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Liquid-Phase Adsorption of Olefin/Paraffin Mixtures on Ion-Exchanged X Zeolite

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Abstract

Adsorption studies of normal paraffins, monoolefins, and their mixtures on X-type zeolites are reported. Adsorption isotherms at ambient temperature for single components, viz., *n*-octane, 1-octene, and water, were measured in the vapor phase. Adsorption measurements for mixtures were carried out in the liquid phase in a specially designed cell. The various systems studied include *n*-octane/1-octene, *n*-decane/1-decene, *n*-undecane/1-undecene, *n*-dodecane/1-dodecene, and *n*-dodecane/1-tetradecene. X-type zeolites with Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, or their mixtures as compensation cations were used for the study. Separation factors calculated from the adsorption data show that olefins are preferentially adsorbed on X-type zeolites. An attempt is made to correlate the separation factors with the charge density of the compensation cations.

INTRODUCTION

Linear alkanes having carbon numbers over 10 find application in the manufacture of detergent alkylates, detergent alcohols, plasticizers, etc.

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(*1*). One of the methods for the commercial production of higher olefins is by the catalytic dehydrogenation of their corresponding paraffins (*2*), followed by the separation of the product olefins from the unconverted paraffins. Adsorptive separation has been shown (*3*) to be superior for the separation of olefins from olefin–paraffin mixtures. Studies reported (*4–6*) on the subject have generally employed faujasite-type zeolites. However, equilibrium adsorption studies on such systems are scanty and confined to molecules having lower chain lengths (*7–9*). In the present paper we report a liquid-phase adsorption study from mixtures of higher olefins and paraffins on different ion-exchanged forms of zeolite type X. An attempt has been made to correlate the separation factors with the nature of the compensation cations of the zeolite. The hydrocarbon mixtures studied include *n*-octane/1-octene, *n*-decane/1-decene, *n*-undecane/1-undecene, *n*-dodecane/1-dodecene, and *n*-dodecane/1-tetradecene.

EXPERIMENTAL

Preparation of Zeolite Samples

Zeolite NaX (SK-20), obtained from Union Carbide Corporation as a binderless crystalline powder, was used (SiO_2/Al_2O_3 ratio = 2.26). Zeolite samples with different compensating cations were obtained by ion-exchange of the sodium cations with K^+, Ca^{2+}, Sr^{2+}, and Ba^{2+}. About 80 g NaX zeolite was refluxed with a 10% aqueous solution of the salt of the cation to be exchanged with. KCl, $CaCl_2$, $Sr(NO_3)_2$, and $BaCl_2$ salts were used for K, Ca, Sr, and Ba exchange, respectively. After refluxing, the solutions were filtered and the filter cake was washed with double distilled water until the filtrate was free of the respective anions. The exchange zeolites were dried at 110°C, followed by activation at 350°C under vacuum for 3 h before their use for adsorption studies. For preparing mixed ion-exchanged zeolites (namely KBaX and KSrX), 5 wt% of each of the respective salts was used during the exchange step. The degree of ion exchange of various samples was estimated by digestion of the zeolite samples in concentrated hydrochloric acid followed by analysis of the resultant solutions with a Varian Techtron model 1200 Atomic Absorption Spectrometer. The cationic compositions various samples are given in Table 1.

TABLE 1
Unit Cell Compositions for Zeolite Samples Used[a]

$Na_{90}[X]$
$Na_{45.9}K_{44.1}[X]$
$Na_{35.5}Ca_{27.3}[X]$
$Na_{40}Sr_{25}[X]$
$Na_{33.5}Ba_{28.3}[X]$
$Na_{10.4}K_{14.9}Sr_{32.4}[X]$
$Na_{4.5}K_{18.7}Ba_{33.5}[X]$

[a] $X = [(AlO_2)_{90}(SiO_2)_{102}]$.

Vapor-Phase Adsorption by Various Zeolite Samples

Adsorption studies of hydrocarbons in the vapor phase over various zeolite samples were carried out using the gravimetric adsorption technique in a McBain balance equipped with a sensitive (30 cm/g) quartz spiral spring (Thermal Syndicate Ltd., U.K.). A cathetometer with a precision of ±0.001 cm was used for measuring the extension of the spring. Vapor pressures of the adsorbates were measured by means of a closed limb mercury manometer.

Liquid-Phase Adsorption Studies

Adsorption studies in the liquid phase were carried out in a specially designed glass cell (5 mL capacity) made from a 8-mm i.d. glass tube. The cell was closed by means of a silicone rubber septum and a screw cap which served as a sampling point. The cell could be evacuated via a narrow side arm having a high vacuum greaseless stopcock. A known quantity (~0.4 g) of the zeolite was taken in the cell and activated at 350°C for 7–8 h under vacuum. The dry weight of the sample was taken. A known quantity of the hydrocarbon mixture of known composition was added to the zeolite by means of a syringe. The cell was kept for equilibration at a constant temperature (30°C) in a water bath and stirred periodically.

The compositions of liquid mixtures were determined by Varian Gas Chromatograph model 6000 VISTA series with DS-604 data system. The analytical conditions were as follows:

Column, 25% polyphenyl ether (6 rings) on chromosorb P (60–80 mesh)
Column temperature, 150–200°C
Detector, TCD and hydrogen (60 mL/min) as a carrier gas
GC analyses were accurate within ±0.02%

Materials

The normal alkanes and alkenes used were of high purity grade procured from E. Merck and Fluka AG. 1-Tridecene, and 1-tetradecene were obtained from Gulf Oil Company. The purity of the chemical was confirmed by gas chromatographic analyses.

RESULTS

The adsorption isotherms obtained based on the equilibrium data for water, *n*-octane, and 1-octene on zeolite samples are given in Figs. 1–4. These data, which follow Type I isotherms, could be fitted into the Langmuir equation. The saturation adsorption capacities and the micropore volumes calculated from the adsorption data are given in Table 2. Table 2 also shows the number of molecules adsorbed per unit cell of the zeolites. It can be seen that the saturation adsorption values of *n*-octane and 1-octene are in the range of 1.4 to 1.9 mmol/g of zeolite. These values agree closely with the data of Herden et al. (*9*) for 1-octene and *n*-octane on NaX, BaX, and KX (1.637 to 1.893 mmol/g). The adsorption capacities for water on these samples also agree with Herden et al. (*9*).

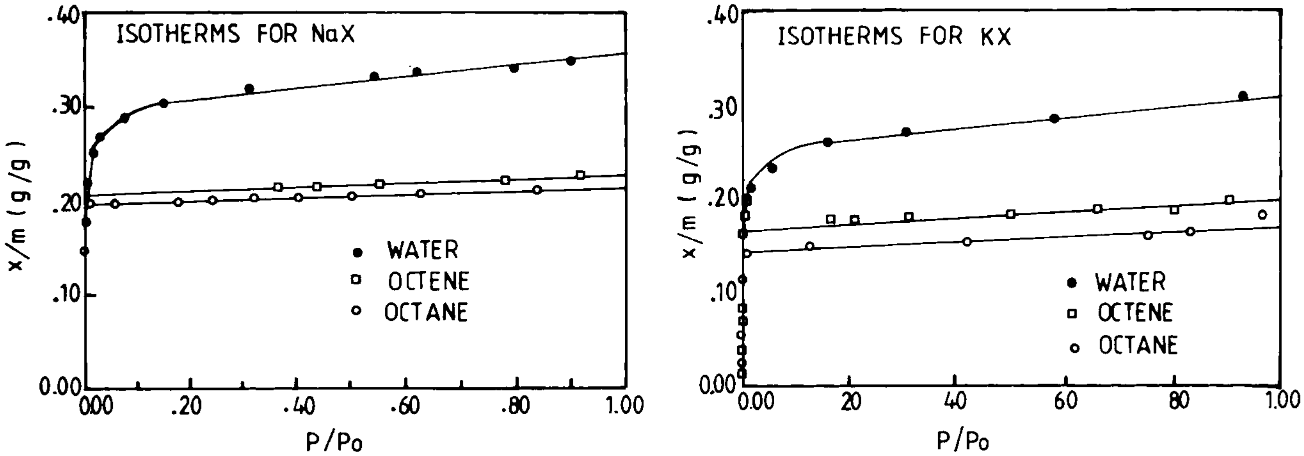

FIG. 1. Individual adsorption isotherms for *n*-octane, 1-octene, and water at 298 K on NaX and KX zeolites.

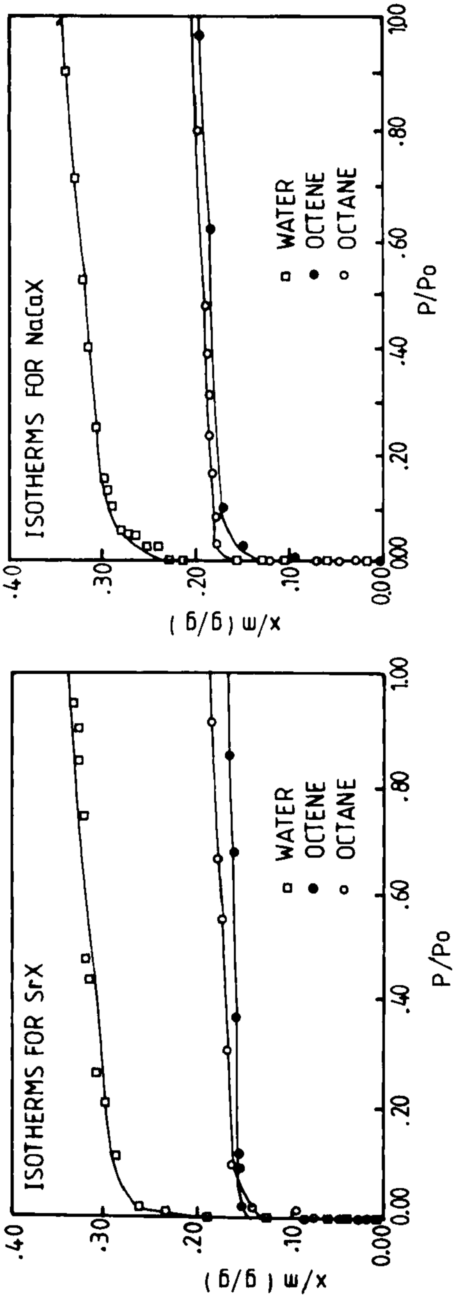

FIG. 2. Individual adsorption isotherms for *n*-octane, 1-octene, and water at 298 K on NaCaX and SrX zeolites.

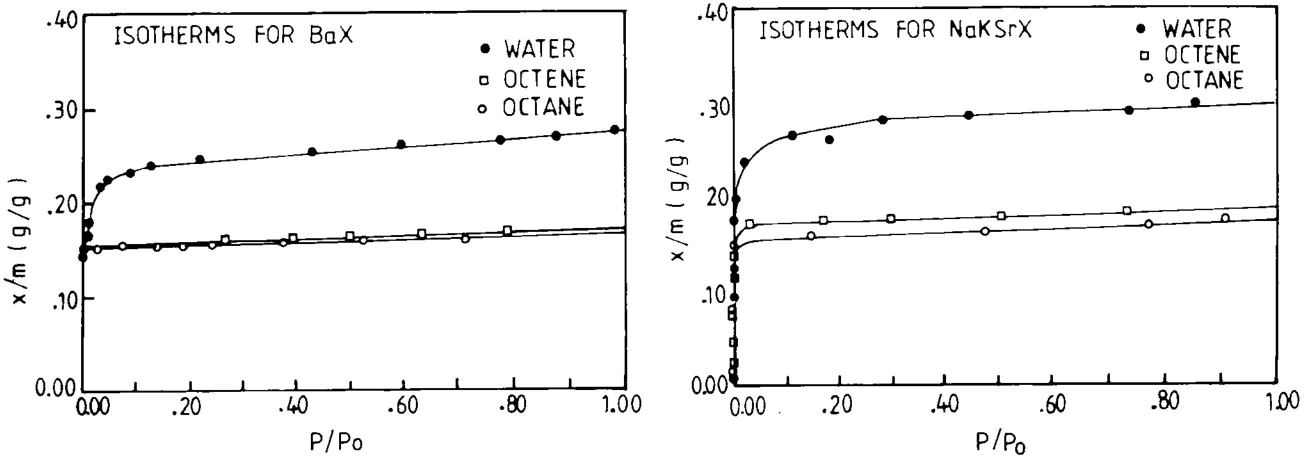

FIG. 3. Individual adsorption isotherms for *n*-octane, 1-octene, and water at 298 K on BaX and NaKSrX zeolites.

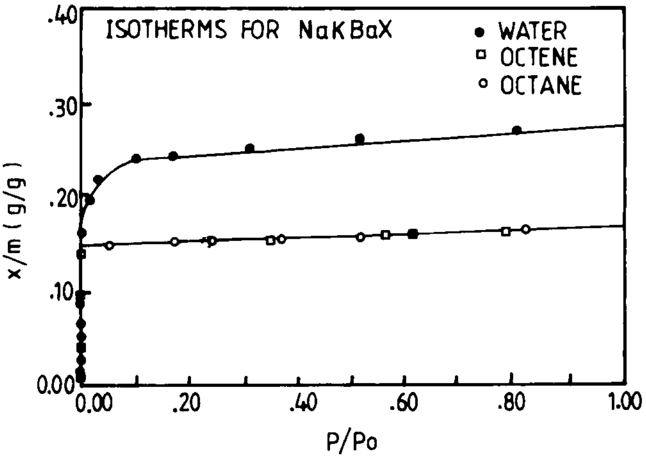

FIG. 4. Individual adsorption isotherms for *n*-octane, 1-octene, and water at 298 K on NaKBaX zeolite.

Calculation of Separation Factor (α)

Separation factors of olefins over paraffins are defined by

$$\alpha_{O/P} = \frac{\text{concentration of olefins in the adsorbed phase}}{\text{concentration of olefins in the bulk}} \times \frac{\text{concentration of paraffins in the bulk}}{\text{concentration of paraffins in the adsorbed phase}}$$

where the concentrations indicated are the equilibrium concentrations.

The amounts adsorbed were estimated from the amounts of the paraffins and olefins initially taken and the amounts present during equilibrium in the bulk phase. The latter quantities are obtained by a knowledge of the bulk composition determined by gas chromatography and the total amount of the mixture in the bulk phase before and after equilibration. The total amount of liquid present in the bulk phase at equilibrium was estimated by carrying out a separate experiment with 90:10 wt% ratio of olefin and paraffin in a mixture. It was assumed that at such a high olefin concentration the paraffin adsorbed in negligible and hence the amount of paraffin in the bulk phase remained the same even after equilibration.

TABLE 2
Equilibrium Adsorption Capacities on Different Zeolites

	Adsorbate								
	Water			*n*-Octane			1-Octene		
Zeolite	mmol/g	No. of molecules per unit cell	Pore volume (mL/g)	mmol/g	No. of molecules per unit cell	Pore volume (mL/g)	mmol/g	No. of molecules per unit cell	Pore volume (mL/g)
NaX	19.0	254.9	0.333	1.937	26.0	0.302	1.982	26.6	0.316
NaKX	16.3	229.7	0.284	1.517	21.4	0.230	1.693	23.9	0.268
NaCaX	19.2	254.8	0.336	1.788	23.7	0.280	1.723	22.9	0.272
NaSrX	18.5	266.6	0.333	1.696	24.4	0.263	1.491	21.5	0.234
NaBaX	14.8	234.6	0.274	1.482	23.5	0.234	1.491	23.7	0.232
NaKSrX	16.4	254.3	0.297	1.607	24.8	0.258	1.710	26.3	0.267
NaKBaX	14.7	244.9	0.263	1.455	24.2	0.237	1.429	23.8	0.233

From GC percentages after equilibration and the initial amount of paraffin, the total amount in the bulk phase can be calculated. The initial and final amount of olefin in the bulk phase can be used to determine the percentage adsorption per gram of the zeolite for an olefin. This adsorption capacity per gram of the zeolite can be used to calculate the amount adsorbed at other lower compositions where both paraffins and olefins are adsorbed. During these calculations, the adsorption capacity for olefins and paraffins having the same carbon number is assumed to be the same which appears to be quite reasonable, as seen for *n*-octane and 1-octene in Table 2. Detailed calculations are given elsewhere (*10*).

As far as the catalytic activity of these zeolites is concerned, no additional products were observed during GC analysis. Isomerized olefins, if any, were not seen appearing as separate peaks. Thus, even if some olefins were isomerized on these zeolites, it did not result into any error in adsorption data or separation factor values.

The adsorptions from various olefin/paraffin mixtures are given in the form of adsorbed phase–liquid phase composition diagrams (X–Y diagram), Figs. 5 and 6.

Figure 5 gives the X–Y diagram for the adsorption of 1-dodecene from its mixtures with dodecane on Na, K, Ca, Sr, Ba, and mixtures of cations forms of X zeolite. It is seen from the figure that in all the three cases the alkene is more selectively adsorbed than the paraffin. The separation factors calculated from the X–Y diagrams are also given in Table 3. The calcium-exchanged X shows the highest selectivity for dodecene.

Figure 6 gives the X–Y diagram for the adsorption of olefin/paraffin pairs of C_8, C_{11}, and C_{12} carbon chains. It is seen that the selectivity for olefins on CaX is high in all cases, and no substantial difference is noticed in the magnitude of the separation factors among C_8, C_{11}, and C_{12} pairs. In fact, as a consequence of the high affinity of bivalent ion-exchanged X zeolite at moderate equilibrium concentration of the olefins, the adsorbed phase nearly fully consists of the olefin molecules. The effect of carbon number on selectivity can be seen only at low olefin equilibrium concentrations. In the same way, the effect of cation types on selectivity can be studied at lower alkane concentrations only. The separation factors for various cation-exchanged X zeolite for C_{12} paraffin–olefin mixtures are given in Table 3. It can be seen that the selectivity values for olefins are in the order NaCaX > NaSrX > NaBaX > NaX > NaKSrX > NaKBaX > NaKX.

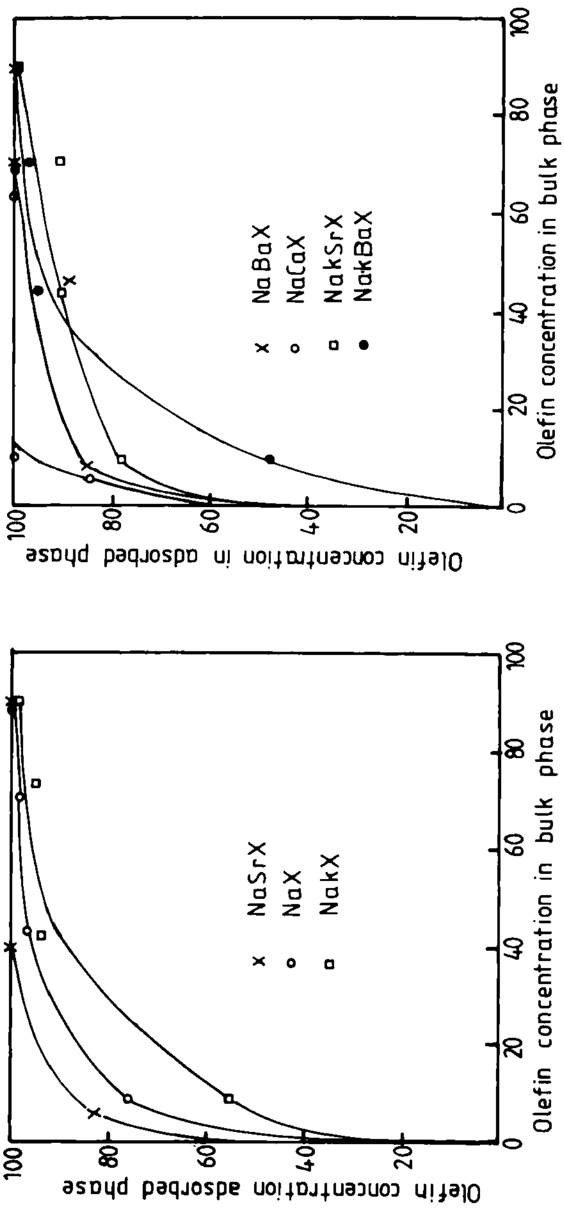

FIG. 5. Phase diagram for adsorption for dodecane/1-dodecene mixture on various zeolites.

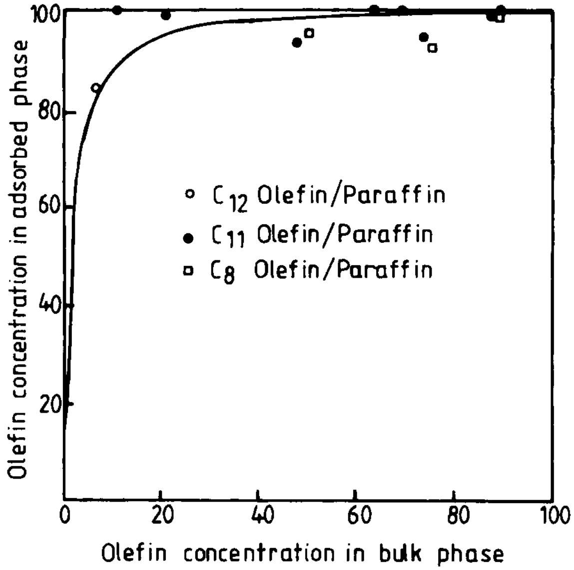

FIG. 6. Phase diagrams for adsorption from olefins/paraffin mixtures on NaCaX zeolite.

TABLE 3
Separation Factors for Various Cation-Exchanged X Zeolites for the Dodecane-1-Dodecene Mixture

Zeolite	$\alpha_{(1\text{-dodecene})/(\text{dodecane})}$
NaCaX	127
NaSrX	76
NaBaX	29
NaX	28
NaKSrX	20
NaKBaX	16
NaKX	10

DISCUSSION

The values of the vapor-phase equilibrium adsorption capacities of various zeolites for water, *n*-octane, and 1-octene shown in Table 2 lead to the following observations:

(a) The pore volume occupied by water molecules is significantly higher than those of *n*-octane and 1-octene.
(b) The number of molecules of octane and octene adsorbed are quite comparable.
(c) The ion-exchanged zeolites containing barium ions showed significantly reduced adsorption capacities.

The adsorption of vapors in zeolite cavities can be described as a pore filling by the adsorbate molecules. Hence the saturation adsorption capacities of zeolites are limited by adsorbate size and shape and the available intrazeolite space. The large number of water molecules adsorbed in the present case compared to the hydrocarbon molecule is the result of its smaller size and closer packing of water molecules. The aluminosilicate network of zeolite X consists of a large cavity (Fig. 7), called the α cage, entered by an aperture of free diameter 7.4 Å and

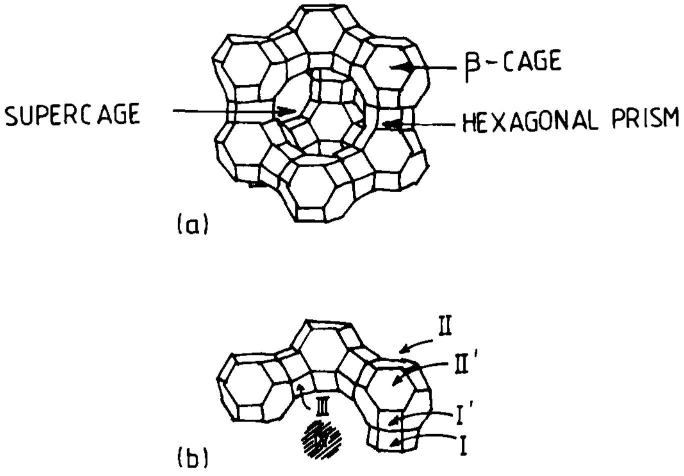

FIG. 7. Framework structure of zeolite X (a). Cation positions in the Na form of zeolite X as indicated by reference to part of the zeolite X framework (b).

sodalite cages (β cages) with apertures of 2.2 Å (*11*). The water molecules have access to both cages, while the hydrocarbon molecules can enter only the α cages by virtue of their larger critical diameter (4.9 Å). Consequently, the pore space available for water molecules is greater than that for hydrocarbon molecules. For molecules of comparable size, e.g., octane and octene, the adsorption capacities are also of similar magnitude, as seen from Table 2.

During adsorption from mixtures, the cations, i.e., the type and their distribution, play a major role in deciding the selectivity of a particular component. In Type X zeolites the accessible cations are located at Sites II and III (Table 4). Herden et al. (*8*, *9*) have shown that equilibrium adsorption of hexane/hexene and octane/octene mixtures depend on the nature of the cations present. The olefins on divalent cation-exchanged zeolite have also shown higher heats of immersion values. Barrer (*12*) observed that as a consequence of the interaction of π electrons of C=C bond with the electrostatic field gradient around the cations, the heat of adsorption of ethylene is higher than that of ethane on the NaX zeolite. This higher heat of adsorption (about 3 kcal/mol) results into a preferential adsorption of the olefins over paraffins. Such an interaction is dependent on the number of cations and the cationic charge density. In the present case a

TABLE 4
Distribution of Cations at Different Sites in Zeolite X Structure

Position	Site	No. of sites/ unit cell	Na^+	K^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
Center of hexagonal prism	I	16	4	9.2	13.3	11.2	7.3
In sodalite cage, adjacent to hexagonal prism	I′	32	32	13.6	5.0	7.0	5.0
In super cage, adjacent to the six ring outside of sodalite cage	II	32	32	25.6	25	19.5	11.3
In sodalite cage, adjacent to the single six ring	II′	32	—	—	6.0	4.2	—
In super cage, neighborhood of the four ring	III IV	48 16	4 —	— —	— —	— —	— —

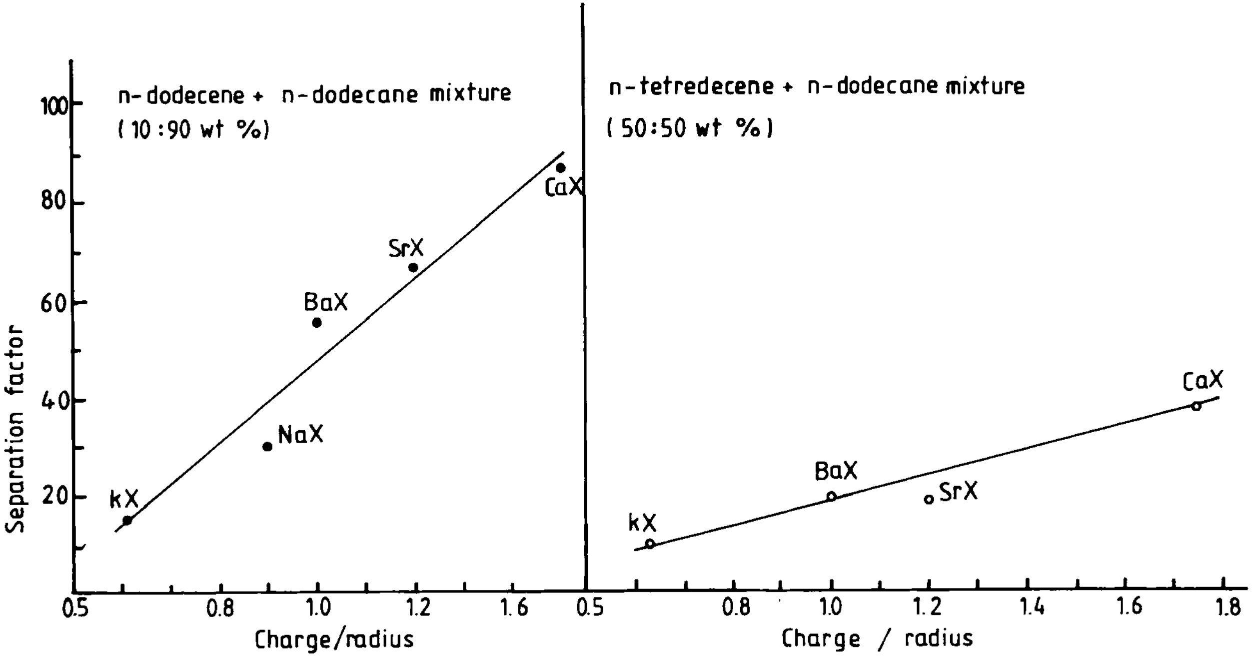

FIG. 8. Correlation of separation factors with the charge/radius ratio of compensation cations.

correlation between the separation factor and the charge/ion radius ratio (*e*/*r*) has been observed. In Fig. 8 the separation factor α for 1-dodecene from its mixtures with *n*-dodecane has been plotted against *e*/*r* for various cations used in the ion-exchanged zeolites. A similar dependence of separation factors on cations was observed by Herden et al. (*7*) for tetradecene/dodecane mixtures.

In Fig. 6 the effect of carbon chain length on selectivity is shown. It is interesting to note that for the pairs of olefins/paraffins, the selectivity did not drastically depend on the carbon numbers. The reasons for this observation may be that the difference in the heat of adsorption between an olefin and a paraffin arising out of the double bond may not depend on the carbon number of the hydrocarbons. As the difference in the heat of adsorption was shown to have an exponential relationship with the separation factor (*13*), we may also expect a similarity among the selectivities of different olefin/paraffin pairs.

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