

Kinetic Study of Liquid-Phase Esterification with Sulfonic Acid Cation-Exchange Resin of the Macroreticular Type. II.¹⁾ Solvent Effects on Resin Catalysis

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The rates of the esterification of octanoic acid with 1-butanol catalyzed by macroreticular sulfonated ion-exchange resin in the presence of various organic solvents and water were measured by the use of a batch reactor. The solvent effects on the rate were investigated by applying the heterogeneous-pseudohomogeneous reaction mechanism. From these results, it was found that the effects can be quantitatively estimated by means of the magnitude of the equilibrium constants, $K_{\text{sol}}^{(S)}$, for the solvent-separated ion-pair formations, which are due to the interaction of the sulfo groups in the resin with the solvents. The correlations of the $K_{\text{sol}}^{(S)}$ value with the physical properties, μ and ϵ ; the solvatochromic parameters, π^* , α , and β , and Gutmann's parameters, AN_E and DN_B , have been examined by using linear regression analysis methods. The results of the correlations in which the protic solvents have been excluded suggest that the positions of the equilibria of solvent-separated ion-pair formations depend mainly on the electron-donor property of the solvents; that is to say, the solvents with a strong donor property diminish the number of un-ionized sulfo groups which act as catalytic species for the heterogeneous reaction.

The advantages cited most frequently for the use of ion-exchange resins as catalysts are the elimination of the necessity for product isolation by distillation or extraction procedures and their possible re-utilization. Therefore, experimental studies of the use of resin have been carried out on almost all the reactions homogeneously catalyzed by acids or bases.²⁾ Little, however, is known concerning the solvent effects on resin catalysis.

Tartarelli et al.³⁾ studied the kinetics of the esterification of benzoic acid with 1-butanol catalyzed by sulfonic acid resin of the standard type and sulfuric acid in the presence of heptane, benzene, and toluene as solvents; they reported that, taking into account the distribution of the components between the external solution and the micropore liquid in the resin, the solvent effects on the reaction rate can be explained on the basis of a mechanism involving the reaction between a positive ion and a dipolar molecule. The kinetics of ethyl acetate reesterification with methanol and 1-propanol catalyzed by a sulfonated ion-exchanger MS-25 in 1,4-dioxane and cyclohexane were likewise investigated by Setinek and Rodriguez,⁴⁾ who noted that cyclohexane behaved as an inert solvent, while 1,4-dioxane interacted with the catalyst. Recently, Regen et al.⁵⁾ pointed out that, from a qualitative point of view, the nature of the organic solvent used for polymer-based triphase catalysts may influence the observed activity of the catalysts in the following ways: (1) it can be important in determining the absorption equilibria for the reactants on the polymer; (2) when a gelular resin is used, it can control the extent of swelling, which in turn will determine the number of active sites available for catalysis, and (3) it may be important in establishing the nature of the microenvironment at the active site.

On the other hand, Gates and his coworkers have

published a series of fundamentally important papers.⁶⁻⁸⁾ These papers have shown that an excess of water or alcohol can shift the catalytic species from the more active undissociated sulfonic acid to the less active solvated proton; this finding was also substantiated by our preceding work.¹⁾ The shift of catalytically active species reveals an important relationship between the solvent system and the nature of the catalytic species.⁹⁾

In this work, in order to clarify the solvent effects on the resin catalysis from such a point of view, we have measured the kinetics of the esterification of octanoic acid with 1-butanol catalyzed by macroreticular sulfonic acid resin (Amberlyst 15) in the presence of various organic solvents and water.

Experimental

Catalyst Preparation and Reagents. The catalyst was a macroporous sulfonated copolymer of styrene and divinylbenzene, Amberlyst 15 (Rohm and Haas Company). The hydrogen-form resin, 0.59–0.84 mm particles, was pretreated as usual¹⁾ and then stored in a desiccator in sealed vials over silica gel. The ion-exchange capacity was 5.05 meq g⁻¹ of dry resin, and the water content was 6.87 wt%.

The octanoic acid (reagent-grade for the automatic analysis of amino acids from Wako Pure Chemical Industries, Ltd.) was used without further purification. The 1-butanol was purified by drying over potassium carbonate and distillation.

Solvents. All the chemicals were of a guaranteed reagent grade. The octane and toluene were distilled and then dried over magnesium sulfate. The anisole was washed with a 0.5 mol dm⁻³ aqueous solution of sodium hydroxide and twice with distilled water, dried over calcium chloride, and then distilled. The dibutyl ether was purified by distillation and passing it through a column of activated alumina. The 2-butanol was purified in the same manner as 1-butanol. The 1,4-dioxane was refluxed over sodium and then dis-

tilled. The dimethyl sulfoxide was dried over calcium chloride and distilled under reduced pressure.

Reaction-Rate Measurement. The apparatus was the same as that described in Part I.¹⁾ The esterification was measured at $80 \pm 0.05^\circ\text{C}$, and the reaction medium was agitated at 250 rpm. In all experiments, the total volume of the reaction mixture, consisting of octanoic acid, 1-butanol (or with water in the runs so denoted in Fig. 2), and a solvent, was kept constant at 30 ml. The initial concentration of octanoic acid and the amount of resin were also held constant at $0.150 \text{ mol dm}^{-3}$ and 1.25 g respectively. The initial ratio of the volume of 1-butanol to that of solvent was changed in every run for the kinetic analysis. After the start of a reaction, 40.0- μl samples were removed by using a microsyringe at appropriate time intervals and then transferred to individual capped microtubes containing a mixture of hexadecane as an internal standard and the solvent used in each run. For gas-chromatographic (GC) analysis, samples of about 1–2 μl were taken from these microtubes. The reaction rates were determined from the analyses of butyl octanoate. The instrument used to carry out the GC analyses and the operating conditions were described in detail in an earlier paper.¹⁰⁾

The ester-concentration increments from 0.0200 to $0.0400 \text{ mol dm}^{-3}$, divided by the time required for the reaction progress, were set equal to the reaction rates for each solution composition at a conversion of 20 % and were adopted as the kinetic data, since a short induction period rarely appeared and since an initial reaction rate could not be employed.

Results and Discussion

Effects of Various Organic Solvents and Water on the Rate. The influences of various organic solvents upon the reaction rate are shown in Fig. 1. When 2-butanol was used as a solvent, *s*-butyl octanoate was formed as a by-product. However, the rate of the by-product reaction was negligibly small compared to that of the reaction of octanoic acid with 1-butanol under the present reaction conditions. In other cases, no side reaction occurred. As can be seen from Fig. 1, dimethyl sulfoxide most strongly interacted with the catalyst and inhibited the reaction, while octane did so most weakly or not at all; octane is, therefore, regarded as an inert solvent.¹¹⁾ Water also inhibited the reaction, as is shown in Fig. 2.

Evaluation of Solvent Effects in the Dielectric Approach. The swelling of an unsulfonated styrene-divinylbenzene copolymer of the macroreticular type was scarcely even observed in either polar or nonpolar organic solvents, whereas the sulfonated ion-exchange resin, Amberlyst 15, was slightly swollen only in polar solvents.¹²⁾ This swelling was considered to be due to the interaction between solvents and sulfo groups in the resin.¹²⁾ In practice, even when a polar reactant or a solvent such as 2-methyl-2-propanol¹³⁾ or 1,4-dioxane⁴⁾ was used, no sulfo groups located within the gelular microspheres in about 20% crosslinked resins took part in the catalytic reaction. Therefore, it is considered that only the sulfo groups residing on the

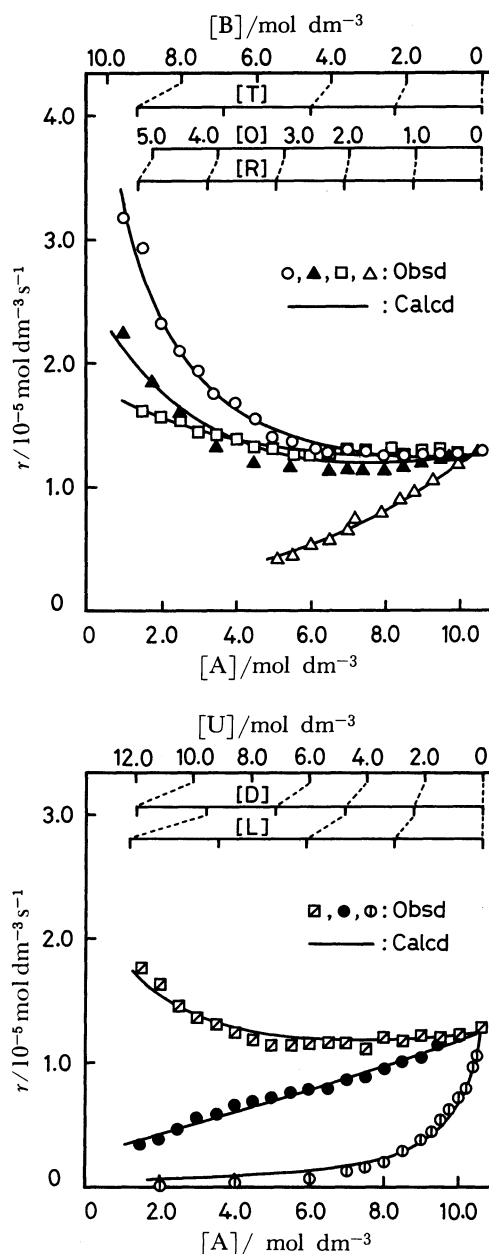


Fig. 1. Solvent effects on reaction rate (r).
 $[F]=0.120 \text{ mol dm}^{-3}$, $[E],[W]=0.030 \text{ mol dm}^{-3}$.
 O; Octane (O), $\blacktriangle$; toluene (T), $\square$; dibutyl ether (R),
 $\triangle$; 2-butanol (B), $\boxtimes$; anisole (L), $\bullet$; 1,4-dioxane (D),
 Φ ; dimethyl sulfoxide (U).

surface of the microspheres are available for a catalytic reaction, that the number of the available sulfo groups varies hardly at all with the polarity of the reaction medium, and that it is not necessary to take into account the distribution of the reactants between an external solution and micropore liquid in the microspheres, which conforms to Helfferich's standpoint.¹⁴⁾

On the assumption that a reaction between a neutral dipolar molecule and a positive ion is the rate-controlling step, Tartarelli et al.³⁾ interpreted the solvent effects on the rate of esterification with sulfonic acid resin in the dielectric approach. According to this treatment, the kinetic data presented in Figs. 1 and 2

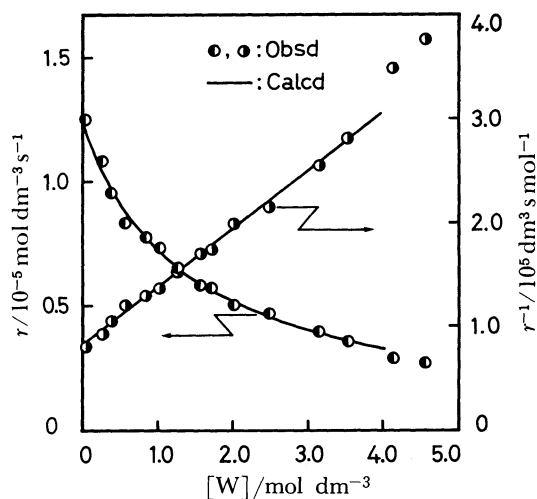


Fig. 2. Effect of water on reaction rate (r).
 $[F]=0.120 \text{ mol dm}^{-3}$, $[A]=9.7 \text{ mol dm}^{-3}$, $[E]=0.030 \text{ mol dm}^{-3}$, solvent; octane.

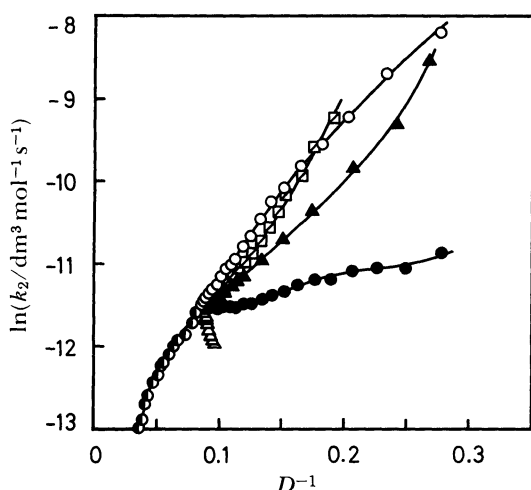


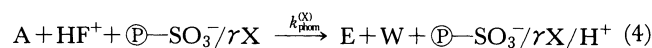
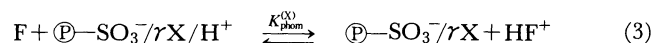
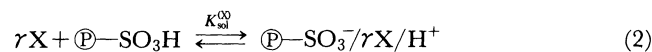
Fig. 3. Dependence of dielectric constant of reaction medium (D) on reaction rate constant ($k_2=r[F]^{-1}[A]^{-1}$). $\circ$; Octane, $\blacktriangle$; toluene, Δ ; 2-butanol, $\square$; anisole, $\bullet$; 1,4-dioxane, $\odot$; water.

should give a straight line in the plot of $\ln k_2$ vs. $1/D$ with a positive slope. As is shown in Fig. 3, however, curves and a line with a negative slope were obtained. These results indicate that the dielectric approach is inadequate to interpret the solvent effects on the resin catalysis.

Application of Heterogeneous-Pseudohomogeneous Reaction Mechanism¹⁾ and Estimation of Solvent Effects by Means of Kinetic Analysis. In the preceding paper,¹⁾ it was reported that water and 1-butanol solvate the matrix-bound sulfo groups, and that the esterification system consists of a heterogeneous reaction catalyzed by matrix-bound sulfo groups which are not ionized and a pseudo-homogeneous reaction by protons solvated with alcohol. Rate Equation 1, values calculated from which were in fair agreement with the observed ones, was presented.

$$r = \frac{\{k_{\text{het}}[F] + k_{\text{phom}}^{(A)} K_{\text{phom}}^{(A)} K_{\text{sol}}^{(A)} [F][A]^{\alpha+1}\} [\text{Cat}] M}{1 + K_{\text{sol}}^{(A)} [A]^{\alpha} + K_{\text{sol}}^{(W)} [W]^{\beta}} \quad (1)$$

In the present case, it is necessary to take into account the interaction of an additional solvent with the catalyst, that is, with sulfo groups in the resin. Assuming that appropriate polar solvents also behave as solvating agents (Eq. 2), and then that the protons solvated with the solvents become catalytic agents (Eqs. 3 and 4), the reaction rate is expressed by Eq. 5.



$$r = \frac{\{k_{\text{het}}[F] + k_{\text{phom}}^{(A)} K_{\text{phom}}^{(A)} K_{\text{sol}}^{(A)} [F][A]^{\alpha+1} + k_{\text{phom}}^{(X)} K_{\text{phom}}^{(X)} K_{\text{sol}}^{(X)} [F][A][X]^{\gamma}\} [\text{Cat}] M}{1 + K_{\text{sol}}^{(A)} [A]^{\alpha} + K_{\text{sol}}^{(W)} [W]^{\beta} + K_{\text{sol}}^{(X)} [X]^{\gamma}} \quad (5)$$

The application of Eq. 5 based on the heterogeneous-pseudohomogeneous reaction mechanism makes it possible to estimate the solvent effects on the resin catalysis in a quantitative way, provided that Eq. 5 gives good representations of the observed data plotted in Figs. 1 and 2. Hence, octane was chosen as the reference solvent, for it does not interact with the sulfo groups, that is to say, $K_{\text{sol}}^{(O)}=0 \text{ dm}^3 \text{ mol}^{-1}$, and the optimum values of α , β , $k_{\text{het}} [\text{Cat}]$, $k_{\text{phom}}^{(A)} K_{\text{phom}}^{(A)} [\text{Cat}]$, $K_{\text{sol}}^{(A)}$, and $K_{\text{sol}}^{(W)}$ were determined from the results observed with octane according to the procedure previously described.¹⁾ Next, in order to determine the values of $k_{\text{phom}}^{(X)} K_{\text{phom}}^{(X)} [\text{Cat}]$ and $K_{\text{sol}}^{(X)}$ for each solvent for integral values of the γ exponent ranging from one to three, the sum of the squares of the deviations of the predicted rates from the observed rates has been calculated with a computer. By substituting the values of these parameters, which are listed in Table 1, into Eq. 5, the most precise representation of the data for each solvent is given. When the calculated values are compared to the data in Figs. 1 and 2, the agreement between the observed and calculated values is satisfactory. These results give support to this approach for the quantitative estimation of the solvent effects on the resin catalysis.

Correlations with Physical Properties and Empirical Parameters of Solvents. The least-squares analyses were carried out for the equilibrium constants for solvent-separated ion-pair formation, $K_{\text{sol}}^{(S)}$, vs. the molecular dipole moment, μ , and the dielectric constant, ϵ . Equation 6 is the least-squares fit for $K_{\text{sol}}^{(S)}$ vs. μ with seven solvents, and Eq. 7, for $K_{\text{sol}}^{(S)}$ vs. ϵ with nine solvents.

$$K_{\text{sol}}^{(S)} = 2.66\mu - 1.19, \quad R = 0.838 \quad (6)$$

$$K_{\text{sol}}^{(S)} = 0.103\epsilon + 0.461, \quad R = 0.814 \quad (7)$$

Table 1. Optimum Values of γ , $K_{\text{sol}}^{(\text{S})}$, and $k_{\text{phom}}^{(\text{S})}K_{\text{phom}}^{(\text{S})}[\text{Cat}]$, and Empirical Parameters of Solvents

No.	Solvent	γ	$K_{\text{sol}}^{(\text{S})}$	$k_{\text{phom}}^{(\text{S})}K_{\text{phom}}^{(\text{S})}[\text{Cat}]$	$AN_E^{\text{a,b)}}$	$DN_B^{\text{a,c)}}$	$\pi^{*\text{d)}}$	$\alpha^{\text{d)}}$	$\beta^{\text{d)}}$
		(α , β)	$\text{dm}^3 \text{mol}^{-1}$	$10^{-6} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \text{g}^{-1}$					
1	Octane (O)	—	0	—	—	—	(-0.08 ^f)	(0.00 ^f)	(0.00 ^f)
2	Toluene (T)	1	0.133	0.00	3.3	3.9	0.54	0.00	0.11
3	Anisole (L)	1	0.205	0.00	7.6	7.9	0.73	0.00	0.22
4	Dibutyl ether (R)	1	0.384	9.36	2.6	18.1	0.24	0.00	0.46
5	1-Butanol ^{e)} (A)	1	0.823	4.23	24.4	24.0	0.47	0.79	0.88 ^{g)}
6	1,4-Dioxane (D)	1	2.08	4.86	6.0	18.0	0.55	0.00	0.37
7	2-Butanol ^{e)} (B)	2	2.59 ^{h)}	4.86	—	—	—	—	—
8	Water ^{e)} (W)	1	6.07	0.00	41.0	17.0	1.09	1.17	0.18 ^{g)}
9	Dimethyl sulfoxide (U)	1	9.88	0.00	17.6	30.1	1.00	0.00	0.76

a) Values taken from Ref. 22. b) AN_E values are calculated from the E_T values using $AN_E = -40.52 + 1.29E_T$.

c) DN_B values are calculated from the B^* or B values using $DN_B = -6.36 + 0.19B^*$. d) Values taken from Ref. 19.

e) Highly-structured protic solvents. f) Values of hexane and heptane. g) Data are relatively less certain.

h) $\text{dm}^6 \text{mol}^{-2}$.

These correlation coefficients for Eqs. 6 and 7 are not statistically acceptable. This result is consistent with the information¹⁵⁾ that the extent of ionization is governed by the ability of a solvent to heterolyze covalent bonds and not by its dipolar characteristics, such as the dipole moment or the dielectric constant.

Recently, an empirical solvent scale based on the solvatochromic comparison method¹⁶⁾ and an equation based on the linear solvation energy relationship,¹⁷⁻¹⁹⁾ which expresses the role of the contributions of individual types of solvent-solute interactions, have been proposed by Kamlet, Taft, and their co-workers.²⁰⁾ In general form, this solvatochromic equation is given by

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta, \quad (8)$$

where XYZ is the measured quantity (a free energy or heat of transfer between solvents, the logarithm of a reaction rate or an equilibrium constant, etc.) in the given solvent, and where XYZ_0 is the same quantity obtained for a reference solvent. The π^* scale is an index of solvent dipolarity/polarizability (SPP). The α scale of hydrogen-bond donor (HBD) acidities describes the ability of the solvent to donate a proton. Similarly, the β scale of hydrogen-bond acceptor (HBA) basicities expresses the solvent's ability to accept a proton (donate an electron pair). The s , a , and b terms in Eq. 8 are measures of the responses of XYZ to changing SPP, HBD acidity and HBA basicity; they are called the solvatochromic coefficients.

For the seven solvents whose solvatochromic parameters are known, the multiple-parameter least-squares correlation of $\ln K_{\text{sol}}^{(\text{S})}$ with the π^* , α , and β values leads to

$$\ln K_{\text{sol}}^{(\text{S})} = -3.72 + 3.88\pi^* + 0.26\alpha + 2.57\beta, \quad (9)$$

$$R = 0.827.$$

If the data for 1-butanol and water, which are highly-structured protic solvents, are excluded, a correlation equation with an acceptable correlation coefficient,

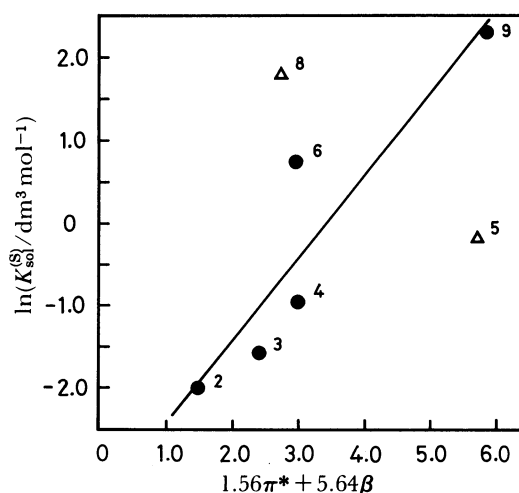


Fig. 4. Relationship between equilibrium constants ($K_{\text{sol}}^{(\text{S})}$) and solvatochromic parameters (π^* and β). Δ ; Highly-structured protic solvents.

represented by the regression line in Fig. 4, is given by

$$\ln K_{\text{sol}}^{(\text{S})} = -3.43 + 1.56\pi^* + 5.64\beta, \quad (10)$$

$$R = 0.917.$$

It is considered that, since the data points representing 1-butanol and water, which can also act as stronger hydrogen-bond donors, are not displaced from the regression line in the same direction in Fig. 4, there is no contribution of solvent HBD acidities to the $K_{\text{sol}}^{(\text{S})}$. Furthermore, because the π^* , α , and β parameters are roughly normalized to cover the range from near 0.0 to near 1.0,¹⁹⁾ the b/s (5.64/1.56) ratio obtained from Eq. 10 may indicate that the positions of the equilibria of solvent-separated ion-pair formations depend largely on the solvent HBA basicities.

In contrast to the solvatochromic parameter scales of Kamlet and Taft, Gutmann and his coworkers^{15,21)} have proposed a "donor-acceptor" approach to describe the total solvent effects in terms of the electron-donor and electron-acceptor properties of the solvent.

As quantitative measures of these solvent properties, two empirical parameter scales, termed "donor number" (DN) and "acceptor number" (AN), have been introduced. The DN was defined as the negative ΔH° value for the interaction between the reference acid, $SbCl_5$, and a basic solvent in a highly dilute 1,2-dichloroethane solution. The AN was derived from the infinite-dilution ^{31}P NMR solvent shifts (relative to hexane) of triethylphosphine oxide in the bulk solvents.

The plot of $\ln K_{sol}^{(S)}$ vs. $DN_B^{(22)}$ values is shown in Fig. 5. If the points for the highly-structured protic solvents are excluded, the correlation with DN_B leads to

$$\ln K_{sol}^{(S)} = -2.857 + 0.163DN_B, \quad R = 0.934. \quad (11)$$

With the allowance of a partial dependence on AN_E also, the multiple linear regression equation becomes

$$\ln K_{sol}^{(S)} = -2.918 + 0.082AN_E + 0.129DN_B, \quad R = 0.953. \quad (12)$$

The $\ln K_{sol}^{(S)}$ values are plotted against the values of $0.082AN_E + 0.129DN_B$ in Fig. 6. By a consideration of the small difference in the magnitude of the correlation coefficient between the two linear regression analyses, it is found that $K_{sol}^{(S)}$ is sensitive mainly to the donor ability of solvents. A comparison of Eqs. 11 and 12 with Eq. 10 shows that the correlations with Gutmann's parameters are somewhat better than those with the solvatochromic parameters. However, since no normalization of the AN_E and DN_B parameters has been carried out, the relative contributions of the individual solvent properties can not be discussed by a direct comparison of the coefficient value of AN_E with that of DN_B .

Taft et al.¹⁸⁾ have examined the relationships between Gutmann's AN and DN and the solvatochro-

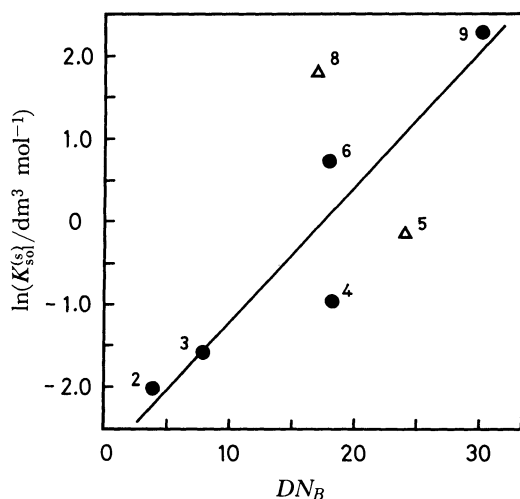


Fig. 5. Relationship between equilibrium constants ($K_{sol}^{(S)}$) and solvent donor numbers (DN_B). Δ ; Highly-structured protic solvents.

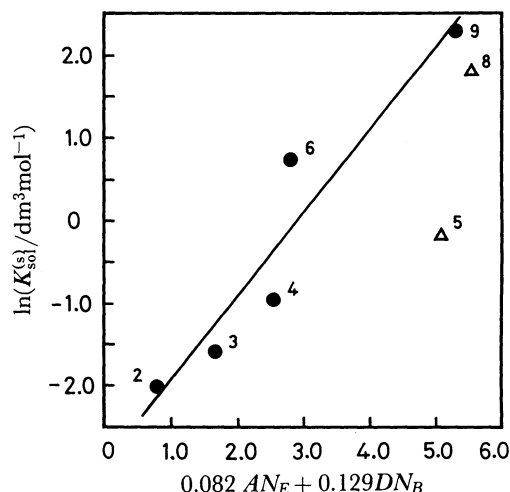


Fig. 6. Relationship between equilibrium constants ($K_{sol}^{(S)}$) and solvent acceptor and donor numbers (AN_E and DN_B). Δ ; Highly-structured protic solvents.

mic parameters, π^* , α , and β ; they have reported that AN correlates well with a linear combination of π^* and α , and that DN is linear with β when the result for pyridine is excluded. Therefore, it seems that the significance of the correlation (Eq. 12) with Gutmann's parameters is essentially the same as that (Eq. 10) with the solvatochromic parameters. These significations are in harmony with Gutmann's description²³⁾ that the formation of solvent-separated ion pairs is primarily influenced by the coordinating properties of the solvent.

As is shown in Table 1, the protons produced by the interaction of the sulfo groups with anisole and toluene, whose $K_{sol}^{(S)}$ values are relatively small, have no catalytic activity as those with water and dimethyl sulfoxide: $k_{phom}^{(S)} K_{phom}^{(S)} [Cat] = 0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ g}^{-1}$. This result may indicate that, when the resins are immersed in anisole and toluene, some of the sulfo groups residing on the surface of the microspheres exist as contact ion pairs (or intimate ion pairs),²⁴⁾ in which cations and anions are considered to be in immediate contact with each other, rather than as solvent-separated ion pairs.

In conclusion, if the solvents with a strong electron-donor property are employed as diluents in the esterification with the macroreticular sulfonic acid resin, this donor property diminishes the number of unionized sulfo groups which act as catalytic species for the heterogeneous reaction and, consequently, a decrease in the total catalytic activity is observed. Hence, it can be presumed that the extent of the selectivity of the resin catalyst related to the alkyl chain length of normal fatty acids, which was reported in an earlier paper,¹⁰⁾ also decreases.

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Notation

A	1-Butanol
F	Octanoic acid
W	Water
E	Butyl octanoate
O	Octane
T	Toluene
L	Anisole
R	Dibutyl ether
D	1,4-Dioxane
B	2-Butanol
U	Dimethyl sulfoxide
X	Additional solvent (O,T,L,R,D,B, or U)
k_2	Specific rate constant, calculated by assuming that the esterification was second-order, $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
D	Dielectric constant of the reaction medium
r	Reaction rate, $\text{mol dm}^{-3} \text{s}^{-1}$
[Cat]	Number of sulfo groups participating in the reaction per g of the resin catalyst, mol of sulfo groups g^{-1}
M	Amount of the resin catalyst, g
$\textcircled{P}\text{--SO}_3\text{H}$	Matrix-bound sulfo group which is not ionized
$\textcircled{P}\text{--SO}_3^-/\gamma\text{X}/\text{H}^+$	Solvent-separated ion pair
α, β, γ	Number of molecules participating in solvation
k_{het}	Specific rate constant for the heterogeneous chemisorption reaction of fatty acid, s^{-1} (mol of $\text{--SO}_3\text{H}$ groups participating in the reaction) $^{-1}$
$K_{\text{sol}}^{(\text{A})}, K_{\text{sol}}^{(\text{W})}, K_{\text{sol}}^{(\text{X})}$	Equilibrium constants for solvent-separated ion-pair formations, $\text{dm}^3 \text{mol}^{-1}$ (except $K_{\text{sol}}^{(\text{B})}/\text{dm}^6 \text{mol}^{-2}$)
$k_{\text{phom}}^{(\text{A})}, k_{\text{phom}}^{(\text{X})}$	Specific rate constants for the pseudo-homogeneous reactions of the protonated fatty acid with alcohol, $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ (mol of $\text{--SO}_3\text{H}$ groups) $^{-1}$
$K_{\text{phom}}^{(\text{A})}, K_{\text{phom}}^{(\text{X})}$	Equilibrium constants for the protonations of fatty acid, dimensionless

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