for the micropore diffusivity, the D_i values given in Table 2 correspond to $r_o = 10$ microns. Such diffusivities are of the order of 1×10^{-11} m²/s and are somewhat lower for the more strongly adsorbed SO_2 and H_2S than for CO_2. Values of the same magnitude were reported by Chihara et al. (1978) for rare-gas adsorbates in molecular-sieving carbon and by Walker et al. (1966) for micropore transport of CO_2 in coal particles. The activation energies obtained from an Arrhenius plot of the D_i/r_o^2 values increase from 1.4 for CO_2 to 1.8 for H_2S and to 5.0 kcal/mol for SO_2. The lower micropore diffusivities for H_2S and SO_2 are expected in view of the stronger attraction between wall atoms and absorbate molecule for the sulfur-containing gases. Further, such results would not be expected if the micropore transport occurred by a pore-volume rather than a surface transport process.

The data for H_2S and SO_2 as well as that for CO_2 indicate that intraparticle transport has a strong effect on the overall adsorption rate. Hence, particle-size and pore-volume distribution information is necessary for a careful design of activated carbon beds for these gases.

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NOTATION

a = pore radius, m
D = composite molecular diffusivity, m²/s
D_a = effective diffusivity in the macropores, m²/s
D_i = effective diffusivity in the micropores, m²/s
d_p = equivalent spherical diameter of carbon particles, m
E = activation energy for micropore diffusion, kcal/mol
E_d = axial dispersion coefficient, based upon cross-sectional area of column, m²/s
ΔH_A = isoteric heat of adsorption, kcal/mol
ΔH_c = heat of condensation of pure adsorbate at normal boiling point, kcal/mol
K_A = adsorption equilibrium constant, m³/kg
k = first-order adsorption rate constant, m³/kg · s
k_f = gas-to-particle mass transfer coefficient, m/s
L = bed length, m
r_o = radius of microparticles in the activated carbon, m
T = absolute temperature, °K
v = gas velocity in interstitial space at temperature of bed, m/s
V = pore volume, m³/kg

Greek Letters

β_a = macropore porosity
ϵ = bed porosity
τ_a = tortuosity factor for macropores

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Estimation of Solvent Effects on Chemical Reaction Rates Using UNIFAC Group Contribution

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The UNIFAC group contribution method, developed by Fredenslund et al. (1975), provides the chemical engineer with a straightforward, reliable method for predicting activity coefficients in nonelectrolyte solutions when little or no experimental equilibrium data exist. The UNIFAC method has been applied to vapor-liquid, liquid-liquid, and solid-liquid equilibria calculations with good results. In the following, UNIFAC is combined with transition state theory to predict thermodynamic solvent effects on chemical reaction rates in solution.

TRANSITION STATE THEORY

Transition state theory (Evans and Polanyi, 1935; Glasstone et al., 1941) postulates the existence of an intermediate species or transition state, M, for any elementary reaction,

$$A + B \rightleftarrows M \rightarrow \text{Products} \qquad (1)$$

The assumption of thermodynamic equilibrium between this transition state and the reactants, A and B, leads to the following expression for reaction rate in a nonideal system (Brønsted, 1922; Bjerrum, 1924),

$$\text{Rate} = k_o \frac{\gamma_A \gamma_B}{\gamma_M} \cdot (A)(B) \qquad (2)$$

where k_o is the rate constant in an ideal reference system ($\gamma_A = \gamma_B = \gamma_M = 1$), γ_i is the activity coefficient for an individual species i, and (A) and (B) are the reactant concentrations. The Brønsted-Bjerrum relationship for the apparent rate constant in a nonideal solution follows directly from this expression,

$$k = k_o \frac{\gamma_A \gamma_B}{\gamma_M} \qquad (3)$$

Equation 3 is not limited by the assumption of equilibrium between the transition state and reactants (Marcus, 1967) and is

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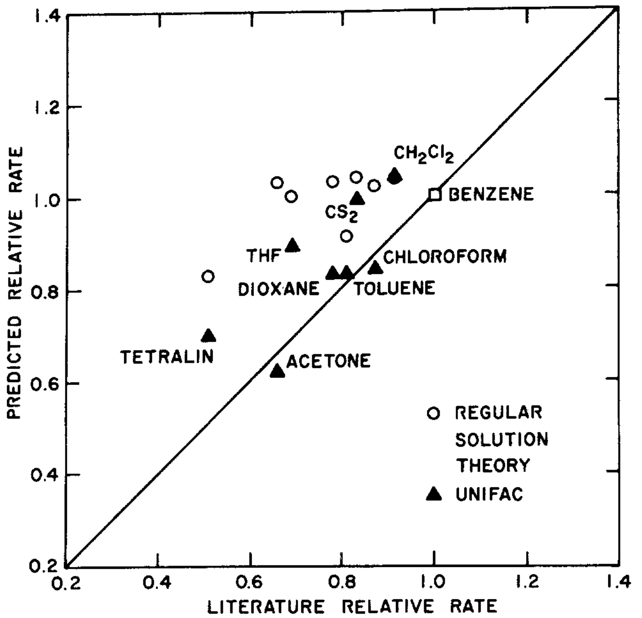

Figure 1. Comparison of predicted and experimental reaction rates in various solvents (relative to benzene) for the Diels-Alder dimerization of cyclopentadiene at 25°C.

useful in correlating and predicting solvent effects for simple reactions. For liquid-phase reactions, a number of different approaches can be used to obtain the activity coefficients in Eq. 3 from excess Gibbs energy expressions for mixtures (Eckert et al., 1974). These approaches have two primary limitations. (1) Application of any solution theory to evaluate γ_M requires some knowledge of the transition state structure and properties, and these data are usually scarce. (2) Predictive solution theories that have been used previously are not adequate for highly nonideal solutions (e.g., polar or associating systems) where the solvent effects on reaction rate are greatest. One advantage of utilizing UNIFAC to predict γ_M is that only the number and types of groups in the transition state are required, physical properties are not necessary. The UNIFAC method is also applicable to a wide range of solution nonidealities, including polar and associating systems, and is limited only by the number of accurate group interaction parameters that are currently available. To demonstrate the use of the UNIFAC method in conjunction with the Brønsted-Bjerrum relationship, predicted solvent effects are compared with experimental data for the Diels-Alder dimerization of cyclopentadiene and the competitive catalytic hydrogenation of cyclohexene and acetone.

RESULTS

The liquid-phase Diels-Alder dimerization of cyclopentadiene to form α-dicyclopentadiene at 25°C has been studied in a number of solvents. Solvent effects have also been predicted by Wong and Eckert (1969) using the Brønsted-Bjerrum relationship in conjunction with the regular solution theory of Scatchard and Hildebrand. From Eq. 3, the reaction rate in any solvent i relative to that in benzene (subscript ϕ) is given by,

$$\text{Relative Rate} = \frac{(k/k_o)_i}{(k/k_o)_\phi} = \frac{(\gamma_A^2/\gamma_M)_i}{(\gamma_A^2/\gamma_M)_\phi} \tag{4}$$

Activity coefficients for cyclopentadiene (γ_A) and the transition state in the solvents of interest are calculated using UNIFAC parameters and procedures given by Fredenslund et al. (1977) and Skold-Jørgensen et al. (1979). The structure of the transition state is assumed to be that of the product, α-dicyclopentadiene. A comparison of measured solvent effects with those calculated by Wong and Eckert and those predicted using UNIFAC are presented in Figure 1. References for the experimental data are compiled by Wong and Eckert (1969).

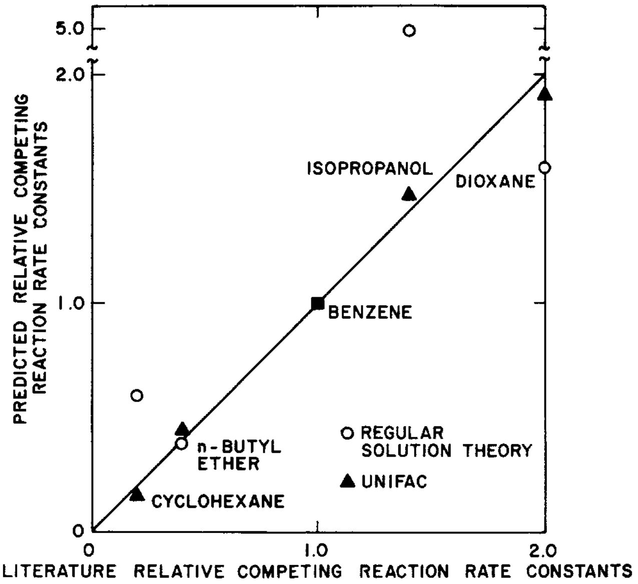

Figure 2. Comparison of predicted and experimental competing reaction rates in various solvents (relative to benzene) for the catalytic hydrogenation of cyclohexene and acetone at 25°C.

The competitive hydrogenation of cyclohexene and acetone over a nickel catalyst at 25°C has been studied in a number of different solvents by Jungers et al. (1958). Solvent effects have also been predicted by Eckert (1967) using Scatchard-Hildebrand regular solution theory to evaluate activity coefficients. The following assumptions are made in determining solvent effects. (1) At 25°C, the chemical reaction is the rate controlling step. The Brønsted-Bjerrum relationship is applicable to this surface reaction, with activity coefficients corresponding to the surface species. (2) Since an adsorption equilibrium is implied, the reactants on the surface are in equilibrium with reactants in the bulk phase. The transition state, however, exists only as a surface species, independent of the bulk phase except through the chemical equilibrium with the reactants on the surface. In this case, the activity coefficient of the transition state is independent of the solvent used, and the relative competing reaction rate in solvent i compared to benzene is,

$$\begin{matrix}\text{Relative Competing} \\ \text{Reaction Rate}\end{matrix} = \frac{(k_1/k_2)_i}{(k_1/k_2)_\phi} = \frac{(\gamma_{A1}/\gamma_{A2})_i}{(\gamma_{A1}/\gamma_{A2})_\phi} \tag{5}$$

where subscripts A1 and A2 refer to cyclohexene and acetone, respectively; and subscripts 1 and 2 refer to the hydrogenation of A1 and A2, respectively. Activity coefficients for cyclohexene and acetone in the various solvents are calculated using UNIFAC parameters and procedures referenced previously. A comparison of the results with the experimental data and with the predictions using regular solution theory (Eckert, 1967) are given in Figure 2.

CONCLUSIONS

In both examples, solvent effects predicted using the UNIFAC method are superior to predictions using Scatchard-Hildebrand regular solution theory. These results are not unexpected since UNIFAC is applicable to a wider range of solution nonidealities and UNIFAC parameters are evaluated from an extensive correlation of published vapor-liquid equilibrium data. The limitations of regular solution theory are clearly exemplified for highly polar solvents, such as acetone in Figure 1 and isopropanol in Figure 2.

The overall agreement between experiment and UNIFAC-predicted solvent effects is very good—especially for the competitive catalytic hydrogenation of cyclohexene and acetone—and suggests that quantitative predictions of solvent effects on chemical reaction rates are possible. At present, the UNIFAC method is limited by the number of available UNIFAC parameters, although experimental determination of new parameters is proceeding rapidly. As more parameters become available, a more extensive evaluation of this method should be accomplished.

NOTATION

A = reactant
B = reactant
k = reaction rate constant
M = activated complex
γ = activity coefficient

Subscripts

$A1$ = cyclohexene reactant
$A2$ = acetone reactant
i = arbitrary solvent
ϕ = benzene solvent
o = ideal solution
1 = cyclohexene hydrogenation reaction
2 = acetone hydrogenation reaction

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Correlation of Hydrogen Solubilities in Nonpolar Solvents Based on Scaled-Particle Theory

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Recent developments in heavy fossil-energy technology have renewed interest in hydrogen-heavy hydrocarbon vapor-liquid equilibria, especially at higher temperatures. In this work we present a correlation for Henry's constants for hydrogen in typical hydrocarbons and nonpolar solvents in the temperature range 248-700°K.

HENRY'S CONSTANT

For hydrogen (2) dissolved in a solvent (1), Henry's constant H is defined by:

$$H \equiv \lim_{x_2 \to 0} f_2/x_2 \qquad (1)$$

where x is the liquid-phase mole-fraction and f is the fugacity given by:

$$f_2 = \phi_2 y_2 P \qquad (2)$$

where P is the total pressure and y is the vapor-phase mole fraction. The vapor-phase fugacity coefficient ϕ can be calculated from an equation of state (Prausnitz, 1969).

The well-known K factor is related to Henry's constant by:

$$K \equiv y_2/x_2 = \frac{\gamma_2^* H}{\phi_2 P} \qquad (3)$$

where γ_2^* is the (unsymmetric) liquid-phase activity coefficient. Since the solubility x_2 is normally small and since hydrogen's gas-phase properties are normally well approximated by those of an ideal gas, the ratio γ_2^*/ϕ_2 is close to unity even at moderately high pressures, provided only that the temperature of the system is well below the solvent's critical.

Figure 1 shows experimental Henry's constants for hydrogen in 14 solvents in the region 248-700°K. Note the scale at the right which refers to carbon disulfide and benzene. For hydrogen in this temperature range, Henry's constants uniformly fall with rising temperature. Over the temperature range indicated, Henry's constants vary by one order of magnitude, depending on temperature and solvent.

SCALED-PARTICLE THEORY

To correlate H, we use the scaled-particle theory of Reiss et al. (1959, 1960) as discussed by Pierrotti (1963, 1976). The partial Gibbs energy of dissolving a solute in a liquid consists of two parts: first, the work needed to create a cavity in the solvent to place a solute molecule and second, the energy of interaction between the dissolved solute and the surrounding solvent. (The entropy of interaction is neglected.)

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