Accelerating Diffusion with Mixed Solvents

The experiments reported here show how diffusion rates in liquids can be increased by as much as an order of magnitude by use of coupled diffusion fluxes in mixed solvents. Solutes whose diffusion can be accelerated in this way include simple electrolytes, essential oils, dyes, and antibiotics. These increases are primarily caused by thermodynamic interactions and can be estimated from solubilities.

E. L. CUSSLER
and M. M. BREUER
Unilever Research
Isleworth, Middlesex, England

SCOPE

This study aims at sharply increasing diffusion rates in liquids by means of coupled diffusion fluxes. Such increases are important because diffusion in liquids is slow and is often the rate-limiting step of an industrial process. Coupled diffusion fluxes occur when the flux of a solute is altered by the concentration gradient of a second solute. For example, the flux of sodium acetate in aqueous solution can be increased nine times by a gradient of acetone.

The feature of this work which distinguishes it from past studies is the large magnitude of the coupled diffusion effects observed. These effects are well understood: most of the theoretical work is over ten years old (*1*, *2*) and the experimental observations go back at least to 1892 (3). But past physical chemical studies have concentrated on the accurate experimental verification of the Onsager reciprocal relations and hence required an emphasis on experimental detail (*4*). Strongly coupled diffusion fluxes are observed in biological systems, but the interpretation of experimental results in these cases is hindered by the inexact knowledge of the chemical composition of the systems used (*5*). Engineering studies of coupled diffusion have focused on estimation methods which can avoid the tedious experiments characteristic of exact analysis (*6-7*). In contrast, this work is not interested in accurately studying small effects but aims at approximately predicting and experimentally discovering greatly accelerated diffusion rates.

CONCLUSIONS AND SIGNIFICANCE

There are three conclusions from these experiments:

1. The diffusion of simple electrolytes can be accelerated by an order of magnitude by means of coupled fluxes in mixed solvents.
2. These increased diffusion rates are primarily caused by thermodynamic interactions and can be estimated from solubilities.
3. The diffusion of dyes, antibiotics, and essential oils can also be accelerated several hundred percent, but the increases are generally less than those observed for simple electrolytes.

While the experiments reported here all involve increases in diffusion rates, parallel experiments could also achieve decreases in these rates.

The accelerated diffusion rates reported here offer a means by which the rate of almost any mass transfer process can be increased. In practice, these increases will be useful if the industrial situation fulfills three requirements:

1. the process is diffusion limited;
2. it involves small amounts of valuable materials; and
3. it is restricted to short process times.

Such processes occur most commonly in the photographic, pharmaceutical, and toiletry industries.

THEORY

Before discussing our experimental results, we develop a guide for choosing systems in which the diffusion will be accelerated. The diffusion of a solute in a mixed solvent is most easily described by use of ternary flux equations of the form suggested by Onsager (*8*):

$$-j_1 = D_{11}\,\nabla c_1 + D_{12}\,\nabla c_2 \tag{1}$$

For most chemical systems

$$|D_{11}\,\nabla c_1| >> |D_{12}\,\nabla c_2| \tag{2}$$

In other words, the flux of 1 is primarily governed by its own gradient. However, we are interested in cases where

$$|D_{11}\,\nabla c_1| \leq |D_{12}\,\nabla c_2|, \tag{3}$$

that is, in cases where the flux of 1 is controlled not by its own gradient but is strongly affected by that of the solvent 2.

There are three causes for nonzero values of D_{12}: reference velocity changes, mobility differences, and thermodynamic interactions. While reference velocity changes can cause D_{12} to be positive or negative, they do not have a large effect (*1*, *4*). Similarly, the effect on D_{12} of differences in mobility is found not to be large except in systems containing high polymers (*9*). We believe that the key factor governing D_{12} is thermodynamic.

To test this belief, we assume that the flux of each solute present is given by

$$-j_i = \frac{Dc_i}{RT}\,\nabla\mu_i \tag{4}$$

E. L. Cussler is with the Department of Chemical Engineering, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213.

where D is a diffusion coefficient taken as equal for all solutes. This assumed equality of D quantifies our belief that mobility differences rarely contribute significantly to D_{12}. Equation (4) also implicitly assumes that changes in reference velocity also have little effect on D_{12}. Strictly speaking, $\nabla\mu_i$ should be replaced by a more general chemical force, a weighted sum of chemical potential gradients leading to a bewildering phalanx of conventions related to reference velocity (*1, 4*). These are ignored.

If we rewrite Equation (4) in the form of Equation (1) we see that

$$D_{ij} = \frac{Dc_i}{RT}\left(\frac{\partial\mu_i}{\partial c_j}\right)_{c_{k\neq j,3}} \tag{5}$$

The main term diffusion coefficients ($i = j$) now behave in a fashion similar to that suggested by the Nernst-Hartley equation, and the cross term diffusion coefficients ($i \neq j$) depend on removing some of species 2 and replacing it with solvent 3.

We now estimate the chemical potential derivatives in Equation (5). We are particularly interested in cases where 1 is an expensive valuable species and is present in small concentration only, since this is probably the case of industrial importance. Since c_1 is small, species 1 behaves ideally, so that

$$D_{11} = \frac{Dc_1}{RT}\left(\frac{\partial\mu_1}{\partial c_1}\right)_{c_2} = D \tag{6}$$

The derivative in the cross term diffusion coefficient is approximated by a difference:

$$D_{12} = \frac{Dc_1}{RT}\left(\frac{\partial\mu_1}{\partial c_2}\right)_{c_1} \doteq \frac{Dc_1}{RT}\left(\frac{\mu_1{}^0(2) - \mu_1{}^0(3)}{c_2{}^0 - 0}\right) \tag{7}$$

where $\mu_1{}^0(j)$ indicates the partial molar Gibbs free energy of species 1 at infinite dilution in solvent j, that is, in the standard state. The magnitude of this difference can be estimated from the solubility, since at saturation

$$\mu_1{}^0(j) + RT \ln c_1{}^S(j) = \mu_1{}^0 \text{ (pure 1)} \tag{8}$$

where $c_1{}^S(j)$ is the concentration of 1 in j at saturation. Thus

$$D_{12} \doteq \frac{Dc_1}{c_2{}^0} \ln\left[\frac{c_1{}^S(3)}{c_1{}^S(2)}\right] \tag{9}$$

The cross term diffusion coefficient can be large if 1 shows very different solubilities in 2 and 3.

Application to the Diaphragm Cell

The flux equations with their estimated parameters must now be applied to the specific experimental geometry to be used in these experiments, which is that of the diaphragm cell. We first assume that the ternary diffusion coefficients D_{ij} are not functions of concentration. Equation (1) may then be solved to give (*10-11*)

$$\Delta c_1 = \frac{(D_{11} - \sigma_2)\,\Delta c_{10} + D_{12}\,\Delta c_{20}}{\sigma_1 - \sigma_2}\, e^{-\sigma_1\beta t} + \frac{(D_{11} - \sigma_1)\,\Delta c_{10} + D_{12}\,\Delta c_{20}}{\sigma_2 - \sigma_1}\, e^{-\sigma_2\beta t} \tag{10}$$

where the eigenvalues σ_i are

$$\sigma_{\frac{1}{2}} = \frac{1}{2}\left[D_{11} + D_{22} \pm \sqrt{(D_{11} - D_{22})^2 + 4\,D_{12}\,D_{21}}\right] \tag{11}$$

But when species 1 is present at very small concentration, we know that D_{12} becomes small so that

$$D_{11}\,D_{22} >> |D_{12}\,D_{21}| \tag{12}$$

so that $D_{11} \doteq \sigma_1$ and $D_{22} \doteq \sigma_2$. Expanding the exponentials in Equation (10) and neglect all but the linear terms, we obtain

$$\begin{aligned}\frac{\Delta c_1}{\Delta c_{10}} &= 1 - \left[D_{11} + D_{12}\frac{\Delta c_{20}}{\Delta c_{10}}\right]\beta^t + \dots \\ &= 1 - D_1\,\beta^t + \dots\end{aligned} \tag{13}$$

where D_1, which equals the quantity in square brackets, is a pseudo binary diffusion coefficient. Combining Equations (6), (9), and (13) this coefficient becomes

$$D_1 = D\left(1 + \frac{c_1}{c_2{}^0}\,\frac{\Delta c_{20}}{\Delta c_{10}} \ln\left[\frac{c_1{}^S(3)}{c_1{}^S(2)}\right]\right) \tag{14}$$

Because all terms except the linear one in Equation (13) are neglected, this relation is restricted to small times. In our experiments, we have taken this to mean that $D_1\,\beta\,t \leq 0.2$.

EXPERIMENT

All materials except for the dyes were reagent grades and were used as received. Recrystallization of some of the salts and drying of the solvents had no significant effect on the measured diffusion rates. Most of the dyes were prepared in this laboratory and frequently contained significant quantities of impurities such as sodium chloride. Repeated recrystallizations of the dyes were found to have only a minor effect on the diffusion.

All experiments were made in duplicate with the diaphragm cell apparatus which has been described elsewhere (*12-13*). The only difference was in the type of diaphragm which was a new piece of Whatman 42 filter paper for each run; and in the stirring which employed Teflon coated magnetic stirrers. The top stirrer was supported above the paper with a glass spacer ring, while the bottom stirrer was mounted on a shaft so that it revolved directly below the paper. Cell constants under these conditions were about 7 cm^{-2}. These changes in the diaphragm and the stirring decrease the accuracy of the measurements to about 5%, but the experiments now take a few hours, compared with several days for a conventional cell with a glass frit.

The concentrations of solutions containing simple sodium salts or antibiotics were measured with a Gallenkamp FH 500 flame analyzer. Solutions containing dyes were greatly diluted to minimize the effect of different solvents and then analyzed with a Unicam SP500 spectrophotometer. Concentrations of organic solutions were measured with a Perkin Elmer F-11 chromatograph fitted with a dual flame ionization detector.

RESULTS AND DISCUSSION

This section contains typical experimental results showing accelerated diffusion caused by coupled diffusion fluxes, and a test of the guide developed above for qualitatively predicting these increases. Our discussion will be greatly simplified if we adopt a convention for labelling the components. We choose as component 1 the species present in small amounts whose diffusion we are trying to accelerate. We choose as component 2 the solvent in which 1 is relatively insoluble, and as component 3 the solute in which 1 is relatively soluble. In addition, we will discuss only experiments in which $\Delta c_{10}/\Delta c_{20}$ is positive so that D_{12} is positive and the diffusion is accelerated. Obviously we could make experiments in which D_{12} would be negative and the diffusion rate would be decreased, but this is not our objective here. Also, since

TABLE 1. PSEUDO-BINARY DIFFUSION COEFFICIENTS OF SODIUM SALTS AT 25°C[a]

Salt 1	Sodium acetate	Sodium lactate	Sodium dodecyl sulphate	Sodium sulphate	Sodium bromide
Value in pure water[b]	1.16(1.16)	1.00	0.99	1.23(1.23)	1.70(1.63)
Solvent 2[c]					
Acetone	9.9	6.7	7.9	8.8	3.1
Acetonitrile	8.9	4.6[b]	3.5	10.0	8.2
t-Butanol	4.3	1.2_6	1.8_6	9.4	4.5
Furfural alcohol	1.4_5	2.0	1.1_6	2.6	1.7_7
Dioxane	5.1	3.5	1.0_9	2.7	2.1_0

[a] All diffusion coefficients have units of 10^{-5} cm²/s.

[b] Literature values in parentheses.[12]

[c] $\frac{c_1}{c_2^0}\frac{\Delta c_2}{\Delta c_1} = 0.45$ except where indicated.

[d] $\frac{c_1}{c_2^0}\frac{\Delta c_2}{\Delta c_1} = 0.40.$

TABLE 2. OVERALL SUMMARY OF ESSENTIAL OIL DIFFUSION IN BENZENE AT 25°C[a]

Diffusion of accelerated with	*d*-limonene	α-pinene	*dl*-menthone	*d*-carvone
benzene (binary)	0.5_5	0.5_4	0.7_3	0.5_6
acetone	1.0_0	0.8_8	0.7_9	0.5_7
acetonitrile	1.1_7	0.9_0	0.9_4	0.8_8
furfural alcohol	2.0_6	0.5_2	0.3_5	
methanol	0.8_7	1.4_0	0.6_6	
tetrahydrofuran			0.6_8	

[a] $\frac{c_1}{\Delta c_{10}}\frac{\Delta c_{20}}{c_2^0} = 0.35$ in all experiments.

species 2 accelerates the diffusion of 1, then species 1 may be shown to accelerate the diffusion of 2; but again, this symmetrical effect is not of present interest.

The magnitude and extent of the acceleration of diffusion by use of mixed solvents is illustrated in Tables 1 to 3. The important quantity reported is the pseudo binary diffusion coefficient D_1, defined by the square brackets in Equation (13). Table 1 gives the increases in pseudo binary diffusion coefficient for a variety of simple sodium salts. Experimental values of the binary diffusion coefficients in water are also included in the table. These are in good agreement with values reported in the literature (*12*), in support of the accuracy of the experimental technique. The increases in pseudo binary diffusion coefficients are comparable for most of the compounds studied. The greatest increases are generally observed in acetone and acetonitrile, in which these salts are very insoluble. However, these solvents will not always give increased diffusion rates. For example, for sodium tetraphenyl boride, acetonitrile is a better solvent than water. We found that this salt diffused from a water-rich region into an acetonitrile-rich region 200% faster than it diffused in pure acetonitrile alone.

The important relationship between accelerated diffusion in Table 1 and the nature of the anion seems to be that expected from solubility. Sodium lactate and sodium acetate give very different results in *t*-butanol, which is certainly inconsistent with ionic size but in accord with solubilities (*14*). A surfactant like sodium dodecyl sulphate is not greatly accelerated in most of the solvents used probably because its strongly hydrophilic and hydrophobic portions make it soluble in a wider range of solvents.

Table 2 shows the increase in pseudo binary diffusion coefficient obtained for four essential oils. Test experiments on a variety of other purely organic systems gave similar results. In general, the acceleration of diffusion in organic systems is smaller than that observed in ionic systems. This is because the solubilities of the essential oils in various nonpolar solvents will be more similar than the solubilities of electrolytes in water and in nonpolar solvents. The best solvent for accelerating essential oils is

TABLE 3. PSEUDO-BINARY DIFFUSION COEFFICIENTS OF DYES AND ANTIBIOTICS AT 25°C

dye 1	formula	solvent 3	solvent 2	Δc_{20}	$D_1 \cdot 10^5$
orange II		H_2O	—	—	0.66
			acetone	−0.90	0.83
			acetonitrile	−0.90	1.06
			dioxane	−0.90	0.54
			t-butanol	−0.90	0.28
			tetracthylene glycol	−0.90	0.30
		methanol	benzene	0.66	1.36
methylene blue		methanol	—	—	0.72
			benzene	0.80	1.79
18 × 164		methanol	—	—	0.37_0
			benzene	0.61	0.65
		water	acetonitrile	−0.90	1.86
Fourrine BDN		methanol	—	—	0.71
			dichloroethane	+0.90	0.77
CIBA red		dioxane	—	—	0.37
			water	−0.46	0.68
Fourrine 4G		methanol	—	—	0.75
			benzene	+0.90	1.7_2
Monensin		ethanol	—	—	0.19
			water	+0.40	0.30
benzyl penicillin		water	—	—	0.97
			dioxane	+0.35	1.5_4
ampicillin		water	—	—	1.21
			dioxane	+0.66	2.73

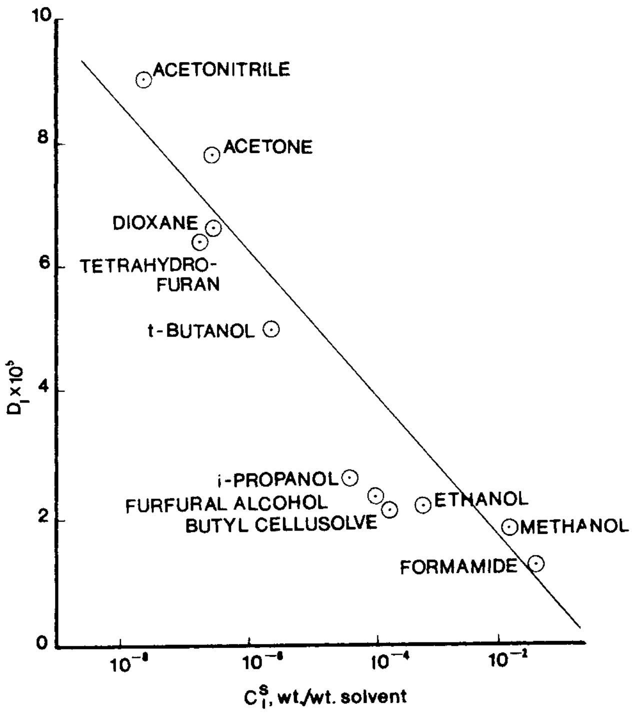

Fig. 1. Amount of increased diffusion as a function of solubility (c_1^s) in nonsolvent units; as: ($c_1 \Delta c_2 / c_2^0 \Delta c_1 = 0.45$).

acetonitrile, which shows increases of more than 300%. Acetone gives increases of better than 100%, which is of interest because acetone-benzene mixtures are currently used industrially for essential oil extractions.

Examples of accelerated diffusion of dyes and antibiotics are given in Table 3. In these experiments, the objective was not the systematic investigation of one type of compound, but the more general study of valuable compounds with very different chemical structures. The object was to discover one or two systems in which the diffusion was accelerated by more than 100%. In this, we were generally successful, but again we did not find increases as large as those reported in Table 1. This was particularly true for dyes. Like sodium dodecylsulphate, many dye molecules have both hydrophilic and hydrophobic groups, and so tend to be sparingly soluble in a wide variety of solvents. The increases which are observed for dyes contribute to, but in general do not dominate, the effect of solvent dyeing (*15*).

The guide for choosing systems for accelerated diffusion, represented by Equation (14), predicts that the accelerated diffusion of species 1 should be proportional to the logarithm of the solubility of species 1 in the solvent 2. Figure 1 shows that this is indeed so for sodium chloride. In all of these experiments, a solution containing 50 ppm sodium chloride (1), 90 wt % solvent 2, and 10% water (3) was allowed to diffuse into pure water. The deviations of the observed apparent diffusivities from the expected linear behavior are not surprising in view of the major approximations in the theory. Specifically, the neglect of preferential solvation, electrostatic interaction, ion pair formation and viscosity effects must lead to considerable error. However, we believe that more exact theories are necessary only if a more complete understanding of a specific system becomes commercially desirable. At the moment, the return is not worth the major experimental effort.

The predictions of Equation (14) are also supported by other experimental tests. For example, Equation (14) predicts that D_1 should remain constant as c_1 is changed if the ratio $\Delta c_{10}/c_1$ is kept constant. We tested this on the system sodium chloride (1)-dioxane (2)-water (3), and found an increase of less than 25% in D_1 with an increase of 400 times in c_1. In addition, Equation (14) correctly predicted that D_1 should vary linearly with c_1 if the concentration difference Δc_{10} was held fixed. However, the experiments did not always support the prediction that D_1 should vary linearly with Δc_{20}.

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NOTATION

c_i = concentration of species i, g cm.$^{-3}$
$c_i^S(j)$ = concentration of i at saturation in j [Equation (12)]
D = binary diffusion coefficient of all species [Equation (8)]
D_1 = pseudo binary diffusion coefficient [Equation (14)]
D_{ij} = ternary diffusion coefficient [Equation (1)]
$\mathcal{D}_{ij}$ = binary diffusion coefficients in gases [Equation (6)]
D_{ij} = generalized Stefan-Maxwell diffusion coefficient [Equation (7)]
j_i = mass flux relative to volume average velocity [Equation (1)]
t = time
β = diaphragm cell calibration constant [Equation (14)]
Δc_{10}, Δc_i = concentration differences of i in diaphragm cell at times zero and t, respectively [Equation (14)]
μ_i = chemical potential of i
$\mu_i^0(j)$ = chemical potential of i in standard state of infinitely dilute j [Equation (11)]
σ_i = eigenvalue [Equation (15)]

Subscripts

1 = species whose diffusion is to be accelerated
2 = solvent in which 1 is relatively insoluble
3 = solvent in which 1 is relatively soluble

LITERATURE CITED

1. de Groot, S. R., and P. Mazur, Non-Equilibrium Thermodynamics, North-Holland, Amsterdam (1962).
2. Katchalsky, A., and P. F. Curran, Non-Equilibrium Thermodynamics in Biophysics, Harvard Univ. Press, Cambridge, Mass. (1965).
3. Arrenhius, S., *Z. Physik. Chem.*, **10**, 51 (1892).
4. Woolf, L. A., D. G. Miller, and L. J. Gosting, *J. Amer. Chem. Soc.*, **84**, 317 (1962).
5. W. D. Stein, Movement of Molecules across Cell Membranes, Academic Press, New York (1967).
6. Cullinan, H. T., and M. R. Cusick, *Ind. Eng. Chem. Fundamentals*, **6**, 73 (1967).
7. Kett, T. K., and D. K. Anderson, *J. Phys. Chem.*, **73**, 1268 (1969).
8. Onsager, L., *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).
9. Cussler, E. L., and E. N. Lightfoot, *J. Phys. Chem.*, **69**, 1135 (1965).
10. Gilliland, E. R., R. F. Baddour, and D. J. Goldstein, *Can. J. Chem. Eng.*, **35**, 10 (1957).
11. Cussler, E. L., and P. J. Dunlop, *J. Phys. Chem.*, **70**, 1880 (1966).

12. Robinson, R. A., and R. H. Stokes, Electrolyte Solutions, Butterworths, London (1965).
13. Bremer, M. F., and E. L. Cussler, *AIChE J.*, **16**, 832 (1970).
14. Seidell, A., Solubilities of Inorganic Compounds, 4th ed., W. F. Linke (ed.), Am. Chem. Soc., Washington (1965).
15. Medley, J. A., and M. W. Andrews, *Textile Res. J.*, **30**, 855 (1960).

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Counterdiffusion of Liquid Hydrocarbons in Type Y Zeolite: Effect of Molecular Size, Molecular Type, and Direction of Diffusion

This paper presents experimental results on the counterdiffusion of liquid hydrocarbons in the Y zeolite as determined by an unsteady state technique using the zeolite powder. The critical diameter of aromatic molecules counterdiffusing with respect to cyclohexane into NaY zeolite has a marked effect upon the counterdiffusion rate. For a given molecular type, the single parameter of critical molecular diameter correlates the size effect well. Molecular type, for example, toluene vs. phenol, also has a pronounced effect on the counterdiffusion rate. Those molecules showing stronger interactions with the zeolite have lower counterdiffusion rates. In both NaY and SK-500, the diffusion coefficients for adsorptive counterdiffusion are an order of magnitude greater than the diffusion coefficients for desorptive counterdiffusion indicating that factors other than simple intracrystalline diffusion as such are also important in zeolite counterdiffusion. Simple diffusion models do not account for the differences observed indicating that a more sophisticated approach is necessary.

REBECCA M. MOORE and
JAMES R. KATZER
Department of Chemical Engineering
University of Delaware
Newark, Delaware 19711

SCOPE

Zeolites play a very important role in the chemical and petroleum industry as both adsorbents and catalysts (Collins, 1968). Adsorbent applications utilize the strong selective adsorption which zeolites often show toward a compound or a class of compounds or the very fine, uniform pore structure which permits the adsorption of molecules smaller than a given critical diameter. Adsorbent applications involve the diffusion of at least one species and often the counterdiffusion of different species within the pore structure, and thus design of adsorption units requires information on diffusion and/or counterdiffusion rates (Roberts and York, 1967; Gehrhardt and Kyle, 1967; Fukunaga et al., 1968). Such information is not generally available, and thus the design of such units remains mainly an empirical art. In catalytic applications since the locus of catalytic activity for many reactions is within the pore structure, the simultaneous counterdiffusion of reactants and products must occur within the structure. The presence of diffusion limitations in zeolite catalysts would reduce the activity observed and for multiple-step reactions could also alter the selectivity. Thus a quantitative understanding of counterdiffusion in zeolites is important to the engineering design of zeolite catalysts and of processes utilizing them.

Very little information is available on counterdiffusion in zeolites. Furthermore, counterdiffusion rates are grossly different from single component unidirectional rates, cannot be estimated from single component rates, and thus must be determined independently (Satterfield and Katzer, 1971). Studies of the counterdiffusion of hydrocarbons in large pore zeolites under practical conditions are necessary to provide an understanding of the important variables affecting it. Such work will probably not immediately result in the development of theoretical models for zeolite

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Correspondence concerning this paper should be addressed to J. R. Katzer. R. M. Moore is with the University of Technology, Loughborough, England.