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REVIEW

Separation of Closely Related Systems by Molecular Sieve Zeolites

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Abstract

Molecular sieve zeolites are robust, thermally stable selective absorbents. They are chemically pure crystalline aluminosilicates with up to 50% of their crystal volume available for adsorption. Zeolites are widely used for industrial drying, purification, and separation, as well as catalysts and ion exchangers. They can be synthesized, on a plant scale, from silica (or sodium silicate) and sodium aluminate. The product is a powder which is pellitized and "activated" before use. Their structures are regular arrangements of channels and cavities entered through "windows" of molecular dimensions which aid their molecular sieving action. Further control of the property comes from their cation content, temperature, and, in some cases, by the preabsorption of small polar molecules. Industrial separations commonly achieved on zeolites include: (1) *n*-paraffins from isoparaffins, aromatics, and naphthenes (e.g., to produce high octane petrol); (2) *p*-xylene from other xylene isomers and ethyl benzenes; and (3) cryogenic separation of permanent gases. Zeolites are also useful for a wide range of analytical separations by gas–solid chromatography and more recently they have been used as high-pressure chromatographic media. Some naturally occurring zeolite minerals may find a future use as selective adsorbents.

INTRODUCTION

The term "molecular sieve" is commonly appended to materials such as carbon, cellulosic, and silica gels, but the term was first used in 1932 by McBain (*1*) to describe the selective sorption properties of the natural zeolite mineral chabazite. This early work was expanded by

Barrer who, in 1945, published the first definitive work (*2*) on the separation of gaseous mixtures by dehydrated chabazite.

From that data zeolites increasingly have been recognized as a class of materials whose industrial use is unrivaled by any other group of compounds. In the recent authoritative text on zeolites by Breck (*3*), he estimates that from 1948 to 1972 over 7000 papers and 2000 U.S. patents were published dealing with zeolite science and technology. This intense interest still continues.

There are about 40 natural zeolite minerals but there are few commercially workable deposits, and the bulk of published work refers to synthetic zeolites, not all with natural counterparts, which can be relatively easily prepared on a laboratory or plant scale. These synthetic zeolites are available in a highly pure form, and it is these materials which are widely used to separate gas and liquid mixtures, as drying agents, and as catalysts.

ZEOLITE STRUCTURES

General

Zeolites are highly crystalline aluminosilicates with framework structures in which $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra are assembled to give porous three-dimensional arrays which early investigators aptly described as "sponge-like." The frameworks enclose highly regular networks of interconnected channels and cavities which contain mobile water molecules and cations. A detailed survey of known zeolite structures is given by Breck (*3*).

The "activation" of the structure, by removal of water, usually creates a stable lattice into which molecules can permeate subject to restrictions on their entry caused by the individual zeolite structure (and the cations they contain). It is these restrictions which give rise to molecular sieving as the dimensions of the entrance to the cavities and channels within zeolite structures are of the same order of magnitude as the "kinetic diameter" of many organic and inorganic gas molecules. A bonus is the high voidage available in activated sieves (Table 1).

Molecular Sieve Zeolite A

In zeolite A the structure consists of small cages (cavities) linked to create a series of larger cages (Fig. 1). Entry to the small cage is through

TABLE 1

Comparison of Molecular Sieves

Sorbent	Pore dimension molecular size range (Å)	Pore volume (cm^3/g)
Coal	4–5	0.07–010
Glass	3–10	0.01–0.04
Silica gel	4–10	0.09–0.35
Carbon (Saran type)	4.5–5.7	∼0.4
Zeolites	Free aperture(s) of main channel	Pore volume (cm^3/g)
Chabazite	3.7 × 4.2	0.47
Zeolite A	4.2	0.47
Zeolite X	7.4	0.50
Mordenite	6.7 × 7.0 2.9 × 5.7	0.28

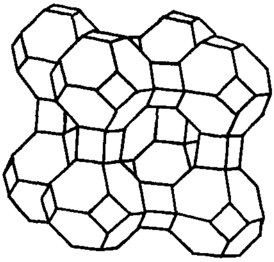

Fig. 1. Structure of zeolite A. The oxygen windows are represented by straight lines joining Si/Al atoms.

a hexagonal window, bounded by six oxygen atoms, giving a restricting dimension of 2.2 Å (Angstrom units will be used, rather than pm, to correspond to the commercial practice in describing sieving action.), and to the large cage through an octagonal oxygen window diameter 4.3 Å. Each unit cell ideally contains 12 sodium ions and 27 water molecules. Zeolite A has no known natural counterpart.

Molecular Sieve Zeolite X

Zeolite X (Fig. 2) resembles A but the smaller cages are linked to each other via one-half of the hexagonal windows to give a large cavity bounded

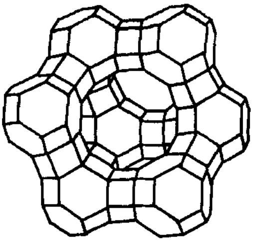

FIG. 2. Structure of zeolite X.

by a 12-oxygen window of crystallographic diameter 7.4 Å. Zeolite X is isomorphous with the naturally occurring faujasite which differs in cation composition and has a different Si/Al ratio in its framework. Another isomorph is the synthetic zeolite Y.

Other Useful Zeolites

Chabazite can be synthesized on plant scale and its structure (Fig. 3) is based on "double hexagonal rings" i.e., two hexagonal arrangements of [Si/AlO$_4$] tetrahedra linked together. These provide the basis for a framework enclosing larger cavities with octagonal windows. Synthetic chabazite is marketed as AW 500 (Linde) and Zeolon 500 (Norton).

Synthetic mordenite has a structure which is an arrangement of chains of tetrahedra, linked to give 5-membered oxygen windows, which are then arranged to provide a two-dimensional channel system (see Table 1). It is marketed as AW 300 (Linde) and Zeolon 900 (Norton).

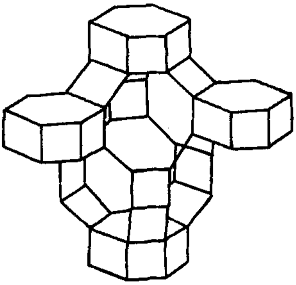

FIG. 3. Structure of chabazite.

SYNTHESES

Zeolites can be produced from an aluminate gel into which a source of silica has been introduced. Normally the cation present is sodium but many synthetic zeolites are known in which other alkali and alkaline earth metals are used to produce different zeolites, and a series can also be prepared in the presence of a quaternary ammonium cation (see Ref. *3*, Chap. 4). The source of silica can be glass, aerated silica, colloidal silica, or a sodium silicate. An industrial preparation can be low temperature (e.g., 90°C for A and X) or high temperature (~300°C for mordenite) with crystallization times of 2 to 30 hr. The final product is a power, with crystallites of 1 to 5 μm, and is pelletized for plant and laboratory use. The size of the aggregate produced can be tailored to prospective use, e.g., small cylinders (1 × 5 mm) for laboratory use and spheres (to $\frac{1}{4}''$ diameter) for plant use. The binder is usually a clay mineral of the kaolin type.

FACTORS CONTROLLING MOLECULAR SIEVE PROPERTIES

The number of oxygen atoms forming a zeolite aperture is an obvious indication of the molecular size capable of entering the internal structure, as is the shape of the aperture (e.g., the 8-ring in A is planar but that in chabazite is puckered). Crystallographic dimensions change with dehydration which can be due to framework distortion or to relocation of cations.

Further selectivity can be achieved by ion exchange, i.e., the introduction of a larger cation to partially block windows or a more subtle effect relying on a cation resiting to restrict bulk access to part of the zeolite channels. In zeolite A the replacement of Na^+ by 25% K^+ causes a sharp reduction in effective window size whereas the replacement of Na^+ by by Ca^{2+} gives an equally sharp increase at 34% exchange (Fig. 4).

These effective pore sizes are reflected in the commercial names for the K, Na, and Ca exchanged forms of A, viz., 3A, 4A, and 5A (A originally ≡ Angstrom). Chabazite behaves in a similar way but the exact mechanism of these sieving actions is not fully understood.

Effective window size can be controlled by temperature, a 200°C change causing a variation in amplitude of vibration of the encircling atoms of about 0.2 Å, but, probably more significant, selectivity can be a function of the temperature-dependent activated diffusion of molecules. This has formed the basis for a commercial separation of permanent and inert gases at cryogenic temperatures (*4*).

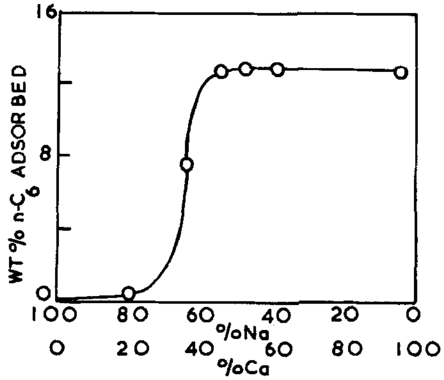

FIG. 4. Effect of ion exchange ($Na^+ \rightleftharpoons \frac{1}{2}Ca^{2+}$) on the absorption of *n*-hexane by A.

Other controls of effective pore size can be by partially blocking the channels by the presorption of small polar molecules (e.g., H_2O) in, say, chabazite or mordenite, or by creating a stable inorganic complex in a wider pored zeolite (e.g., the Cu-pyridine complex in X). Pore closures in A can be obtained by steaming at 550°C, and this is sufficient to exclude refrigerant gases so that A can be used for refrigerant drying.

To conclude this brief survey, it must be stressed that all molecular sieve separations are judged by "effective pore size" (*5*) which will be larger than the measured crystallographic dimensions (for dehydrated zeolites). This is a practical concept taking into account the foregoing factors as well as expressing effects arising from polarizability and steric hindrance differences between similar molecules.

Table 2 presents some molecular sieve possibilities.

USES OF MOLECULAR SIEVES FOR SEPARATION, ANALYSIS, ETC.

Breck (*6*) lists 165 adsorption processes of which 112 are commercial applications. Most of these are concerned with drying and catalysis, and are outside the scope of this article. The list is not complete and many hundreds of separations are reported in the literature. The remainder of this account will be concerned with the uses of zeolites to separate closely related systems. They can be conveniently cataloged under three headings:

1. Gas chromatographic analyses
2. Other analyses and separations of an analytical nature
3. Plant scale separations

Use of Zeolites in Gas Chromatographic Analyses

Hydrocarbon Separations. Examples of the general analytical use of zeolite columns for the separation of C_1–C_8 hydrocarbons are summarized in Table 3.

In these analyses both binderless zeolite and sieved fractions from ground pelletized zeolites were used. Helium was the most common carrier gas but air and hydrogen were often used. Columns were about 4 mm × 2 m, and some form of preactivation was always used. Flow rates were about 40 cm^3/min and temperature programs to 300°C were used. Most authors treated the zeolite with sodium hydroxide solution before use. This was to neutralize the surface which tends to acquire protons due to excess washing. Protonated sieves are powerful catalysts, and the general catalytic activity of zeolites restricts their gas-chromatographic use. More recent work has been concerned with new zeolites (*11*) (e.g., L) and the attainment of better separations by using ion-exchanged forms of X and Y (*8*, *9*, *12*, *13*) (Fig. 5).

Several authors have devised methods for the determination of hydrocarbons in crude oil fractions involving a presorption onto molecular sieve. Eggertsen and Groennings (*20*) used a 5A column at 190°C to retain *n*-paraffins from platformates. The sieve was cooled and then rapidly

TABLE 2

Some Selective Sorbtions on Zeolite A

Sorbed on 4A and 5A	Sorbed on 5A but not 4A	Not sorbed by A
Ethane, methane	Propane and higher *n*-paraffins	Isobutane and *all* isoparaffins
Ethylene, acetylene, propylene	Butene and higher olefins	
Methanol, ethanol	*n*-butanol and higher *n*-alcohols	Isopropyl alcohol all iso, *sec*, and *tert* alcohols
Water, CO_2, H_2S, SO_2, N_2, O_2	Cyclopropane, Freon 12	Benzene and all aromatics cyclohexane, Freon 11 and 114

TABLE 3

Examples of the General Use of Zeolites in the Separation and Analysis of C_1–C_8 Hydrocarbons by Gas Chromatography

Hydrocarbons analyzed	Other gases present	Zeolite	Experimental comments	Refs.
C_1–C_3 (*n*-paraffins)	O_2, N_2	5A, 10X(CaX), 13X	Presorption of H_2O	*7*
C_1–C_4 (olefins and paraffins)	CO, H_2	X(Ba, Ca), 13X	Catalytic decomposition of propylene noted	*8*
C_1–C_4	CO, H_2	LiX		*9*
C_1–C_4	CO	BaY	Presorption of H_2O	*10*
Unsaturated hydrocarbons	Polar compounds	AgL	Good separation at 200–300 °C	*11*
C_1–C_4	CO	Y	Mg, Cd, Sr, and Ba exchanged forms	*12*
C_1–C_4	CO, H_2	X	Na, Li, K, Rb, and Cs exchanged forms	*13*

reheated to 400 °C, and the *n*-paraffins released were trapped in a silicone oil GLC column at −30 °C. They were then eluted and detected in the normal way. Analyses of C_5–C_{13} was achieved in 90 min. A similar method was used by Chen and Lucki (*21*) for *n*-paraffins in gas oils and by Soulages and Brieva (*22*) for paraffin and naphthene contents of saturated hydrocarbon distillates. The latter uses 13X (CaX) in a porous layer open tubular column (PLOT), and this technique gave analyses times as low as 12 min for some components. Another variation has been to use a mixed 13X, chromosorb column for a similar purpose (*23*) (Fig. 6).

Mordenite has been used to preseparate alkane mixtures derived from oil shales prior to GLC analyses (*24*).

Other Separations. These are summarized in Table 4.

Use of Zeolites for Other Separations of an Analytical Nature

This is principally used to carry out special separations on a laboratory scale for analyses and/or separation. Examples are listed in Table 5.

No special techniques are used beyond activation; a variety of larger columns were used for gram scale separation/purifications.

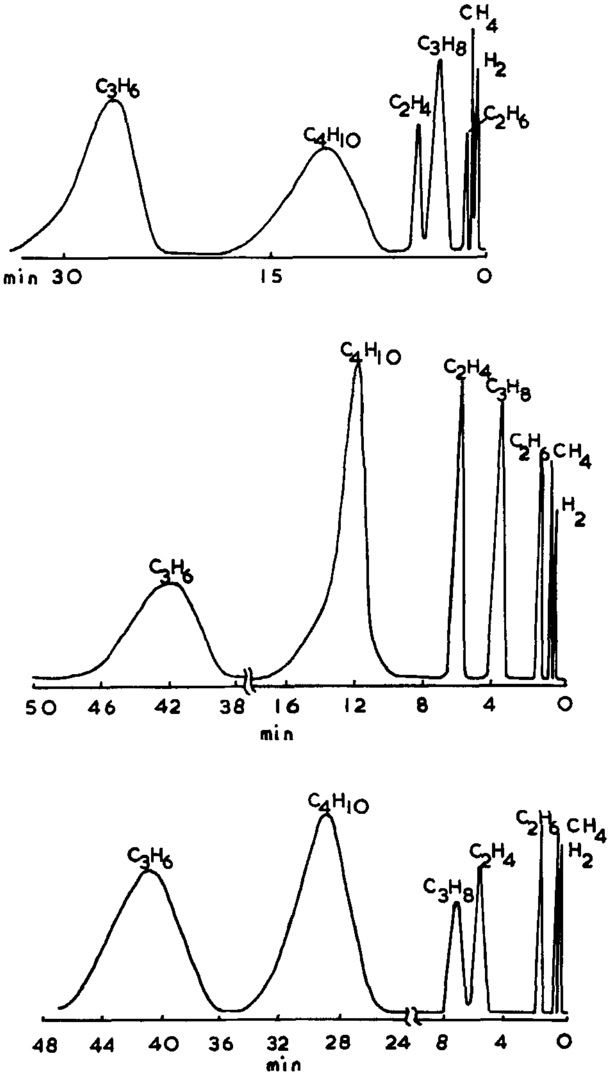

FIG. 5. Effect of cation exchange on gas chromatographic properties (from Ref. *12*). Top: Chromatogram of gas mixture on NaCaX; column temperature, 200°C; flow rate, 100 ml/min. Middle: Chromatogram of gas mixture on NaSrX; column temperature, 200°C; flow rate, 100 ml/min. Bottom: Chromatogram of gas mixture on NaBaX; column temperature, 180°C; flow rate, 100 ml/min.

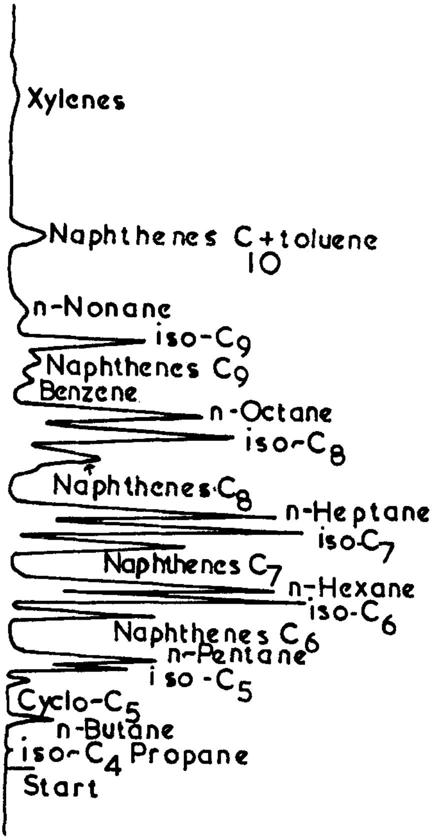

FIG. 6. Gas chromatogram of Occidental virgin naphtha (from Ref. *23*).

TABLE 4

Other Analytical Separations Using Zeolites for Gas Chromatography

Analysis	Zeolite used	Comments	Refs.
Aromatics/ aliphatics	CaA	He carrier at 195–280°C	*14*
CH_4, H_2O, CO	CaA	N_2 carrier at 102°C double column (2 × 2 m)	*15*
Ar, O_2, N_2	L		*16*
O_2, N_2, CO, N_2O, CO_2	Me_4N form of X, Y, and mordenite	He carrier at 66°C	*17*
Butylene isomers	CsY		*18*
Butene isomers	KX		*19*

TABLE 5

Specialized Separations/Analyses on Zeolites

Mixtures	Zeolite	Comments	Refs.
Toluene, *m*-xylene, isopropyl alcohol with *t*-butyl alcohol, acetone, ethyl acetate impurities	A, X	Purification for use in semiconductor preparation	*25*
n-Paraffins	NaA		*26*
m-, *p*-Xylenes in isooctane	NaKBaX	See later	*27*
S compounds in *n*-heptane and propylene	13X	Column chromatography	*28*
Propylene from propane	NaX	99.4 → 99.9% pure C_3H_6	*29*
Heptane/dodecane	NaA, MgA		*30*
Thiols and sulfides in liquid hydrocarbons	13X	Recovery of S	*31*
Monoolein/triolein	10X	2 × 20 g columns (40 g zeolite)	*32*
Toluene/isooctane/*n*-heptane	13X		*33*
2-, 3-, 4-Methylpyridine/2,6-lutidine	X		*34*
n-Tetradecane/isooctane	5A	*n*-Paraffin recovery for detergents and plasticizers (column 2″ × 8′)	*35*
tris/bis-Difluoroamino methanes	4A, 5A, 13X		*36*
Silanes	KZnA	Semiconductor applications	*37*
n-Tetradecane/benzene	5A	12 ml/min, column 4 cm × 1.34 m → 99.9% benzene	*38*
n-Heptane/methyl cyclohexane	5A		*38*

Use of Zeolites on Plant Scale to Separate Similar Molecules (*39, 40*)

These are somewhat outside the brief of this article, but a short survey of the applications will add balance to that part of the title referring to "closely related systems."

The major commercial "molsiv" processes are:

1. *n*-Paraffin separation to provide feedstock for the production of biodegradeable detergents, jet fuels, linear alcohols, fatty acids, synthetic protein, and lube-oil additives (Fig. 7). The 5A sieve is used to sorb *n*-paraffins from the iso-fraction and aromatics stream component, and subsequently desorbed by displacement (using light hydrocarbons) or by pressure swing techniques. The major processes are UOP Molex, UCC Isosiv, Texaco process, and VEB Leuna Werke Parax.
2. *p*-Xylene separation for terylene intermediates. This uses NaKBaX as the basis of the UOP Parex process. Other similar separations recently have been reported by UOP (*41*) and are summarized in Table 6.
3. Olefin separations. Examples of this are the UOP Olex process (olefins from olefin/paraffin mixtures) and the UCC Olenfinsiv process (*n*-butylene from isobutylene), both based on A sieves.

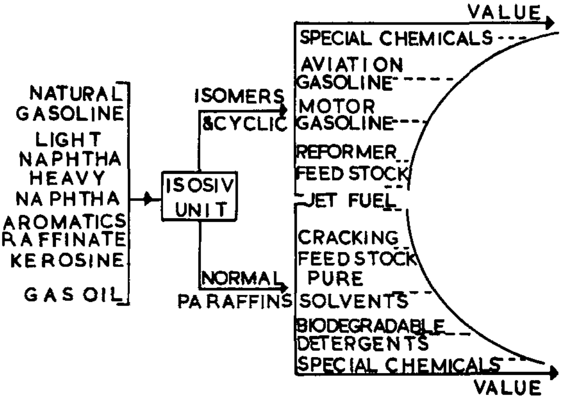

FIG. 7. Possible uses of the Isosiv process (from Ref. *38*).

TABLE 6

Large-Scale Application of Zeolite Adsorbents in Sorbex Processing

Adsorbent no.	Component A/Component B	β^a
1	*p*-Xylene/ethylbenzene	1.6
	p-Xylene/*o*-xylene	3.8
	p-Xylene/*m*-xylene	4.0
2	*p*-Xylene/ethylbenzene	2.1
	p-Xylene/*o*-xylene	2.2
	p-Xylene/*m*-xylene	2.7
3	*p*-Xylene/ethylbenzene	2.2
	o-Xylene/ethylbenzene	2.9
	m-Xylene/ethylbenzene	3.4
4	*p*-Cymene/*o*-cymene	2.0
	p-Cymene/*m*-cymene	3.1
5	*p*-Diethylbenzene/ *m*-diethylbenzene	2.5
6	*p*-Diisopropylbenzene/ *m*-diisopropylbenzene	4.9
7	Butene-1/isobutene	2.2
	Butene-1/*cis*-butene-2	3.1
	Butene-1/*trans*-butene-2	3.5
8	Olefins/aromatics	<0.1
	Olefins/paraffins	10
9	*n*-Paraffins/isoparaffins	>1000
10	*p*-Cresol/*o*-cresol	1.8
	p-Cresol/*m*-cresol	2.0
	p-Cresol/xylenols	>5
11	β-Pinene/α-pinene	2.6
12	Fructose/glucose	7.0
	Fructose/polysaccharides	>50
13	Glucose/fructose	1.7
	Glucose/polysaccharides	>50

[a] β = separation factor of Component A/Component B.

CONCLUSION

The growth of molecular sieve applications seems likely to continue. Eastern block technology uses further separations on an industrial scale (e.g., cyclohexane/benzene to give 99.999% purity) (*42*). More selective analytical uses from new synthetic sieves can be expected and their wider use in other chromatographic techniques is possible.

The investigation of their selective sorbent properties in high-pressure liquid chromatography seems promising (*43*) (Figs. 8 and 9) and their use in TLC (*44*) is possible. These uses are not so limited, as catalysis by the zeolite is less likely to occur under the prevailing experimental conditions.

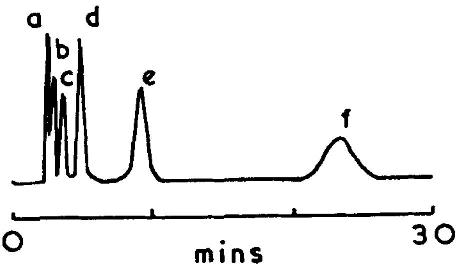

FIG. 8. HPLC separation of alcohols on Pellisieve 8AH (Zeolon 100) (from Ref. *43*): (a) *n*-amyl alcohol, (b) *n*-butyl alcohol, (c) *tert*-butyl alcohol, (d) isopropyl alcohol, (e) ethyl alcohol, and (f) methyl alcohol.

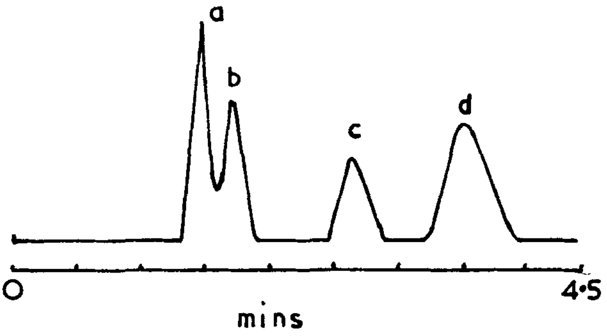

FIG. 9. HPLC separation of polar compounds on diethanolamine modified Pellisieve 8A (Linde 10X) (from Ref. *43*): (a) acetophenone, (b) aniline, (c) benzyl alcohol, and (d) phenol.

Finally, clinoptilolite may be the first natural zeolite to be of commercial value as a molecular sieve because large, relatively pure deposits are now being worked in Japan and the United States.

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