EVALUATION OF BLOCKING EFFICIENCY

In the following, an estimation of the influence of this blocking effect on the probability of penetration of sorbate molecules through the crystal surface will be given. Comparing the equation for barrier limited sorption

$$\gamma = 1 - \exp(-3\alpha t/R) \tag{1}$$

with the approximation formula for intracrystalline diffusion

$$\gamma \approx 1 - (6/\pi^2)\exp(-\pi^2 Dt/R^2) \tag{2}$$

and neglecting the slight difference in the pre-exponential factors, we get

$$\alpha \approx \pi^2 D_{\text{app}}/3R \tag{3}$$

On the other hand, the ratio between the flux density j through the crystal surface and the barrier parameter α is given by

$$\alpha = j/[a_s - a_{s,(\text{eq})}] \tag{4}$$

The comparison of Equations (3) and (4) leads immediately to the proportionality

$$D_{\text{app}}/R \propto \alpha \propto j \tag{5}$$

Taking into account this approximate result and comparing the diffusion coefficients derived from uptake curves (Figure 1), one can show that by using cyclohexane instead of ethylbenzene as a solvent the probability of n-decane entrance into the zeolite micropores through the crystal surface is at least three orders of magnitude higher than by using ethylbenzene. This should be caused by a more weak interaction of the cyclohexane molecules with the outer crystal surface due to the differences in the molecular structure between cyclohexane and ethylbenzene.

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NOTATION

D = Fickian diffusion coefficient
D_{app} = apparent diffusion coefficient obtained by best fitting of uptake curves of sorption processes different from intracrystalline ones to appropriate diffusion equations
R = zeolite crystal 'radius' (the half of the edge length of the cubic A type crystals used)
$a_{s,(\text{eq})}$ = sorbate concentration at the crystal surface (in equilibrium with the surrounding liquid phase)
j = flux density of sorbate through the outer crystal surface
α = barrier parameter
γ = relative amount of adsorbed compound

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Binary Diffusion in Liquid Systems

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Diffusion in liquid systems plays an important role as far as industries and fundamental research are concerned. Mass transfer in absorption, solvent extraction, distillation and other diffusional operations need basic data.

No completely theoretical equations for estimating the diffusion coefficients for all the systems encountered in chemical engineering operations are available in the literature. Thus, empirical and semitheoretical methods of estimating physical properties play an important role in design calculations and for many other purposes in engineering and applied science. A number of workers have developed some correlations for calculating diffusion coefficients. Sometimes the predictions based on these expressions may differ from the true values by as much as 50%. Each expression holds for a certain set of systems. The Wilke and Chang (1955) system fails for highly viscous solvents. For such systems, the correlation given by

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TABLE 1

Solvent	Solutes	Range of percent errors
Chloroform	Acetone, Benzene, n-butyl acetate Ethanol, Ether, Ethyl acetate M. E. K.	-22 % to +16.5 %
Benzene	Acetic Acid, Aniline, Bromobenzene Cyclphexane, Ethanol, n-Heptane M. E. K., Toluene, Anylalcohal, n-Propanol, Ether, Chloroform, Chlorobenzene, ccl_4	- 9.5 % to +20.2 %
Acetone	Acetic acid, Nitrobenzene, Water Chlorobenzene, ccl_4, Benzene	- 7.4 % to +20.5 %
n-hexane	ccl_4, Dodecane, n-Hexane, Toluene, M. E. K.	-15.2 % to + 9.1 %
Ethanol	Idobenzene, water, ccl_4	- 2.4 % to +34.5 %
n-butanol	Methanol, water	- 1.7 % to + 1.6 %
Ethyl acetate	Acetic acid, Acetone, M. E. K. Nitrobenzene, water	-26.1 % to +10.6 %
Methanol	Acetone, M. E. K., Aniline, ccl_4 Chloroform, Nitromethane, Ethyl Aacetate, Alkyl alcohal, Methanol	-12.29% to +16.6 %
Toluene	Acetic Acid, M. E. K., ccl_4 Chloroform	-10.5 % to +11.4 %
m-xylane	Bromobenzene	-2.63%
Water	Acetone, Acetic Acid, Ethyl acetate, Ethanol	- 5.66% to + 1.68%

Olander (1961) is more successful. For water solvent systems, the equation given by Othmer and Thaker (1953) has been recommended. It is therefore clear that the available expressions have only been partially successful, and thus the problem of accurate prediction of diffusion coefficients still remains to be solved. An attempt was therefore made to develop a general expression to predict diffusivities more accurately. Based upon the concept that diffusion coefficient depends primarily on the solvent viscosity, the absolute temperature, the concentration, the molar volumes and the latent heats of vaporization of the mixture components, an equation predicting liquid-liquid diffusivities is

$$D_{AB} = 0.003975\,\frac{T}{\mu_B} \times \frac{m_{cB}}{m_{cA}}^{1/3} \times \left[\frac{H_B}{H_A} \quad \frac{(M_A^2 + M_B^2)}{2M_A M_B}\right]^{1/6}$$

The correlations of the earlier workers involve molar volume of the solute at their normal boiling point. The molar volume is computed in an additive fashion from individual atoms. These values differ considerably (Sovova, 1976). Sridhar and Potter (1977) have used critical molar volume in their expression which gives reasonable predictions for both gas-liquid and liquid-liquid systems. The equation predicted uses critical molar volumes and critical densities.

As mass is related to volume and concentration, it is worthwhile to introduce critical mass factor into the correlation. One of the earlier equations (Sitarama et al., 1963) which, unlike Wilke and Chang (1955), is said to hold for the diffusion of water at low concentrations in organic solvents justifies the dependance of diffusion coefficient on the latent heats of vaporization.

On the microscale, the viscosity reflects the effect of molecular motions and interaction. If these two properties are taken into consideration, it can be claimed that the important variables of diffusion, namely, the shape and volume of component molecules, have been introduced. This is the basis for Wilke's development. But in my opinion viscosity alone is not sufficient to bring out the effect of interatomic distance. As molecular weight is closely associated with molecular diameter and volume, I considered it worthwhile to introduce this factor into the correlation. The applicability of the earlier equations is valid to a restricted range of solute-solvent systems and deviates from one or the other class of systems (Table 1). The predicted equation has been tried for seventy-three systems, giving an average error of 7.73%.

NOTATION

H = latent heat of vaporization
m_c = critical mass
M = molecular weight
T = temperature
μ = viscosity

Subscripts

A = solute
B = solvent

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