

## Studies on Rare Earth Exchanged Zeolites: Part I—Sorption Properties of Rare Earth Exchanged Zeolites\*

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The sorption properties of a series of rare earth exchanged zeolites type X and Y have been determined as a function of rare earth content. The sorption capacity of nitrogen is found to decrease with the increase in rare earth content in the zeolites. This is correlated with the reduction in the void volume from 0.36 cc/g in NaX to 0.29 cc/g in RE(4)X in which 97% Na<sup>+</sup> ions have been replaced with RE<sup>3+</sup> ions. The pore volume modification is further substantiated by the lower sorption rates and equilibrium sorption capacities for water, benzene, ethanol and ethylbenzene vapours. The free energy for sorption of nitrogen and diffusion coefficients for the sorption of water, ethanol and benzene have been estimated from the kinetic data. The results indicate that the number and size of cations in the cavity and the polarizability of the sorbate molecules influence the sorption properties of zeolites.

THE rare earth forms of zeolites are active catalysts for a wide range of reactions<sup>1-3</sup>. The activity of such catalysts depends on the mode of preparation and the relative number of exchanged cations. We have prepared a series of rare earth exchanged X and Y zeolites and studied (unpublished data) their catalytic activity for ethylation of benzene in relation to the degree of exchange. In this paper we report the sorption characteristics of rare earth modified zeolites.

### Materials and Methods

The binder-free zeolite type X was synthesized<sup>4</sup> from sodium silicate, sodium aluminate and sodium hydroxide. The type Y zeolite (SK-40) in the sodium form was obtained from the Union Carbide Corporation (USA). The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio was 2.52 in zeolite X and 4.26 in zeolite Y.

Mixed rare earth chloride (RECl<sub>3</sub>) solution was prepared by dissolving pure didymium oxide and a mixture of lighter rare earths (La, Pr, Sm and other heavy rare earths) in AR HCl solution. The pH was adjusted to 5. The mixed rare earth (RE) and rare earth-ammonium (RENH<sub>4</sub>) forms of the zeolites were prepared by the following two methods. The zeolite was treated with (a) 5% rare earth chloride solution or with 5% RECl<sub>3</sub>+2% NH<sub>4</sub>Cl to obtain REX, REY, RENH<sub>4</sub>X, RENH<sub>4</sub>(1)Y, and (b) NaY was first exchanged with 2% ammonium chloride solution and then treated with RECl<sub>3</sub> solution to replace part of the NH<sub>4</sub><sup>+</sup> ions with RE<sup>3+</sup> to obtain RENH<sub>4</sub>(2)Y. The exchanged zeolites were filtered, washed free of chloride, dried at 120° and equilibrated over saturated ammonium chloride solutions at 25°. The zeolites of higher degree of exchange were obtained by repeated treatments. The REHY

was subsequently prepared by thermal treatment of RENH<sub>4</sub>Y at 500°. The X-ray powder patterns showed that all the zeolite samples were fully crystalline.

The composition of the exchanged zeolite was determined by conventional gravimetric analysis. The rare earths were estimated as oxalates and sodium by flame photometry. Ammonium ion was estimated separately by Kjeldahl's method. Doubly distilled water was used for sorption studies. Organic liquids were purified and dried over molecular sieve 3A.

The sorption measurements were carried out at liquid nitrogen or liquid air temperature in an all-glass BET unit using purified nitrogen gas<sup>5</sup>. Spectrally pure helium (British Oxygen, UK) was used for dead space calibration. The sorption of condensable vapours were measured with a conventional McBain type gravimetric unit. The sensitivity of the silica spring was  $\approx 50$  cm/g. Prior to sorption measurement a known weight of zeolite was evacuated to about 10<sup>-5</sup> torr and gradually heated to 360° and evacuated under reduced pressure for 12 hr to constant weight.

### Results and Discussion

The sorption isotherms of nitrogen on exchanged zeolites type X and Y are plotted in Fig. 1. The isotherms are of type-I. The sorption capacity follows the order RE(1)X > RE(2)X > --- > RE(4)X for zeolite X and NaY > REH(2)Y > REH(1)Y > REY for zeolite Y. The zeolites REHX and REH(2)Y sorb more nitrogen than RE(4)X and REH(1)Y. This may be attributed to the presence of larger number of hydrogen ions in REH(2)Y as compared to REH(1)Y. These results support an earlier finding<sup>6</sup> that the exchange of Na<sup>+</sup> ions by smaller H<sup>+</sup> ions increase the sorption capacity of the zeolite.

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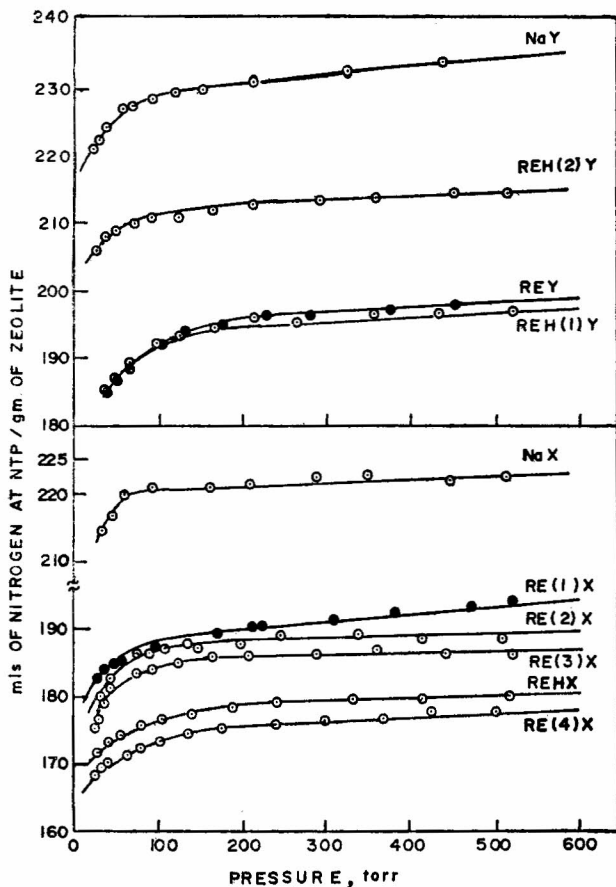


Fig. 1 — Adsorption of N<sub>2</sub> on X and Y type zeolites

With a view to calculating the saturation values and the surface areas, the sorption data have been analysed in the light of BET, and Langmuir isotherm equations. Typical Langmuir and BET plots for zeolite NaX and NaY are illustrated in Fig. 2. The plots clearly show a linear relation for Langmuir adsorption and non-linear relation for the BET adsorption. Similar behaviour is shown by all the exchanged zeolites. The values of surface area computed from BET and Langmuir plots (Table 1) decrease with the progressive exchange with rare earth ions. This is also in the order of decrease in the sorption capacities. The surface areas calculated from the Langmuir equation are generally higher as compared to corresponding BET values. The values of intercept on the BET (Langmuir) plots are very small. This means that the constant *C* in the BET (constant *K* in the Langmuir) equation is very large. The analysis therefore suggests the applicability of Langmuir isotherm equation to the sorption phenomenon in the zeolite.

*Polanyi sorption potential*—The free energy of sorption is given by Eq. (1)

$$\Delta G = -RT \ln P/P_s \quad \dots(1)$$

The value of  $\Delta G$  for the adsorbate-adsorbent system is related to the Polanyi potential ( $\epsilon$ ) which is expressed by Eq. (2).

$$\epsilon = RT \ln P_s/P \quad \dots(2)$$

According to the potential theory the sorption space in the vicinity of a solid surface is characterized by a series of equipotential surfaces. The filling of total adsorption space occurs as the adsorp-

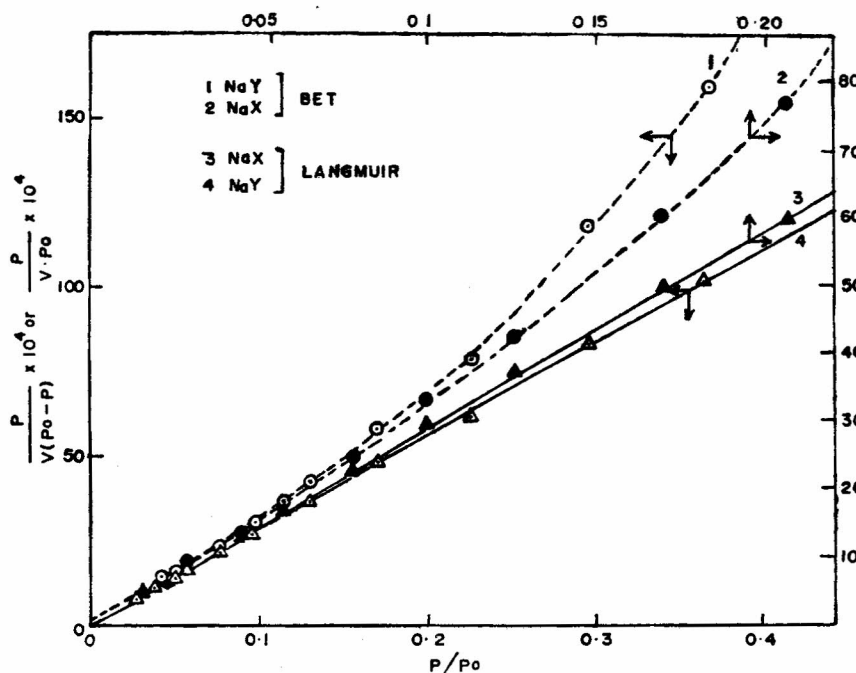


Fig. 2 — Typical Langmuir and BET plots for NaX and NaY zeolites

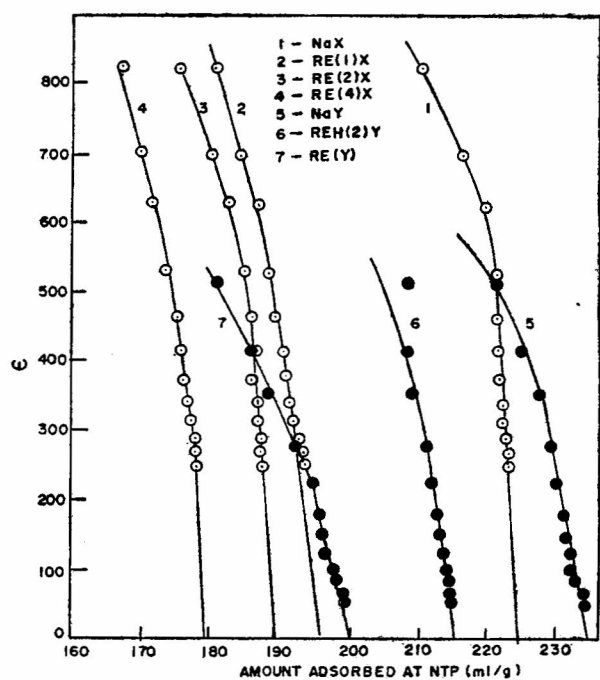


Fig. 3 — Change in Polanyi sorption potential ( $\epsilon$ ) for nitrogen adsorption for X and Y type zeolites

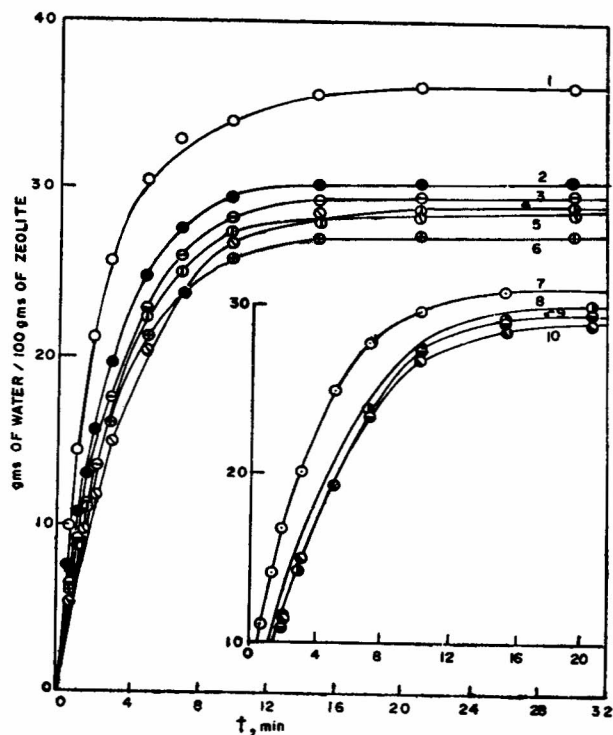


Fig. 4 — Rate of adsorption of water vapour on zeolites [1-NaX, 2-RE(1)X, 3-RE(2)X, 4-RE(3)X, 5-REH(4)X, 6-RE(4)X, 7-NaY, 8-REH(2)Y, 9-REY, 10-REH(1)Y]

tion proceeds. Therefore, with increasing  $\theta$ , the value of  $\epsilon$  should fall. This is indicated in Fig. 3 for the sorption of nitrogen in various zeolites.

*Void volume* — In order to get an idea of the effect of exchange on the microporosity of the zeolite, the nitrogen sorption data have been analysed by the Dubinin-Radushkevich equation (3)

$$\log V = \log V_0 - D \left[ \log \frac{P_s}{P} \right]^2 \quad \dots(3)$$

where  $V$  is the amount sorbed at relative pressure  $P/P_s$  and  $V_0$  is the pore volume; the constant  $D = (0.434 k R^2 T^2) / \beta^2$  where  $\beta$  is the affinity coefficient of the sorbate,  $k$  is a constant and  $R$  and  $T$  have their usual significance.

The plots of  $\log V$  against  $(\log P_s/P)^2$  for various zeolites before and after exchange are linear. The intercept of the plot at  $(\log P_s/P)^2 = 0$  gives the value of  $V_0$ ; while the value of  $D$  is obtained from the slope. The void volumes evaluated from the Dubinin equation are summarized in Table 1. The void volume of NaX as determined from nitrogen adsorption is  $0.37 \text{ cm}^3/\text{g}$  and that of NaY is  $0.36 \text{ cm}^3/\text{g}$ . These values are in close agreement with the values reported<sup>6,7</sup>. Total void volume in the exchange zeolites decreases with the increase in the rare earth content in the zeolite. However, partial exchange of  $\text{Na}^+$  with  $\text{H}^+$  ions appears to increase the void volume. This is confirmed from the data for the total void volumes for REH(1)Y and REH(2)Y.

*Sorption of water and organic vapours* — The sorption kinetics of water, ethanol, benzene and ethylbenzene vapours on various zeolites are plotted in Figs. 4 and 5. The kinetic curve is highest for the  $\text{Na}^+$ -form and lowest for rare earth form of zeolite containing maximum  $\text{RE}^{3+}$  ions. Cations in zeolite act as active centres for the sorption of polar molecules such as water. As number of cations per unit cell in the zeolite Y is less as compared to X type (Table 1), the sorption capacity in the former is expected to be lower. The extent of sorption in a zeolite falls with an increase in the size of the adsorbate molecule and follows the order:  $\text{H}_2\text{O} > \text{C}_2\text{H}_5\text{OH} > \text{C}_6\text{H}_6 > \text{C}_6\text{H}_5\text{C}_2\text{H}_5$ . Tsitsishvili and Andronikashvili<sup>9</sup> also observed a fall in sorption of water in  $\text{La}^{3+}$  zeolite at higher degree ( $\alpha > 0.60$ ) of exchange. They, however, attributed this to the weakening of the zeolite lattice. The sorption of benzene vapour, on the other hand, was found to decrease even at lower degree of exchange in  $\text{LaY}$  zeolite.

One of the primary characteristics of a particular zeolite is its adsorption property. Complete adsorption isotherms are particularly helpful in determining equilibrium sorption capacities which can be useful in the evaluation of specific separation and purification processes. Ion exchanges of parent cations present in a zeolite with other cations can have profound effect on the sorptive properties of the zeolite. For example, the effective pore diameter of zeolite A and zeolite X decrease respectively from 4 to 3 Å and from 10 to 7 Å as the parent  $\text{Na}^+$  ions are replaced by larger  $\text{K}^+$  ions<sup>8</sup>. Similar effects on the pore size are observed on replacing monovalent sodium with multivalent  $\text{Ca}^{2+}$  or  $\text{RE}^{3+}$  ions. The above changes in the sorptive capacities may pri-

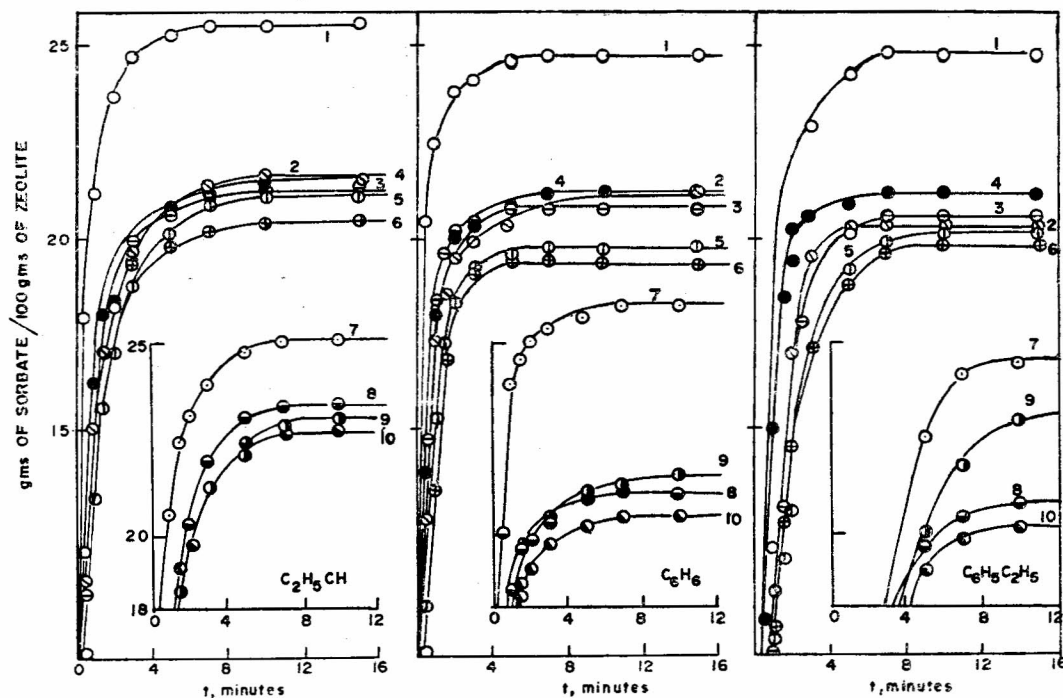


Fig. 5 — Rate of adsorption of vapours of organic solvents on zeolites. [1-NaX, 2-REHX, 3-RE(2)X, 4-RE(1)X, 5-RE(3)X, 6-RE(4)X, 7-NaY, 8-REY, 9-REH(2)Y, 10-REH(1)Y]

TABLE 1 — COMPOSITION, SURFACE AREA AND VOID VOLUMES OF ZEOLITES

Zeolite	Exchange (%)	RE <sub>2</sub> O <sub>3</sub> (%)	Unit cell composition	Surface area (m <sup>2</sup> /g)		Void volume cc/g
				Langmuir	BET	
NaX	—	—	Na <sub>85</sub> (AlO <sub>2</sub> ) <sub>85</sub> (SiO <sub>2</sub> ) <sub>107</sub>	970.6	896.6	0.37
RE(1)X	88.80	26.38	Na <sub>29.6</sub> RE <sub>21.1</sub> (AlO <sub>2</sub> ) <sub>85</sub> (SiO <sub>2</sub> ) <sub>107</sub>	844.7	783.2	0.32
RE(2)X	90.54	26.58	Na <sub>3.0</sub> RE <sub>21.2</sub> (AlO <sub>2</sub> ) <sub>85</sub> (SiO <sub>2</sub> ) <sub>107</sub>	823.1	817.4	0.31
RE(3)X	94.42	27.29	Na <sub>4.8</sub> RE <sub>21.8</sub> (AlO <sub>2</sub> ) <sub>85</sub> (SiO <sub>2</sub> ) <sub>107</sub>	820.0	780.6	0.30
RE(4)X	97.06	29.24	Na <sub>2.5</sub> RE <sub>23.4</sub> (AlO <sub>2</sub> ) <sub>85</sub> (SiO <sub>2</sub> ) <sub>107</sub>	769.5	758.0	0.29
REHX	97.31	28.36	Na <sub>2.4</sub> RE <sub>22.6</sub> (NH <sub>4</sub> ) <sub>1.04</sub> (AlO <sub>2</sub> ) <sub>85</sub> (SiO <sub>2</sub> ) <sub>107</sub>	791.3	769.0	0.30
NaY	—	—	Na <sub>55</sub> (AlO <sub>2</sub> ) <sub>61</sub> (SiO <sub>2</sub> ) <sub>131</sub>	1024.7	936.7	0.36
REY	95.89	22.12	Na <sub>2.2</sub> RE <sub>17.32</sub> (AlO <sub>2</sub> ) <sub>61</sub> (SiO <sub>2</sub> ) <sub>131</sub>	876.0	747.3	0.31
REH(1)Y	95.78	20.33	Na <sub>2.28</sub> RE <sub>15.93</sub> (NH <sub>4</sub> ) <sub>2.71</sub> (AlO <sub>2</sub> ) <sub>61</sub> (SiO <sub>2</sub> ) <sub>131</sub>	849.7	730.0	0.30
REH(2)Y	97.22	15.40	Na <sub>1.55</sub> RE <sub>12.08</sub> (NH <sub>4</sub> ) <sub>10.34</sub> (AlO <sub>2</sub> ) <sub>61</sub> (SiO <sub>2</sub> ) <sub>131</sub>	942.5	828.3	0.33

marily be attributed to the site selectivity of the exchanged ions in the zeolite lattice. For example, it has been reported<sup>9</sup> that in the higher range of exchange ( $\alpha > 60\%$ ), the rare earth ions preferentially occupy site II which are situated in the  $\alpha$  cages. The sorbed molecules interact strongly with the cations in the  $\alpha$  cages which are comparatively less screened.

**Diffusion coefficient** — The diffusion in porous zeolites is often the rate limiting process in adsorption. The inter-diffusion coefficient as defined by Barrer<sup>10</sup> is also influenced by cation exchange process. The diffusion coefficient is obtained from relation (4)

$$\frac{Q_t - Q_0}{Q_\infty - Q_0} = \frac{2A}{V} (Dt/\pi)^{\frac{1}{2}} \quad \dots (4)$$

where  $Q_t$ ,  $Q_0$  and  $Q_\infty$  are the amounts of sorbate sorbed at time  $t$ , zero and at equilibrium respectively,

TABLE 2 — DIFFUSION COEFFICIENT OF SORBATES IN ZEOLITES

Zeolite	Diffusion coefficient ( $D$ ) $\times 10^{12}$			
	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> OH	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>5</sub> .C <sub>2</sub> H <sub>5</sub>
NaX	4.52	2.46	1.73	13.59
RE(1)X	3.45	7.95	2.97	12.82
RE(2)X	3.12	7.95	5.13	16.93
RE(3)X	2.79	6.92	12.21	12.31
RE(4)X	2.79	4.51	15.90	8.98
REHX	3.02	6.40	7.95	12.31
NaY	3.02	3.08	6.92	4.62
REY	2.55	7.95	7.69	9.75
REH(2)Y	2.28	5.39	5.90	5.90
REH(1)Y	2.50	5.39	4.10	6.92

$V$  is the volume of the zeolite powder and  $A$  is the external surface area and  $D$  is the diffusion coefficient.

The external surface area of the zeolite was calculated by the method described by Barrer<sup>11</sup>. Knowing  $V$  and  $A$  the diffusion coefficients were calculated for different zeolites using the above relation. The data summarized in Table 2 indicate that, in general, the diffusion coefficient for water decreases with the increase in the exchanged of sodium ions. The values of  $D$  for the other sorbates studied do not show any significant relationship with respect to the size of the molecules or rare earth content of the zeolite. It has also been reported<sup>9</sup> that the effective diffusion coefficient for  $H_2O$  gradually decrease in A-type on replacing  $Na^+$  ions with other monovalent alkali ions ( $Na^+ \rightarrow Cs^+$ ).

From the above results it may be concluded that cavities in the voids in the zeolites are modified by the cation exchange which in turn predominantly influences their sorption characteristics.

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