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Charge Transfer Complexes between Methylviologen and Aromatic Donors within Faujasite Y: Influence of the Alkaline Metal Counter Cations

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***Abstract*:** Charge-transfer complexes between methylviologen and anthracene or 1,4-dimethoxybenzene have been formed within the cavities of a series of faujasites Y containing different alkaline metal ions. It was observed that for the same uptake of donor, the intensity of the complex band in the diffuse reflectance spectra is always higher for Cs^+ and decreases progressively as the ionic radius of the accompanying alkaline cation decreases. According to molecular modeling, these results can be interpreted in terms that a reduction in the free volume available inside the zeolite supercage favours the complex formation. Copyright © 1996 Elsevier Science Ltd

In a series of pioneering articles, Kochi, Yoon and coworkers have shown that charge transfer (CT) complexes between methylviologen (MV^{++}) and aromatic donors (D) can be formed within the voids of zeolites by a stepwise assembly consisting in the doping of the zeolite by ion exchange and subsequent incorporation of the aromatic compound.[1-4] Zeolites are microporous crystalline aluminosilicates, whose voids contain a variable number of charge-balancing cations to compensate the negative charge of the lattice introduced by the isomorphic substitution of Si by Al.[5, 6] Thus, in the case of as-synthesized faujasite Y the unit cell contents 56 Na that corresponds to 7 ion per supercage distributed in three different locations. Four of these charge balancing cations are in the supercage. Consequently, when the MV^{++}-D complex is formed within the supercages two of these charge balancing cations are also present sharing the space of the reaction cavity.[7]

In the present communication, we report that the apparent equilibrium constant for the CT complex formation depends on the size of the alkaline metal ionic spectator in a way that can be related to the free volume available in the reaction cavity. Samples of the alkaline metal ion exchanged Y zeolites were obtained starting from commercial NaY (Si/Al 2.6) by consecutive ion exchanges using aqueous solutions of M^+ (M^+: Li^+, K^+, Rb^+, Cs^+) in a solid:liquid ratio 1:10 wt/wt. Subsequently the corresponding exchanged zeolites were doped with MV^{++} by stirring a suspension of the corresponding MNaY with aqueous $(MV^{++})Cl_2$. The chemical composition of the zeolites before and after exchange is summarized in Table 1.

Table 1. Chemical composition of the initial alkaline metal exchanged MNaY zeolites and level of supercage occupancy after doping with MV^{++}.

Sample	Unit cell composition[a,b]	MV^{++} content (mmol x g^{-1})[c]	Loading of MV^{++} per supercage[d]
LiNaY	$Na_{17}Li_{36}Al_{53}Si_{139}O_{384}\cdot 84H_2O$	0.1980	0.34
NaY	$Na_{53}Al_{53}Si_{139}O_{384}\cdot 176H_2O$	0.2200	0.44
KNaY	$Na_8K_{45}Al_{53}Si_{139}O_{384}\cdot 133H_2O$	0.1800	0.35
RbNaY	$Na_{22}Rb_{31}Al_{53}Si_{139}O_{384}\cdot 165H_2O$	0.2165	0.47
CsNaY	$Na_{22}Cs_{31}Al_{53}Si_{139}O_{384}\cdot 134H_2O$	0.2103	0.48

[a] Calculated by chemical analyses of the Na^+ left in the zeolite and M^+ (Li^+, K^+, Rb^+ or Cs^+) incorporated after the ion exchange before MV^{++} doping; [b] water content measured by thermogravimetry; [c] obtained by combustion analysis; [d] estimated from the formula weight of the unit cell and MV^{++} content.

Stepwise assembly of the CT complexes of MV^{++} with anthracene (AN) and 1,4-dimethoxybenzene (DMB) was accomplished by stirring suspensions of partially dehydrated MV^{++}-doped zeolites (150°C, 1 Torr, 2 h) with CH_2Cl_2 solutions of the aromatic donor at different concentrations (between 2 to 50 mg of D in 25 ml of solvent) under identical conditions. Figure 1 shows some selected diffuse reflectance spectra for the CT MV^{++}-D complexes within zeolite Y.

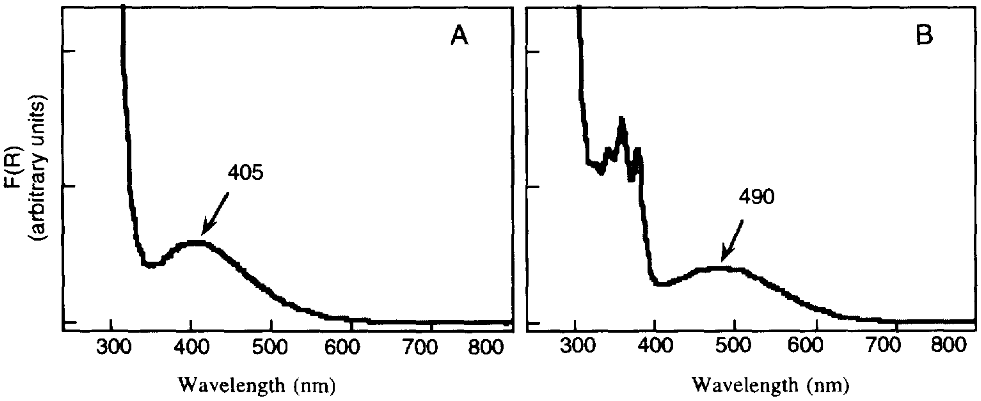

Figure 1. Diffuse reflectance spectra (F(R)) of the MV^{++}-DMB (A) and MV^{++}-AN (B) charge transfer complexes within zeolite NaY.

Only very minor shifts (<10 nm) in the wavelength maximum of the CT band was observed for the series of MY zeolites containing different alkaline metal ions. In contrast, we noted that the intensity of the diffuse reflectance spectra expressed as the Kubelka-Munk function of the reflectivity increases along with the uptake of the donor and with the ionic radius of the residual alkaline metal ion (Figure 2). Both donors, AN and DMB, exhibited the same trend. We noted that the amount of DMB that was adsorbed in the MV^{++}-doped zeolites was consistently much higer than that for AN under the same conditions and concentrations. This fact has to be related with the different diffusion coefficient and molecular size of these donors.

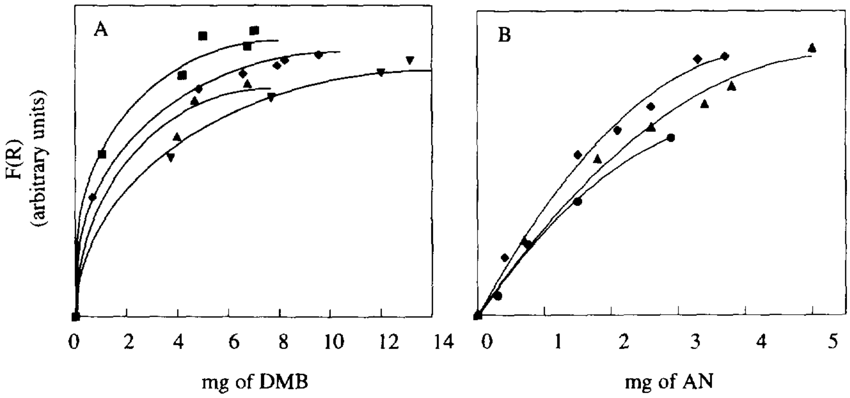

Figure 2. Plots of the intensity of the CT complexes (A: MV^{++}-DMB, B: MV^{++}-AN) measured as the Kubelka-Munk equation (F(R), estimated error < 2%) versus the uptake of D adsorbed on the zeolite (difference between the initial amount and the recovered in the supernatants after incorporation) in a series of alkaline metal exchanged Y zeolites (● LiNaY, ▼ NaY, ▲ KNaY, ◆ RbNaY, ■ CsNaY). The curves correspond to the best second order polynomial fitting of the data.

A reasonable rationalization to account for the influence of nature of the associated alkaline metal cation on the diffuse reflectance intensity of the complex band is that for a given uptake of D more complex is formed when the free volume of the reaction cavity is reduced. Since the interaction between MV^{++} and D is weak, the tighter the fit of the zeolite framework holding the complex, the closer is the contact between MV^{++} and D. As consequence, the complex formation is favored.

An analogous explanation introducing the concept of internal pressure has been given to understand the role that coadsorbed water plays in the shift of the wavelength maxima for these complexes within mono directional zeolites.[4] However, no such effect of coadsorbed water could be observed in the case of zeolite Y.[4] It was suggested that the dimensions of the supercages of zeolite Y are too large to observe any internal pressure exerted by water. Our present observation for zeolite Y will be in line of the influence of water for other zeolites.

In order to justify these results we performed a molecular modeling of our complexes in totally exchanged LiY and CsY zeolites.[8] Recent XRD has provide experimental evidence of the location of Cs^{+} ions in the supercages for partially exchanged CsNaY samples (70% ion exchange).[9] Selected visualizations of the docking showing the higher pressure for MV^{++}-DMB within CsNaY compared to LiNaY are presented in Figure 3.

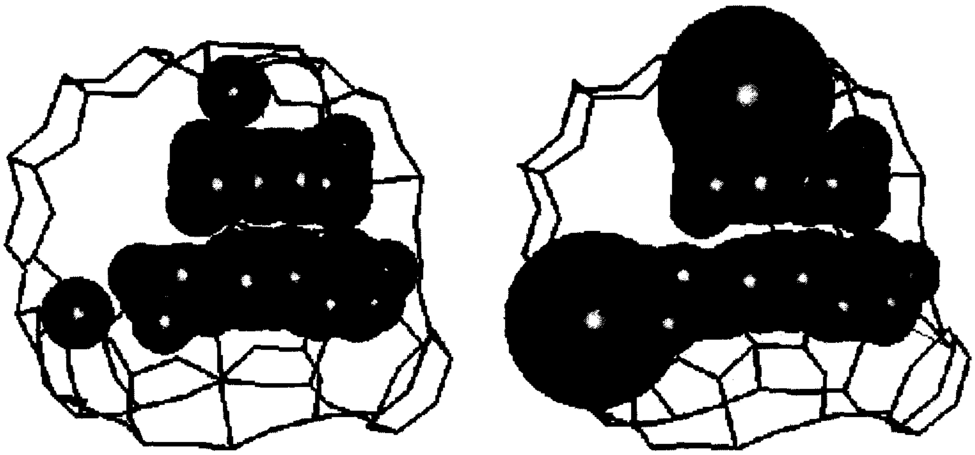

Figure 3. Molecular modeling visualization of CT MV^{++}-DMB complex inside the supercages of LiNaY (left) and CsNaY (right) samples. Two of the original SIII cations have been replaced by MV^{++}.

In conclusion, we have shown that by varying the size of the accompanying charge balancing cation from Li$^+$ to Cs$^+$, an increase of the apparent constant for the formation of CT complexes between MV^{++} and aromatic donors assembled in the zeolite Y supercage is observed. This finding is complementary with the internal pressure effect of coadsorbed water previously established for other zeolites with smaller cage dimensions.

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