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Kinetic Study of Liquid-Phase Esterification with Sulfonic Acid Cation-Exchange Resin of the Macroreticular Type. I. Heterogeneous-Pseudohomogeneous Resin Catalysis[1)]

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The rates of the esterification of octanoic acid with 1-butanol catalyzed by macroreticular sulfonated ion-exchange resin were measured by the use of a batch reactor. The effects on the rate were investigated for variations in the amount of the catalyst, the temperature, and the reactant alcohol concentrations as well as those of water and butyl octanoate. From these data, it is considered that alcohol and water solvate the matrix-bound sulfo groups, and so this esterification system consists of a heterogeneous reaction catalyzed by un-ionized sulfo groups and a pseudo-homogeneous reaction catalyzed by solvated protons; in other words, catalysis by sulfonic acid resin is both heterogeneous and pseudo-homogeneous in liquid-phase esterification.

In organic reactions catalyzed by acids or bases, the use of ion-exchange resins as catalysts offers the following advantages over that of homogeneous catalysts:[2—4)] (1) the resins are easily separated from the reaction mixture, (2) undesirable side reactions are frequently avoided, (3) resin catalysis can afford a degree of selectivity unattainable in homogeneous catalysis, (4) resins permit operation in either continuous or batch processes, and (5) corrosion is eliminated or reduced significantly. Therefore, experimental studies of the use of resin as catalysts have been carried out on many reactions. The major groups of these reactions are acetal-formation, dehydration, esterification, etherification, hydration, hydrolysis, and isomerization. The range of practical application of ion-exchange catalysts has, consequently, been extended. Theoretical problems in ion-exchange catalysis have also been discussed in several reviews.[5—7)]

The esterification of acids with alcohols, which is one of the most active areas for the application of resin catalysis, has usually been catalyzed by the use of a sulfonic acid cation-exchanger and has been carried out in both gas[8—10)] and liquid phases.[11—22)] Kinetic studies of the esterification have been reported in numerous reports on the reaction. In gas-phase esterification, it is known that the experimental data agree well with the estimate obtained by the use of a Langmuir-Hinshelwood model, which demonstrates that the resin catalysis is heterogeneous.[8,10)] In the case of liquid-phase esterification, several authors have preferred Helfferich's classical explanation[23)] based on a pseudo-homogeneous system assumption,[11,13—21)] although others have reported that the kinetics of heterogeneous catalytic reactions provide a satisfactory fit of the data.[12,21)] At present, there is no unified opinion about the liquid-phase catalysis with sulfonic acid resin, as has been mentioned above. Gates and his co-workers, however, pointed out that an excess of water or alcohol can shift the catalytic species from the more active undissociated sulfonic acid (general acid catalysis) to the less active solvated proton (specific acid catalysis), which was substantiated by a series of fundamentally important investigations of the dehydration of 2-methyl-2-propanol,[24)] olefin and paraffin formation from butyl alcohols,[25)] and benzene propylation.[26)] Recently, Gomzi et al.[21)] studied the kinetics of the esterification of acetic acid with 1-butanol catalyzed by sulfonic acid resin of the standard type; they reported that the best model for explaining the reaction rate with a partially wet ion-exchanger (27% water contents) is obtained by assuming a pseudo-homogeneous system, while the kinetics of a dry one is best represented by a model derived from assumptions based on a heterogeneous system. However, in the report of Gomzi et al.[21)] the catalytic species in these reactions were not mentioned at all.

In this work we have measured the kinetics of the esterification of octanoic acid with 1-butanol catalyzed by macroreticular sulfonic acid resin (Amberlyst 15) in order to clarify the catalysis by the resin in liquid-phase esterification. Furthermore, this work should help to elucidate the selectivity behavior of the resin catalyst in relation to the alkyl-chain length of normal fatty acids, which was reported in the preceding paper.[22)]

Experimental

Catalyst Preparation and Materials. A macroporous sulfonated copolymer of styrene and divinylbenzene was prepared from commercial ion-exchange resin, Amberlyst 15. The resin, 0.59—0.84 mm particles, was washed with distilled water and cycled between the hydrogen and sodium forms according to a conventional column method. The hydrogen-form resin to be used as a catalyst was dried in an oven at a temperature below 110 °C to 5.81% water and then stored in a desiccator in sealed vials over silica gel. The ion-exchange capacity was 4.99 meq/g of dry resin.

Guaranteed reagent-grade octanoic acid and butyl octanoate were used without further purification. The toluene and 1-butanol were purified by distillation, and then the former was dried over anhydrous magnesium sulfate.

Reaction-Rate Measurement. The esterification with an ion-exchanger as a catalyst was usually measured at 80±0.05 °C in a 100-ml three-necked flask equipped with a magnetic stirrer (about 250 rpm) and a condenser, and heated in an oil bath. In all experiments, the volume of the reaction mixture, consisting of octanoic acid, 1-butanol, and toluene as a diluent, was kept constant at 30 ml. A timer was started on the addition of the catalyst to the reactor, and 40-μl samples were removed by using a microsyringe at appropriate time intervals and then transferred to individual capped microtubes containing a toluene solution of hexadecane as an internal standard. For gas-chromatographic (GC) analysis, samples of about 1—2 μl were taken from these microtubes. The only product detected, except water, was butyl octanoate. Therefore, the rates were determined from the ester analyses. The molar concentrations of the ester in each original sample were obtained by determining the ratio of the areas of the ester peaks to that of the hexadecane peak and by comparing these with the calibration curves.

The instrument used to carry out the GC analyses and the operating conditions were described in detail in an earlier paper.[22]

Results

Catalyst Amount and Temperature Dependence of Apparent Rate Constant. For determining the order of octanoic acid, the half-life periods were measured under the following conditions: initial concentration of 1-butanol, 7.29 mol dm^{-3}; amount of resin, 1.50 g. Figure 1 shows that the dependence of the rate on the concentration of acid is first-order under these experimental conditions. In addition, it is confirmed, by a comparison with the order obtained in the preceding study,[22] that the toluene used as a diluent does not affect the order. The rate of reaction is represented by

$$r = k'_{\text{obsd}}[\text{F}]. \qquad (1)$$

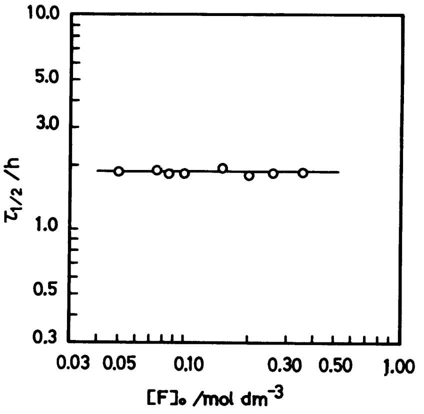

Fig. 1. Relationship between initial concentration of octanoic acid ($[\text{F}]_0$) and half life of esterification ($\tau_{1/2}$).

As is shown in Fig. 2, the pseudo-first-order rate constants, k'_{obsd}, were directly proportional to the amount of the resin catalyst. Hence, the specific rate constant, k_{obsd}, was introduced

$$k_{\text{obsd}} = k'_{\text{obsd}}/M. \qquad (2)$$

The logarithm of k_{obsd} vs. the reciprocal of the absolute temperature, that is, the Arrhenius-type plot, is shown in Fig. 3. As can be seen from the figure, a good straight line was obtained. From the slope of this line, an apparent activation energy of about 14 kcal† mol^{-1} was estimated; this is consistent with the finding of a previous work[22] that neither bulk diffusion nor pore diffusion is a limiting step.

Effects of Alcohol, Water, and Ester. The influence of the concentration of 1-butanol upon the reaction rate is shown in Fig. 4, while the cases of water and butyl octanoate instead of 1-butanol are represented in Figs. 5 and 6 respectively. Water inhibited the reaction, as is shown by the results of Fig. 5, but the ester did not affect the rate over the present range of experimental conditions. In all the

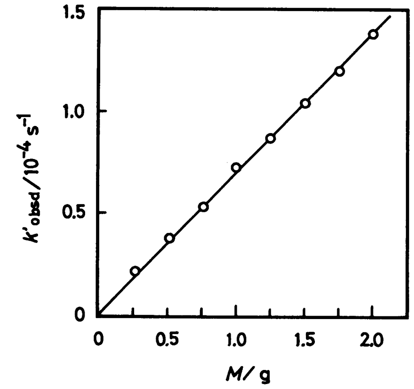

Fig. 2. Dependence of pseudo-first-order rate constant (k'_{obsd}) on amount of Amberlyst 15 (M).

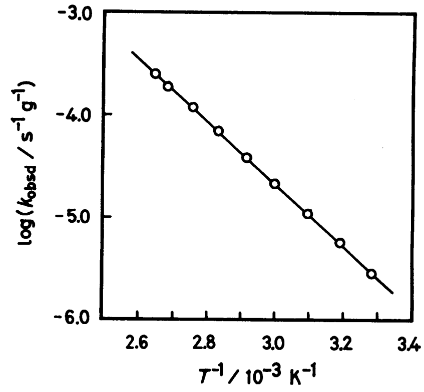

Fig. 3. Dependence of specific rate constant (k_{obsd}) on reaction temperature (T).

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† 1 cal=4.184 J.

runs denoted in Figs. 4—6, the initial concentration of octanoic acid and the amount of resin were held constant at 0.150 mol dm^{-3} and 1.75 g respectively. The ester-concentration increments from 0.0200 to 0.0400 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 appeared rarely and an initial reaction rate could not be employed.

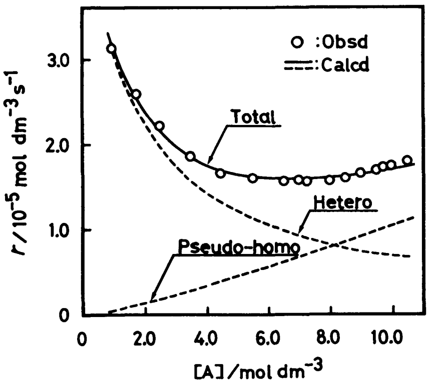


Fig. 4. Influence of concentration of 1-butanol ([A]) upon reaction rate (r).
[F]=0.120 mol dm^{-3}, [W]=0.030 mol dm^{-3}.

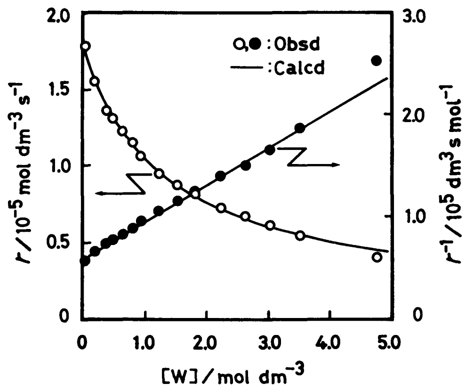


Fig. 5. Influence of concentration of water ([W]) upon reaction rate (r).
[F]=0.120 mol dm^{-3}, [A]=9.8 mol dm^{-3}.

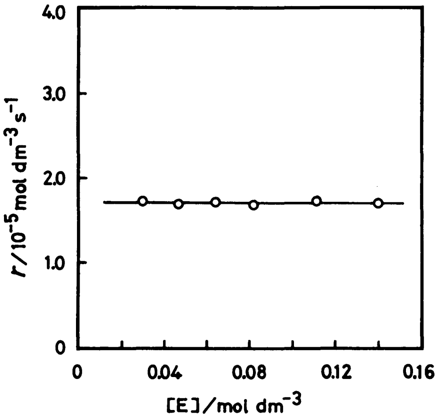


Fig. 6. Influence of concentration of butyl octanoate ([E]) upon reaction rate (r).
[F]=0.120 mol dm^{-3}, [A]=9.7 mol dm^{-3}.

Discussion

Evaluation of Effects of Resin Swelling and the Dielectric Constant of the Reaction Medium on the Rate. Amberlyst 15, which consists of aggreates of very small gelular microspheres, presumably consists of about 20% divinylbenzene.[27] At cross-linker levels above 12%, the resin matrix exhibits great resistance to swelling.[2] Therefore, it is considered[22,27,28] that the gelular microspheres are not greatly swollen by the reaction medium and that only the sulfo groups residing on the surface of the microspheres[29] are available for a catalytic reaction. This conclusion is supported by the curve shown in Fig. 4, for if 1-butanol causes a swelling of the microsphere gel network,[30] the number of directly accesible sulfo groups should decrease with the decrease in its concentration in a reaction solution, and the catalytic activity of the resin should consequently diminish. All this is contrary to the observed curve. From the above evaluation of the resin swelling, it seems that the assumption of Helfferich[23] can not be applied in this case.

The results obtained from Figs. 4 and 5 can not be used in the treatment of the solvent effects for a reaction between a neutral dipolar molecule and a positive ion as the rate-controlling step, because the plot of ln k_2 against $1/D$ is found to be nonlinear.

Nature of the Acid Site in the Resin and Kinetic Analysis. It is considered from Fig. 5 that the product water solvates the matrix-bound sulfo groups and then depresses the catalytic rate.[12,24,25,27,31] Appropriate polar molecules such as alcohol may also participate in a similar solvation to water.[32] Since the ester did not inhibit the reaction, and since the solvating power of the toluene used as a diluent is negligibly small, it is considered that water and alcohol behave as solvating agents under the present reaction conditions. These solvation equilibria may be written as

$$\alpha\text{A} + \text{Ⓟ-SO}_3\text{H} \xrightleftharpoons{K_{\text{sol}}^{(\text{A})}} \text{Ⓟ-SO}_3{}^-/\alpha\text{A}/\text{H}^+, \tag{3}$$

$$\beta\text{W} + \text{Ⓟ-SO}_3\text{H} \xrightleftharpoons{K_{\text{sol}}^{(\text{W})}} \text{Ⓟ-SO}_3{}^-/\beta\text{W}/\text{H}^+. \tag{4}$$

The solvated protons also become catalytic agents.[33] However, it is thought that the specific activity of the hydrated protons is negligible compared with that of those solvated with alcohol; therefore, this 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.

Based on these considerations and the fact that the reaction was first-order in its concentration of fatty acid, the following reaction mechanism may be assumed

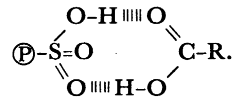
$$\mathrm{F} + \text{Ⓟ-SO}_3\mathrm{H} \xrightarrow{k_{\mathrm{het}}} \text{Ⓟ-SO}_3\mathrm{H} \cdots \mathrm{F}, \tag{5}$$

$$\mathrm{A} + \text{Ⓟ-SO}_3\mathrm{H} \cdots \mathrm{F} \overset{K_{\mathrm{het}}}{\rightleftarrows} \mathrm{E} + \mathrm{W} + \text{Ⓟ-SO}_3\mathrm{H}, \tag{6}$$

$$\mathrm{F} + \text{Ⓟ-SO}_3{}^-/\alpha\mathrm{A}/\mathrm{H}^+ \overset{K^{(\mathrm{A})}_{\mathrm{phom}}}{\rightleftarrows} \text{Ⓟ-SO}_3{}^-/\alpha\mathrm{A} + \mathrm{HF}^+, \tag{7}$$

$$\mathrm{A} + \mathrm{HF}^+ + \text{Ⓟ-SO}_3{}^-/\alpha\mathrm{A} \xrightarrow{k^{(\mathrm{A})}_{\mathrm{phom}}} \mathrm{E} + \mathrm{W} + \text{Ⓟ-SO}_3{}^-/\alpha\mathrm{A}/\mathrm{H}^+. \tag{8}$$

Reaction (5) corresponds to the chemisorption of octanoic acid on the acid site in the resin, and it appears that the fatty-acid molecule is associated with the un-ionized sulfo group by means of the formation of a doubly hydrogen-bonded structure:[34)]



If the Ⓟ-SO3H $\cdots$ F and HF+ species are present in very small amounts, which implies $K_{\mathrm{het}} \gg 1 \gg K^{(\mathrm{A})}_{\mathrm{phom}}$, the following equation can be set up

$$[\mathrm{Cat}] = [\text{Ⓟ-SO}_3\mathrm{H}] + [\text{Ⓟ-SO}_3{}^-/\alpha\mathrm{A}/\mathrm{H}^+] + [\text{Ⓟ-SO}_3{}^-/\beta\mathrm{W}/\mathrm{H}^+]. \tag{9}$$

For the two equilibria (3) and (4), it is possible to write as follows:

$$[\text{Ⓟ-SO}_3{}^-/\alpha\mathrm{A}/\mathrm{H}^+] = K^{(\mathrm{A})}_{\mathrm{sol}}[\mathrm{A}]^\alpha[\text{Ⓟ-SO}_3\mathrm{H}], \tag{10}$$

$$[\text{Ⓟ-SO}_3{}^-/\beta\mathrm{W}/\mathrm{H}^+] = K^{(\mathrm{W})}_{\mathrm{sol}}[\mathrm{W}]^\beta[\text{Ⓟ-SO}_3\mathrm{H}]. \tag{11}$$

The substitution of (10) and (11) into (9) gives

$$[\text{Ⓟ-SO}_3\mathrm{H}] = [\mathrm{Cat}]/(1+K^{(\mathrm{A})}_{\mathrm{sol}}[\mathrm{A}]^\alpha+K^{(\mathrm{W})}_{\mathrm{sol}}[\mathrm{W}]^\beta). \tag{12}$$

The rate of the heterogeneous reaction which contains the chemisorption reaction (5) as its rate-determining step is represented by

$$r_{\mathrm{het}} = k_{\mathrm{het}}[\mathrm{F}][\text{Ⓟ-SO}_3\mathrm{H}]M. \tag{13}$$

Equation (13) may be transformed into

$$r_{\mathrm{het}} = \frac{k_{\mathrm{het}}[\mathrm{F}][\mathrm{Cat}]M}{1+K^{(\mathrm{A})}_{\mathrm{sol}}[\mathrm{A}]^\alpha+K^{(\mathrm{W})}_{\mathrm{sol}}[\mathrm{W}]^\beta}. \tag{14}$$

For the pseudo-homogeneous reaction, where only the protonated form of fatty acid HF+ reacts with alcohol at a measurable rate, the rate equation is given by

$$r_{\mathrm{phom}} = k^{(\mathrm{A})}_{\mathrm{phom}}[\mathrm{A}][\mathrm{HF}^+][\text{Ⓟ-SO}_3{}^-/\alpha\mathrm{A}]M. \tag{15}$$

Equilibrium (7) can be expressed by

$$[\mathrm{HF}^+][\text{Ⓟ-SO}_3{}^-/\alpha\mathrm{A}] = K^{(\mathrm{A})}_{\mathrm{phom}}[\mathrm{F}][\text{Ⓟ-SO}_3{}^-/\alpha\mathrm{A}/\mathrm{H}^+], \tag{16}$$

and by using Eqs. (10), (12), and (16) r_{phom} is given as follows:

$$r_{\mathrm{phom}} = \frac{k^{(\mathrm{A})}_{\mathrm{phom}}K^{(\mathrm{A})}_{\mathrm{phom}}K^{(\mathrm{A})}_{\mathrm{sol}}[\mathrm{F}][\mathrm{A}]^{\alpha+1}[\mathrm{Cat}]M}{1+K^{(\mathrm{A})}_{\mathrm{sol}}[\mathrm{A}]^\alpha+K^{(\mathrm{W})}_{\mathrm{sol}}[\mathrm{W}]^\beta}. \tag{17}$$

Therefore, the total reaction rate is expressed by

$$r = \frac{\{k_{\mathrm{het}}[\mathrm{F}]+k^{(\mathrm{A})}_{\mathrm{phom}}K^{(\mathrm{A})}_{\mathrm{phom}}K^{(\mathrm{A})}_{\mathrm{sol}}[\mathrm{F}][\mathrm{A}]^{\alpha+1}\}[\mathrm{Cat}]M}{1+K^{(\mathrm{A})}_{\mathrm{sol}}[\mathrm{A}]^\alpha+K^{(\mathrm{W})}_{\mathrm{sol}}[\mathrm{W}]^\beta}. \tag{18}$$

The straight line in the plot of [W] vs. $1/r$ in Fig. 5 indicates that the sulfo groups are solvated by one molecule of water per group at values of $[\mathrm{W}]<4$ mol dm^{-3}: $\beta=1$. Therefore, the data shown in Figs. 4 and 5 were compared with the values calculated from Eq. (18), in which $\beta=1$ had been substituted. In order to determine the optimum values of $k_{\mathrm{het}}[\mathrm{Cat}]$, $k^{(\mathrm{A})}_{\mathrm{phom}}K^{(\mathrm{A})}_{\mathrm{phom}}[\mathrm{Cat}]$, $K^{(\mathrm{A})}_{\mathrm{sol}}$, and $K^{(\mathrm{W})}_{\mathrm{sol}}$ for integral values of the α exponent ranging from one to three, the sum of the squares of deviations of the predicted rates from the observed ones has been calculated with a computer. The most precise representation is given by

$$r = \frac{\{k_{\mathrm{het}}[\mathrm{F}]+k^{(\mathrm{A})}_{\mathrm{phom}}K^{(\mathrm{A})}_{\mathrm{phom}}K^{(\mathrm{A})}_{\mathrm{sol}}[\mathrm{F}][\mathrm{A}]^2\}[\mathrm{Cat}]M}{1+K^{(\mathrm{A})}_{\mathrm{sol}}[\mathrm{A}]+K^{(\mathrm{W})}_{\mathrm{sol}}[\mathrm{W}]}, \tag{19}$$

where the values of $k_{\mathrm{het}}[\mathrm{Cat}]$, $k^{(\mathrm{A})}_{\mathrm{phom}}K^{(\mathrm{A})}_{\mathrm{phom}}[\mathrm{Cat}]$, $K^{(\mathrm{A})}_{\mathrm{sol}}$, and $K^{(\mathrm{W})}_{\mathrm{sol}}$ were 2.85×10^{-4} s^{-1} g^{-1}, 5.66×10^{-6} dm^3 mol^{-1} s^{-1} g^{-1}, 0.769 dm^3 mol^{-1}, and 5.30 dm^3 mol^{-1} respectively. In view of the polarity of 1-butanol and water, it seems reasonable that the equilibrium constant, $K^{(\mathrm{W})}_{\mathrm{sol}}$, is greater than the $K^{(\mathrm{A})}_{\mathrm{sol}}$.

When the values calculated from Eq. (19) are compared to the data in Figs. 4 and 5, the agreement between the observed and calculated values is satisfactory. These results give support to the assumptions that this esterification involves both the heterogeneous and pseudo-homogeneous catalyses and that, in the heterogeneous one, the rate-determining step is the chemisorption reaction of fatty acid. As may be seen from Fig. 4, at the lower alcohol concentrations the rate of the heterogeneous reaction catalyzed by the un-ionized sulfo groups[35)] substantially governs the total reaction rate, while at the higher ones the rate is roughly equal to that of a pseudo-homogeneous reaction catalyzed by the solvated protons with alcohol.

It is considered that, since the positions of equilibria (3), (4), and (7) are affected by the reaction temperature, the activation energy for both the heterogeneous and pseudo-homogeneous reactions are different from the apparent one estimated from the slope of the straight line in Fig. 3. Furthermore, it is presumed that the selectivity behavior of the resin catalyst related to the alkyl-chain length of normal fatty acids, which was reported in the preceding paper,[22)] is due to differences in the rate constant, k_{het}, for the heterogeneous chemisorption reaction (5).

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Notation

A	1-Butanol
E	Butyl octanoate
F	Octanoic acid
W	Water
M	Amount of resin catalyst, g
T	Absolute temperature, K
D	Dielectric constant of reaction medium
r	Reaction rate, mol dm^{-3} s^{-1}
k'_{obsd}	Pseudo-first-order rate constant, s^{-1}
k_{obsd}	Pseudo-first-order rate constant per g of resin catalyst, s^{-1} g^{-1}
k_2	Specific rate constant, calculated by assuming that the esterification was second-order, dm^3 mol^{-1} s^{-1} g^{-1}
[Cat]	Number of sulfo groups participating in the reaction per g of resin catalyst, mol of sulfo groups g^{-1}
Ⓟ-SO_3H	Matrix-bound sulfo groups which are not ionized
Ⓟ-$SO_3^-/\alpha A/H^+$, Ⓟ-$SO_3^-/\beta W/H^+$	Solvent-separated ion pair
α,β	Number of molecules participating in solvation
r_{het}, r_{phom}	Rates of heterogeneous and pseudo-homogeneous reactions with ion-exchange resin, mol dm^{-3} s^{-1}
k_{het}, $k^{(A)}_{\mathrm{phom}}$	Specific rate constants for the reactions represented by Eq. (5) and (8), s^{-1} (mol of -SO_3H groups participating in the reaction)$^{-1}$ and dm^{-3} mol^{-1} s^{-1} (mol of -SO_3H groups)$^{-1}$, respectively
$K^{(A)}_{\mathrm{sol}}$, $K^{(W)}_{\mathrm{sol}}$	Equilibrium constants for solvent-separated ion-pair formations (3) and (4), dm^3 mol^{-1} (α, β=1)
K_{het}, $K^{(A)}_{\mathrm{phom}}$	Equilibrium constants for reactions (6) and (7), dm^3 mol^{-1} and no dimension, respectively

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35) The proportion of the un-ionized sulfo groups is given by

$$[\text{Ⓟ-SO}_3\text{H}]/[\text{Cat}] = 1/(1+K^{(A)}_{\text{sol}}[\text{A}]+K^{(W)}_{\text{sol}}[\text{W}]).$$

For example, when the concentrations of 1-butanol are 2.00, 6.00, and 10.00 mol dm^{-3}, the proportions are calculated to be 0.371, 0.173, and 0.113 respectively. From these proportions and the values of r_{het} and r_{phom} for each solution composition, it is considered that the un-ionized sulfo groups are very active compared to the solvated protons with alcohol.