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UV-Vis Spectroscopic Study on Effects of Pressure for Adsorption of *p*-Nitrotoluene at Liquid-Solid Interface

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Abstract. The behavior of *p*-nitrotoluene adsorbed at zeolite/*n*-heptane interface has been investigated by the electronic spectroscopy under pressures up to 300 MPa. The uv-vis absorption bands of adsorbed *p*-nitrotoluene were deconvoluted into ones for the species adsorbed on the cation sites, and one for that on the pore wall of zeolite. The peak of adsorbed species on the cation site red-shifted by 20–80 nm from the position of the same species in the liquid phase, and their magnitudes of shift depended on the strength of electric field generated by the cation in zeolites. The peak intensities of adsorbed species on the cation site were enhanced but those on the pore wall site were reduced with the increase in pressure, suggesting that a part of *p*-nitrotoluene molecules on the pore wall site desorbed and the adsorption on the cation site was enhanced by compression. The pressure dependence of peak intensity indicated that the behavior of this adsorption system was strongly governed by the solvation structure of the adsorbate in the zeolite pore. In particular, it was found that the adsorption of solvent molecules on the cation site strongly affected the volume change of the adsorption system.

Keywords: electronic spectra, adsorption of liquid, zeolites, *p*-nitrotoluene, high pressure

Introduction

The technology which uses the adsorption at liquid-solid interface has increasingly become important because of the global environmental situation. To attain a high performance of an adsorbent and/or an adsorptive process, it is nowadays necessary to analyze adsorbed species in the order of molecular dimension. Adsorption phenomena on solid surface have often been investigated by spectroscopic technique. In particular, infrared (ir) spectroscopy is frequently used in the analysis of gas-solid adsorption systems because the structure and the microscopic environment of admolecules can be directly reflected in the profile of absorption bands. However, this technique has some weak points when applied to a liquid-solid system. For example, it is frequently difficult to separate the absorption band of the admolecule from that of the same species in the bulk liquid phase because the interaction force in an adsorption is frequently similar to that of a solvation. In addition, only a few solvents can transmit ir light in the wavenumber range of the interest and therefore the number of kinds of usable solvent is restricted. The ultraviolet-visible (uv-vis) spectroscopy has several advantages on this point. Namely, many ordinary solvents (water, alcohols, etc.) are good transmittable media of uv-vis light, and the extinction coefficient of uv-vis absorption is eminently larger than that of ir absorption for certain molecules allowing the analysis at a very low coverage. In addition, the magnitude of peak shift during adsorption is frequently large, and the analyses using the MO calculation may provide a good information on the electronic structure of adsorbate and the adsorptive behavior.

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Fundamental studies of adsorption on acidic solid surfaces using uv-vis spectroscopy were reviewed by Okuda (1965). Spectra of strongly interacting species had mainly been studied, and measurements of catalyst acidity and the assignment of the absorption bands had been discussed. Drushel et al. (1966) analyzed systems of some Hammett indicators adsorbed on an alumina and some cracking catalysts, and observed absorption peaks of the protonated species adsorbed on the acid site, as well as that of the physisorbed neutral species. They reported that the red-shift of the physisorbed species was due to an interaction between π-electron of the adsorbate and the surface. Umansky et al. (1990, 1991) proposed a method to determine the acid strength of sites in zeolites using the uv-vis peak shift of adsorbed *p*-nitrotoluene.

However, in spite of many studies on admolecules, specific phenomena of adsorption at liquid-solid interface, such as the solvation of the adsorbate and the competitive adsorption of solvent, has scarcely been discussed; it may be attributed to the shortage of operational parameters for liquid adsorption. The pressure has been used as a probe for analysis of the mechanism in liquid phase reaction. For instance, pressure effects on the reaction rate of mutarotation of α-*D*-glucose by homogeneous acid or base catalysts gave estimation of the activation volume and the rate-determining step (Sander, 1943; Anderson and Broe, 1972; Anderson and Gronlund, 1979; O' Connor et al., 1983; Anderson, 1984). The method was also applied to heterogeneous catalysis (Nobel, 1987, 1988; Eldik, 1986; Noguchi et al., 1980; Sato et al., 1988).

In the present study, the uv-vis spectroscopy was combined with the high pressure technique in order to analyze the adsorptive behavior of *p*-nitrotoluene at *n*-heptane/zeolites interface, and the adsorptive structure were discussed through the thermodynamic analysis and the molecular orbital (MO) calculation.

Experimental

Materials. *p*-Nitrotoluene (Tokyo Kasei, Extra Pure grade), a Hammett indicator of $pK_{BH+} = 10.5$, was used as the adsorbate. *n*-Heptane (Wako Pure Chemicals, Guaranteed Reagent grade) was used as the solvent. This solvent does not freeze under pressures up to 300 MPa at the ambient temperature, and is capable of transmitting uv-vis light between 220 and 800 nm. The *p*-nitrotoluene/*n*-heptane solution was degassed before use by repeated evacuation at liquid nitrogen temperature and warming to ambient temperature.

The adsorbents used in the present study were listed in Table 1 with their fundamental properties. H, Li, and K-ZSM-5 zeolites were prepared by conventional ion exchange of Na-ZSM-5 (Tosoh; $SiO_2/Al_2O_3 = 23.3$), and the silicalite ($SiO_2/Al_2O_3 = 2120$) was kindly presented by Prof. Yashima at Tokyo Institute of Technology. USY zeolite ($SiO_2/Al_2O_3 = 240$) was supplied by Tosoh, and HY zeolite was prepared by a calcination of NH_4Y zeolite (Aldrich; LZY-62, $SiO_2/Al_2O_3 = 2.5$) at 673 K.

Procedure. Amounts of *p*-nitrotoluene adsorbed on the zeolites, evacuated for 4 hours at 673 K, were determined from the difference of concentration of solution between before and after the adsorption. The adsorption equilibrium was reached within 60 min. Uv-vis spectra were measured by the transmission method using a clamp type cell with sapphire windows (Fishman and Drickamer, 1956; Hagiwara, 1995). The adsorbent was pressed into a wafer of 40–80 μm thickness and was activated at 673 K under 1×10^{-1} Pa for 4 h. The wafer cooled to ambient temperature was immersed into the degassed *p*-nitrotoluene/*n*-heptane solution without exposure to atmosphere and equilibrated for 60 min. The solution was poured into the cell after the wet wafer was set. Uv-vis spectra were

Table 1. Characteristic properties of adsorbents.

Adsorbent	Acid strength	Specific surface area (m^2/g)	Pore volume* ml/g	Cation content mmol/g
HZSM-5	$-12.7 < H_0 < -8.7$**	442	0.29	1.32
LiZSM-5	$-10.5 < H_0 < -5.6$	415	0.27	1.31
NaZSM-5	$-5.6 < H_0 < +1.5$	402	0.22	1.28
KZSM-5	$+1.5 < H_0 < +3.3$	372	0.22	1.25
Silicalite	$+3.3 < H_0$	383	0.21	0.02
HY	$-12.7 < H_0 < -8.7$**)	458	0.25	4.90
USY	$+3.3 < H_0$	742	0.47	0.14

*From the amount of nitrogen adsorption at 0.967 relative pressure.

**Umansky et al., 1990.

recorded on Hitachi 330 spectrophotometer under desired pressures from 0.1 to 300 MPa at the ambient temperature (around 15°C). For the purpose of analyzing the spectra, uv-vis spectra for systems without *p*-nitrotoluene nor adsorbents were also recorded at the same conditions.

Results and Discussion

Adsorption Isotherm. Generally speaking, the amount of adsorption at a liquid/solid interface calculated from the concentration change in the liquid phase during adsorption is not the absolute adsorption but an amount of surface excess because the solvent must co-adsorb. However, we approximated the total amount of adsorption by the measured one because the concentration of *p*-nitrotoluene in the equilibrium bulk phase is very low (below 0.5 mmol/g). The adsorption isotherms of *p*-nitrotoluene from *n*-heptane solution over several kinds of zeolite adsorbents are shown in Fig. 1. The isotherms in this concentration region were seemingly obeying Henry's law, and the orders of amount of adsorption are; HY $\gg$ LiZSM-5 > NaZSM-5 > KZSM-5 > HZSM-5 $\gg$ USY > silicalite. This order reflects not only the number of adsorption sites but also the strength of the adsorption interactions. However, the orders in zeolites having the same structure (ZSM-5's and silicalite) indicates that interactions between the electric field formed by the cation and the negative charge of nitro-group in *p*-nitrotoluene strongly governs the adsorptive character. In addition, it can be seen in this figure that HY zeolite adsorbs much more *p*-nitrotoluene molecules than HZSM-5 does because the former has a larger number of the cations and a larger pore space than the later, although these two zeolites have similar acid strength (Table 1).

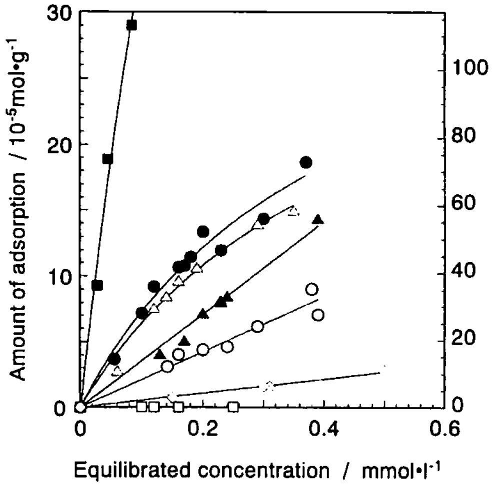

Figure 1. Adsorption isotherms of *p*-nitrotoluene from *n*-heptane solution on several zeolites; ○, HZSM-5; ●, LiZSM-5; △, NaZSM-5; ▲, KZSM-5; □, silicalite; ■, HY zeolite; ◇, USY zeolite.

In order to confirm that both of the external surface and micropore wall in zeolites are available to the adsorption of *p*-nitrotoluene, the magnitude of areas occupied by *p*-nitrotoluene molecule was estimated. The molar area of a *p*-nitrotoluene was set to be 4×10^5 m^2/mol on the basis of van der Waals radii (Bondi, 1977). The largest area occupied exceeded 70 m^2/g for ZSM-5 type zeolite which was about 20% of the total surface areas. Considering from this value and the fact that isotherms were still in the Henry's region, *p*-nitrotoluene must be capable of invading into ZSM-5 zeolite pores and adsorbed on the pore wall as well as on the outer surface.

Uv-Vis Spectra. The uv-vis spectra of *p*-nitrotoluene/zeolite adsorption systems were obtained subtracting the spectra of the adsorbent and those of the solvent at the same pressures from observed ones. The results for ion exchanged ZSM-5 zeolites systems are shown in Fig. 2. The peak positions of absorption bands depended on adsorbents and shifted from that in the solution. In order to analyze the peak profile, absorption bands were deconvoluted. Since the bands were broad without fine structure, we applied following two assumptions: (1) the peak of adsorbed species is symmetric on the linear wavenumber abscissa by analogy with the band of the same species in the solution, (2) the adsorption sites in zeolites consist of cationic sites (site I) and a pore wall site (site II), and the later is similar in nature with the pore wall of silicalite or USY zeolite which scarcely involve cations. Then, firstly the spectra for *p*-nitrotoluene over silicalite and USY zeolite were deconvoluted on the basis of the first assumption, as shown in Fig. 3 using the spectra of *p*-nitrotoluene in *n*-heptane solution. A red-shifted broad band (peak II) around 34000 cm^{-1} (ca. 294 nm) was obtained and it was assigned to the physisorbed *p*-nitrotoluene molecule on site II. The positions of peak II for silicalite and USY zeolite were equal to each other. Therefore, the peak positions of species on pore wall (silicalite) sites seem to be insensitive on pore structure. Nextly, the absorption bands on ZSM-5 and HY zeolite were deconvoluted on the basis of the second assumption using the spectra of *p*-nitrotoluene in solution and adsorbed one on site II, as shown in Fig. 4. A new peak (peak I) was found on the lower

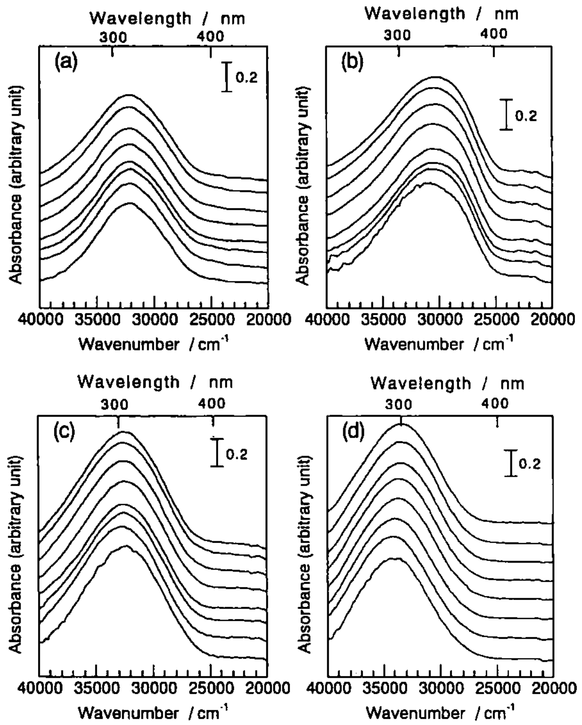

Figure 2. Uv-vis spectra of 0.05 mmol/l p-nitrotoluene n-heptane solution zeolite system under pressure of 0.1 MPa, 25 MPa, 50 MPa, 100 MPa, 150 MPa, 200 MPa, 250 MPa, and 300 MPa. The pressures increase from bottom to top in every figure: (a) HZSM-5, (b) LiZSM-5, (c) NaZSM-5, and (d) KZSM-5.

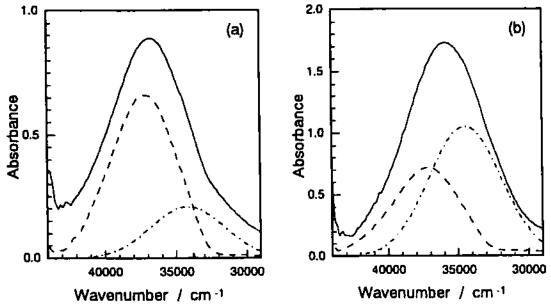

Figure 3. The uv-vis spectra and their deconvoluted spectra of p-nitrotoluene on (a) silicalite (0.05 mmol/l) and (b) USY zeolite (0.5 mmol/l). ———, observed spectra; - - - -, liquid phase; —-—, adsorbed phase.

wavenumber side of peak II in every system and it was assigned to the p-nitrotoluene adsorbed on the cation site. In the case of LiZSM-5 adsorbent, the presence of an additional peak (peak III) was suggested between peak I and peak II on the basis of above assumptions, because the peak I became highly asymmetric if third peak was not considered.

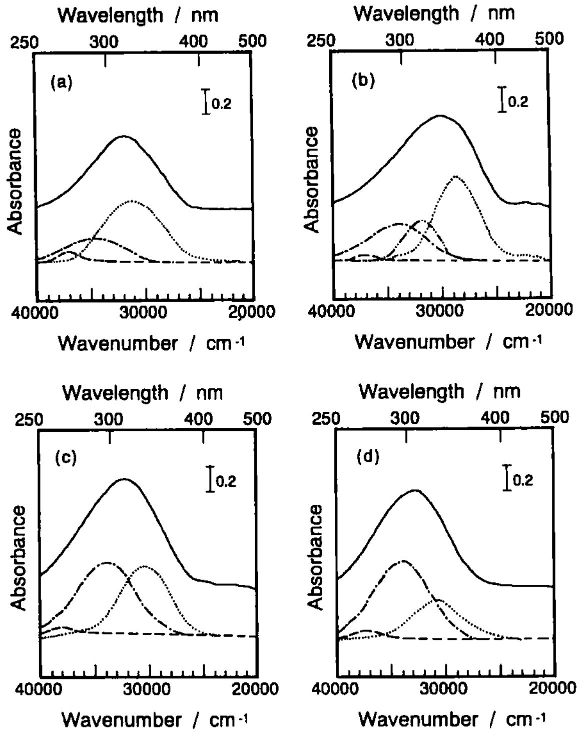

Figure 4. The uv-vis spectra and their deconvoluted spectra of p-nitrotoluene on (a) HZSM-5, (b) LiZSM-5, (c) NaZSM-5, and (d) KZSM-5. ———, observed spectra; - - - -, liquid phase; · · · · ·, peak-I (adsorbed phase); —-—, peak-II (adsorbed phase); —··—, peak-III (adsorbed phase).

Uv-Vis Peak Position. The positions of the peak I were listed in Table 2. It can be seen that a smaller cation induced a larger red shift except for the case of H-type zeolites. Since a small cation forms a strong field in its vicinity, the peak I was assigned to a species perturbed by the electric field of the cation. Shifts of peak I observed on HZSM-5 (318 nm) were smaller than those on the other ZSM-5 zeolites. Umansky et al. (1990, 1991) also found a peak in p-nitrotoluene/HZSM-5 system at a position which coincides with this work, and assigned it to unprotonated species. Considering above mentioned facts, peak I found on H-type zeolites may be assigned to incompletely protonated p-nitrotoluene. The position of peak I for HY zeolite is equal to that of HZSM-5 suggesting that the nature of adsorption sites giving peak I in these zeolites are similar. The position of peak III on LiZSM-5 was nearly equal to that of peak I on HZSM-5. Since the LiZSM-5 zeolite had some proton sites, the peak III was also assigned to an incompletely protonated species on OH site.

Table 2. Observed and estimated uv-vis positions and oscillator strength for *p*-nitrotoluene adsorption system by CNDO/S method.

Interacting species	Peak position Observe/nm Peak I	 Peak II	 Calculated/nm	Estimated oscillator strength
Non		270*	269.4	0.349
Silicalite		294	—	—
USY		294	—	—
HZSM-5	318		412.1	0.565
HY	318		—	—
Li^+	350		372.3	0.450
Na^+	330		359.3	0.412
K^{+}**	325			
$(OH)_3Si$—OH—$Al(OH)_3$	—	—	277.6	0.376

*The value in *n*-heptane solution.

**CNDO/S parameters are not registered.

Brocląwik and Witko (1988) showed using a semi-empirical molecular orbital calculation (MNDO) that the aromatic ring and methyl group in *p*-nitrotoluene bear a positive charge, but the nitro group bears a negative charge. Therefore, peak I and peak II can be assigned to the *p*-nitrotoluene interacting with the cation site through its nitro group, and to a species interacting with the zeolite pore wall through its aromatic ring or methyl group, respectively.

In order to discuss the uv-vis absorption theoretically, CNDO/S MO calculation (Baumann, 1977; Buemi; Kihara, 1993) for *p*-nitrotoluene molecules interacting with H^+, Li^+, and Na^+ cations were carried out. The calculated peak positions and their oscillator strengths were summarized in Table 2.

It is found that addition of H^+, Li^+, and Na^+ give rise to red shifts in uv-vis spectra and a slight enhancement of the oscillator strength in *p*-nitrotoluene. The magnitude of the estimated shift roughly corresponded with observed values except for the case of H^+. It is concluded, therefore, that Li and Na cations in zeolites are completely ionized and a strongly interacting complex is formed. On the other hand, the peak shift for the system including H is overestimated, probably because of an insufficient ionicity of the OH site as mentioned before. To check the validity of this speculation, a calculation on the system of a *p*-nitrotoluene molecule interacting $(OH)_3Si$—OH^+—Al^-—$(OH)_3$ instead of H^+ was carried out, and a small red shift was obtained as shown in the last line in Table 2. It was, therefore, confirmed that the interaction of a *p*-nitrotoluene molecule with OH site in the zeolite is rather weak. Since the magnitude of the peak shift was strongly correlated with the strength of electric field estimated from methane adsorption (Yamazaki, 1991), the observed uv-vis peak shift was probably caused by stabilization of π^*-orbital.

Pressure Effects on Uv-Vis Spectra. The uv-vis spectra of *p*-nitrotoluene in *n*-heptane solution (0.05 mmol/l) at several pressures were shown in Fig. 5. The peak position shifted ca. 700 cm^{-1} to lower

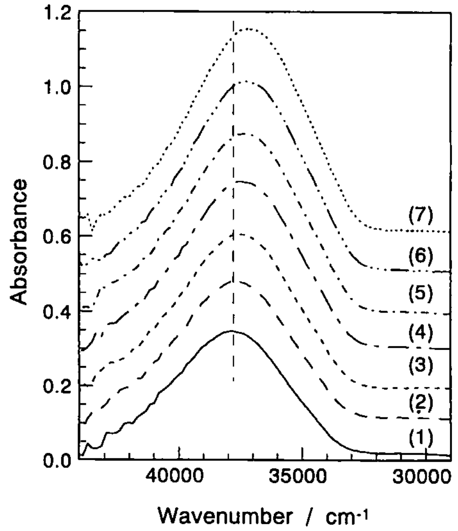

Figure 5. The uv-vis spectra of *p*-nitrotoluene in *n*-heptane solution (0.5 mmol/l) at several pressures: (1) 0.1 MPa, (2) 50 MPa, (3) 100 MPa, (4) 150 MPa, (5) 200 MPa, (6) 250 MPa, and (7) 300 MPa.

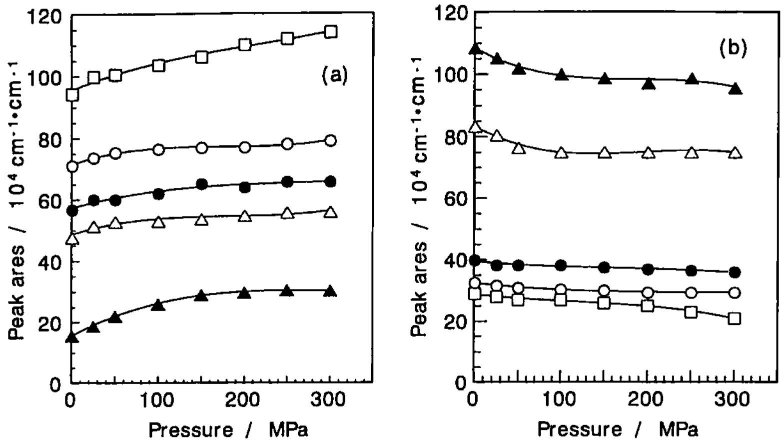

Figure 6. The integrated intensities of (a) peak-I and (b) peak-II as a function of pressure. Equilibrium concentration of *p*-nitrotoluene in *n*-heptane was 0.05 mmol/l except for HY (0.01 mmol/l). ○, HZSM-5; ●, LiZSM-5; △, NaZSM-5; ▲, KZSM-5; □, HY.

wavenumber side by the compression up to 300 MPa. From the MO calculation of the peak position of *p*-nitrotoluene interacting with a hydrocarbon (for simplicity, a methane molecule was used as the hydrocarbon in the calculation), it was found that the small red shift of uv-vis peak was resulted when a hydrocarbon molecule accessed to the nitro group or the aromatic ring of *p*-nitrotoluene. Therefore, we concluded that the red-shift was attributed to the closer access of solvent molecule or the increase in solvation number by compression. On the other hand, the peak positions of adsorbed species were not changed with the increase in pressure. It may mean that a *p*-nitrotoluene molecule in the adsorbed phase is hard to be compressed in the pressure range studied.

The integrated intensities of peak I and peak II were shown in Fig. 6 as a function of pressure. In the cases of zeolites with a smaller cation, the peak I is stronger than the peak II, i.e., the zeolite involving a smaller cation adsorbs *p*-nitrotoluene more selectively on the cation site. The total amounts of adsorption in the uv-vis measurement (0.05 mmol/l equilibrium concentration) were estimated to be in the order of 1×10^{-5} mol/g on the basis of the integrated molar extinction coefficient of *p*-nitrotoluene in *n*-heptane solvent, which was in accordance with adsorption isotherms (Fig. 1). Since these amounts were sufficiently smaller than the estimated monolayer capacities, above mentioned selectivity for adsorption has to be attributed to the potential energy difference between site I and site II. Namely, a small cation such as Li^+ interacts more strongly with a *p*-nitrotoluene molecule than the pore wall does.

The area of peak I in each systems enhanced with the increase in pressure while that of peak II reduced. Nevertheless, the total band areas on each zeolite were almost constant regardless of pressure. Accordingly, it is suggested that admolecules migrates from site II to site I with the increase in pressure keeping the total amount of adsorption constant.

Assuming competitive adsorption between *p*-nitrotoluene and *n*-heptane on each sites, the adsorption equilibrium equations may be represented as follows;

$$\text{on site I:}\quad p\text{-nitrotoluene}_{\text{sol}} + n\text{-heptane}_{\text{ad1}} \rightleftharpoons p\text{-nitrotoluene}_{\text{ad1}} + n\text{-heptane}_{\text{sol}} \qquad (1)$$

$$\text{on site II:}\quad p\text{-nitrotoluene}_{\text{sol}} + n\text{-heptane}_{\text{ad2}} \rightleftharpoons p\text{-nitrotoluene}_{\text{ad2}} + n\text{-heptane}_{\text{sol}} \qquad (2)$$

where subscripts sol, ad1, and ad2 indicate species in the bulk solution and the admolecules on site I and site II, respectively. In the present study, the amount of *p*-nitrotoluene adsorbed was much lower than the monolayer capacity, and the mole fraction of the solution did not vary with compression because a large solution volume in the optical cell was capable of compensating the concentration change by adsorption. In addition, the molar extinction coefficient of admolecules is considered to be constant regardless of pressure because the peak position did not change with pressure. On the basis of above approximation, the partial molar volume change ($\Delta \bar{V}$) can be simply

Table 3. Partial molar volume change in adsorption of *p*-nitrotoluene on site-I and site-II.

Adsorbent	$\Delta\bar{V}_1$/cm^3	$\Delta\bar{V}_2$/cm^3
H-ZSM-5	−3.3	2.4
Li-ZSM-5	−5.0	1.5
Na-ZSM-5	−4.4	4.6
K-ZSM-5	−19.0	3.2
Silicalite		−5.5
HY	−4.2	3.3
USY		−3.0

expressed as follows (Hagiwara et al., 1995)

$$-\Delta Vi = RT\left[\frac{\partial \ln S_i}{\partial p}\right]_{p=0} \tag{3}$$

where S_i is the integrated intensity of the peak i. The values of $\Delta\bar{V}$ were estimated from the slope of the plot of ln S_i vs. p at the zero pressure and listed in Table 3.

$\Delta\bar{V}$ values on site-I were negative while those on site-II were slightly positive for the cation containing zeolites. It means that the adsorption of a *p*-nitrotoluene molecule on site-I and the accompanying desorption of solvent molecules (desolvation) from there bring about a net reduction of the system (partial molar) volume, while the reverse is true on site-II in these adsorbents. Namely, $\Delta\bar{V}$ value of adsorption reflects not only the strength and the number of adsorption bond formed or disappeared but also the change in solvation number of the adsorbate and the adsorption site during the adsorption.

It is well known that the formation of a hydrogen bond and a covalent bond reduces the system volume by about 4 ml/mol and 10–20 ml/mol, respectively (Nobel, 1987). The magnitude of the $\Delta\bar{V}$ values observed in this study were almost order of formation or a disappearance of a hydrogen bond. However, the absolute value of the volume reduction on the Li cation on which *p*-nitrotoluene adsorbed more strongly was smaller than that on a K cation on which adsorption was supposed to be weak. This discrepancy suggested that an action leading to an increase in partial molar volume was involved in the adsorption process on these cation containing zeolites. We can speculate two processes concerning the solvent action. (1) The system volume reduces when either *p*-nitrotoluene or *n*-heptane adsorb, however the volume reduction is larger for *p*-nitrotoluene on site-I than for *n*-heptane on the site-II. (2) Some *n*-heptane molecules solvated to the *p*-nitrotoluene in the liquid phase and they are released in the cause of adsorption of the later onto site-I. The former mechanism seems realistic if *n*-heptane interacts strongly with the electrostatic field formed by a cation. Namely, a volume increase by *n*-heptane desorption will compensate the volume reduction by *p*-nitrotoluene adsorption more on Li^+ site than on K^+ site. The latter mechanism also should increase the volume of the system because *p*-nitrotoluene molecule, having a relatively large polarity, may attract *n*-heptane in the liquid phase while the solvation structure may be restricted in the micropore of adsorbents. Although each mechanism can simultaneously take place, the former is probably dominant because $\Delta\bar{V}$ is depended on the kind of cation.

The $\Delta\bar{V}$ values on site II were slightly positive for zeolites containing cation (or aluminum) while they were slightly negative for silicalite and USY zeolite. This result seems reasonable since *p*-nitrotoluene is a basic indicator, and the pore wall of Al containing zeolite has an anionic nature while those of silicalite and USY zeolites are bearing little negative charge. Namely an weakening of adsorptive interaction of *p*-nitrotoluene is happening on site-II of the former adsorbents which pushes the $\Delta\bar{V}$ value to positive side.

The values of $\Delta\bar{V}_1$ and $\Delta\bar{V}_2$ for HY zeolite were very close to those for HZSM-5, respectively. Together with the equality of peak I position mentioned before, a similar adsorption structures involving solvation structure may be formed on these two zeolites.

Conclusion

Behavior of *p*-nitrotoluene adsorbed at zeolites/*n*-heptane interfaces has been investigated. The results are summarized as follows:

(1) The adsorption isotherms of *p*-nitrotoluene on ion-exchanged ZSM-5 zeolites indicated that the electric field on the surface governs the adsorptive properties.

(2) Respective absorption peaks of species adsorbed on the cations and on the zeolite pore wall were found on uv-vis spectra. Peaks of the species adsorbed on the cation site shifted to lower wavenumber side, and the degrees of shift were depended on the strength of electric field formed by the cation.

(3) The pressure dependence of the adsorption on each site showed that the adsorptive characteristics at the liquid/solid interface was strongly governed by a solvation structure.

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