DEDS and DMDS with double lone pair electrons were less adsorbed than DES. This indicated that the geometric structures were less important than the electronic structure of the adsorbate. These results showed a good agreement with Traube's rule²⁰ which meant that bond length was more important factor than functional group of adsorbate in these adsorbate in the adsorption. The adsorbed amounts of thiophene and its derivatives, BTP and DBTP, however, decreased with the increased electrons. It was highly probable that this tendencies were attributed to the $p\pi$ -conjugation of lone pair electrons of sulfur.¹² Therefore, the more π electron they have, the less amounts adsorbed.

The dependences of equilibrium loading on exchanged cations are shown in Fig. 6~12. The increasing orders of equilibrium loading on the cation saturated zeolites Ca^{2+} -, K^{+} -, Fe^{3+} - and Co^{2+} -zeolite for EM and K^{+} -, Ca^{2+} -, Fe^{3+} -, Co^{2+} -zeolite for DES, DMDS, TP, BTP, and DBTP.

Co^{2+} -zeolite was the most effective adsorbents for any Adsorbates while K^{+} -, Ca^{2+} -zeolites were poor adsorbents.

These results agreed with Henrickson and Eyman's report¹¹ which stated that transition metals made more powerful coordination links than alkali metals. Co^{2+} -zeolites showed the larger adsorption capacities for DES, DEDS, DMDS and EM than for TP, BTP and DBTP. The diminishing electron density around sulfur atoms of TP, BTP and DBTP caused the decrease in adsorbed amounts due to the $p\pi$ -conjugation.¹²

Adsorption Isotherm. The linear relationship in the Fig. 13 indicated that the adsorption pattern followed Langmuir type

$$Q^{-1} = b^{-1} + (bkC)^{-1}$$

where Q , C , b and k are equilibrium loading, concentration and constant, respectively. Fig. 13 represented Langmuir adsorption isotherms of DEDS on several cation exchanged natural zeolites. The adsorption parameters, b and k , evaluated from the slopes and the intercepts were presented in the Table 4.

They were related with adsorption capacities of adsorbents and equilibrium constants, respectively. Polarizing powers of exchanged cations were plotted against adsorption parameter b as shown in Fig. 14. This linear relationship indicated that adsorption capacities were proportionally correlated with polarizing powers of the exchanged cations.

Therefore it could be deduced that the driving force of these adsorption was complex-formation of the exchanged cations with unshared electron pairs of sulfur atom. In the case of Fe^{3+} -zeolite, however, some deviations were shown. This was probably caused by changing of surface oxidation state of Fe^{3+} -ion

Adsorption rate. The great part of adsorption took place within an hour. The relationship between contact time and the loading ratio at the initial adsorption stage is represented in Fig. 15 and was confirmed that the rate determining step of adsorption of DMDS, DES,

DEDS, TP, on Co^{2+} -zeolite at initial stage was intraparticle diffusion into the transitional pores of zeolite.²¹

The following Boyd's equation for the intraparticle diffusion is used in determining the structure effects of adsorbates,

$$Q_t/Q_\infty = (R/6) \times (D_i \times t/\pi)^{0.5},$$

where Q_t and Q_∞ indicated adsorbed amounts

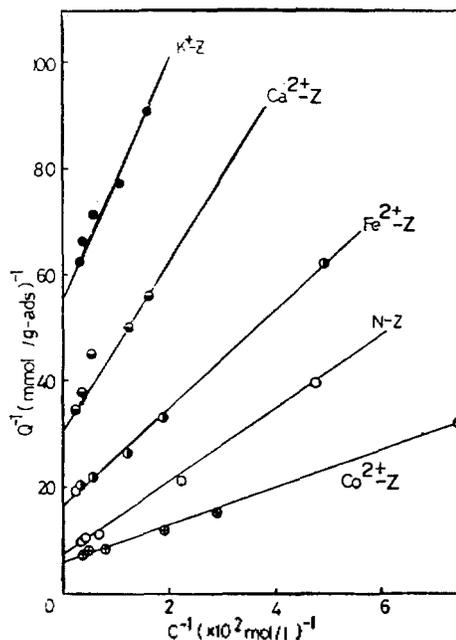


Fig. 13. Langmuir adsorption isotherms of DEDS on Co^{2+} -zeolite.

Table 4. Adsorption parameters for adsorptions of organo sulfur compounds on the cation exchanged natural zeolites

Sulfur compd	Zeol.									
	K ⁺ -Z		Ca ²⁺ -Z		Co ²⁺ -Z		Fe ³⁺ -Z		N-Z	
	b	k	b	k	b	k	b	k	b	k
EM	0.07	1.65	0.07	1.46	0.25	2.72	0.17	1.72	0.27	3.51
DES	0.04	0.71	0.05	0.96	0.23	1.21	0.14	1.32	0.20	1.10
DMDS	0.06	0.70	0.06	0.99	0.19	1.46	0.14	1.45	0.18	1.14
DEDS	0.02	0.68	0.04	0.56	0.17	1.06	0.11	2.13	0.14	1.05
TP	0.01	0.51	0.02	0.54	0.11	1.01	0.06	1.45	0.11	0.65

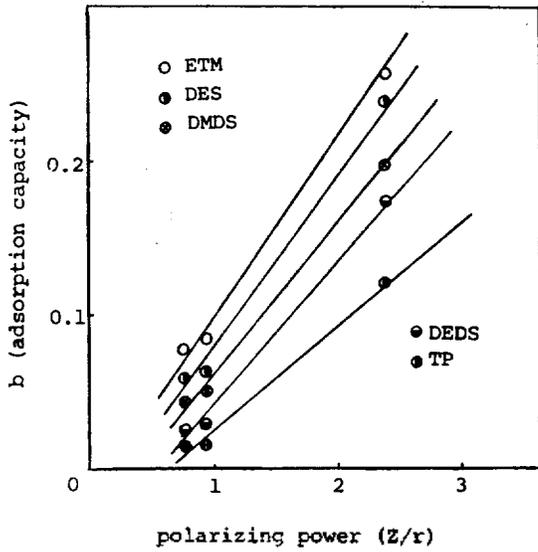


Fig. 14. Relationship between adsorption capacities and polarizing power of exchanged cation.

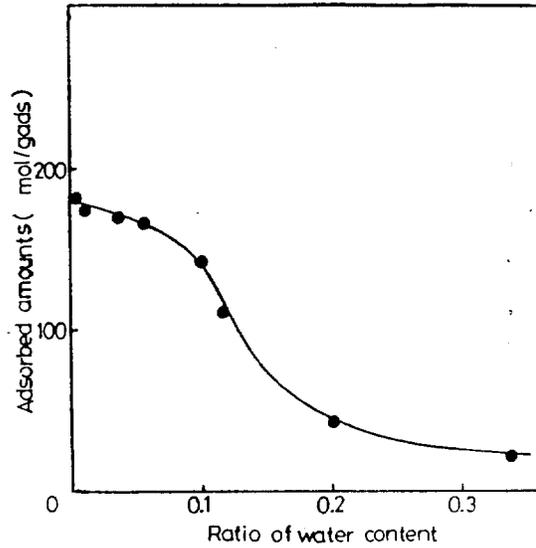


Fig. 16. Effect of preadsorbed water on the adsorption of DEDS on to Co^{2+} -zeolite.

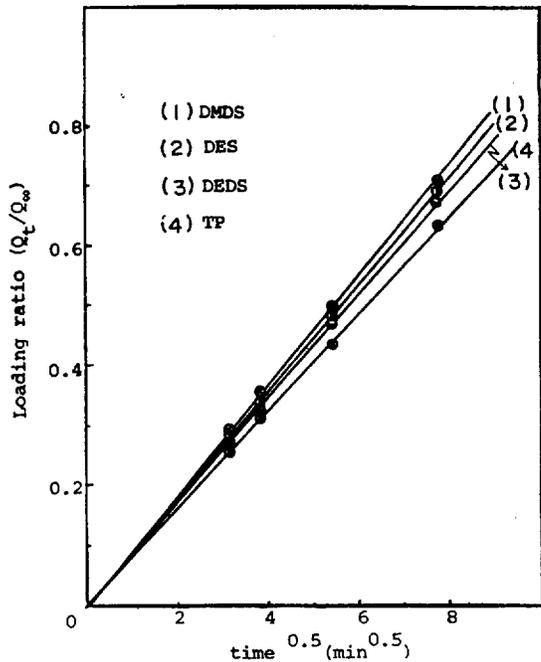


Fig. 15. Linear relationship between loading ratio and contact time^{0.5} of adsorption.

at contact time t at equilibrium. The constant R is the radius of adsorbent. Intraparticle diffusion coefficient, D_p , calculated from the

Table 5. The intraparticle diffusion coefficients of DES, DMDS, DEDS, TP on Co^{2+} saturated natural zeolite ($\times 10^{-4} \text{mm}^2/\text{h}$)

Adsorbate	DMDS	DES	DEDS	TP
D_i	2.511	2.306	2.046	1.574

slopes in Fig. 15 are shown in Table 5.

The increasing order of diffusivity of TP, DEDS, DES and DMDS illustrates that the adsorption rates depend upon the length of adsorbates.

Effect of Preadsorbed Water. Water contents of Co^{2+} -zeolite were plotted against adsorption capacities in Fig. 16. This preadsorbed water, as much as $2.26 \times 10^{-3} \text{mol/g-zeolite}$ (10% to its maximum adsorption capacity of water), affected the adsorption capacities of zeolite, but very insignificant amount.

This meant that small size molecule, like water, preferentially occupied the micro pores of zeolite while the organo sulfur compounds adsorbed onto exchanged cations at transitional pore of cation exchanged natural zeolites.

CONCLUSION

The equilibrium adsorbed amounts are dependent upon the exchanged cation and the nature of adsorbate, such as molecular length, volume and electronic structure. The decreasing orders of equilibrium loadings were EM, DMDS, DES, DEDS and TP for Ca^{2+} - and K^{+} -zeolites, EM, DES, DMDS, DEDS, and TP for Co^{2+} - and Fe^{3+} -zeolites and TP, BTP, DBTP for all adsorbents.

Exchanged cations on the zeolites represented the selectivities of adsorption. The adsorption capacities are proportional to the polarizing power (Z/r) of the exchanged cations. These results indicated that the driving force of these adsorption was complex-formation of the cations with the sulfur atom.

The great part of equilibrium adsorbed amounts were obtained within an hour. The rate determining step of the adsorption at initial stage is intraparticle diffusion of the adsorbate into the transitional pores of zeolite.

The preadsorbed water preferentially occupied the micro pore. And a maximum of 10 % of water adsorption didn't affect the adsorption of organo sulfur compounds which indicate that these adsorbates adsorb on the cation of transitional pores.

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