Effect of solvent on the kinetics of hydration of 2-methylpropene catalyzed by strong-acid ion exchangers

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EFFECT OF SOLVENT ON THE KINETICS OF THE HYDRATION OF 2-METHYLPROPENE CATALYZED BY STRONG ACID ION EXCHANGERS

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Summary

The hydration of 2-methylpropene, catalyzed by strong acid ion exchange resins, was investigated in solvent mixtures of water and either 1,4-dioxan or sulfolane at 25.0 °C. A gel type, an intermediate type and a macroporous resin were all investigated. It appeared that the macroporous resin is the most active catalyst for almost all solvent compositions investigated. The influence of the solvent composition on the rate of the hydration reaction can be explained by the acidity of the acid groups of the resin and by the distribution coefficient, λ , of the alkene defined as the concentration ratio at equilibrium between the resin phase and the liquid phase surrounding the catalyst particles. The solvent also determines the value of the distribution coefficient, λ , of the alkene between the resin phase and bulk liquid. For one resin this effect was determined quantitatively.

A complicating effect is the difference in the composition of the solvent in the resin phase and in the bulk liquid. For mol fractions of the cosolvent above 40%, it appeared that the concentration of sulfolane in the resin phase is considerably larger than that of 1,4-dioxan. As a consequence, the distribution coefficient of the alkene over the resin phase and the surrounding liquid is much higher for mixtures of sulfolane and water than for mixtures of 1,4-dioxan and water. This results in considerably higher hydration rates for sulfolane-water than for the 1,4-dioxan-water mixtures of comparable compositions.

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Introduction

Strong acid ion exchange resins are interesting catalysts for the hydration of alkenes. For example a strong acid ion exchange resin is used for the industrial production of 2-propanol from propene and water, using water as the continuous phase [1 - 3]. The production rates of alkanols per unit of volume of the resin with water as solvent are strongly limited by low solubilities of the alkenes in water, however. Trying to push the rate by increasing the temperature fails as a consequence of the relatively low thermal stability of the catalyst. For temperatures above 150 °C the catalyst deactivates rather quickly as a result of thermal dissociation of the acid groups from the polymer backbone [4].

From the results of a kinetic study of the hydration of *n*-butenes in water catalyzed by a strong acid ion exchange resin [5], it was derived that a production of 5×10^7 kg 2-butanol per annum requires a reactor volume between 100 and 200 m³ [6], which is too large for an economic process. The required volume may be expected to be considerably smaller when instead of pure water homogeneous mixtures of water and an organic co-solvent are used as the liquid phase. The higher solubility of the alkenes in these mixtures will increase the rate of reaction of the alkenes. Some promising examples of the use of the cosolvents 1,4-dioxan and sulfolane are presented in the patent literature [7 - 9].

In the present study the influence of the cosolvents 1,4-dioxan and sulfolane on the rate of hydration of 2-methylpropene is investigated for reactions catalyzed by some types of strong acid ion exchange resins. All resins are completely sulfonated copolymers of styrene and divinylbenzene. In contrast to the hydration of the *n*-butenes, the hydration of 2-methylpropene has a substantial rate already at room temperature and the kinetics are not complicated by side reactions.

In a previous study on the rate of hydration of 2-methylpropene in homogeneous solutions of *p*-toluenesulfonic acid and poly(styrenesulfonic acid) in binary mixtures of 1,4-dioxan and water or sulfolane and water, it was found that the reaction rate is strongly influenced by addition of the cosolvent [10]. From the results collected in this paper, together with those of the previous study, it can be concluded that sulfolane is a suitable co-solvent for the enhancement of the rate of hydration of alkenes heterogeneously catalyzed by strong acid ion exchange resins.

Experimental

Materials

2-Methylpropene and *cis*-2-butene were obtained from Matheson (purity more than 99%).

The ion exchange resins Amberlite IR-120, XE-307 and IMAC C16P were obtained from Serva, Rohm and Haas, and Duolite International,

respectively. These resins are completely sulfonated copolymers of styrene and divinylbenzene and are of the gel type, the intermediate type and the macroreticular type, respectively. Amberlite IR-120 and Imac C16P contain 8 and 16% divinylbenzene, respectively. The divinylbenzene content of XE-307 is not given by the manufacturer. The elemental composition of this resin in wt.% is 45.4% C, 3.7% H, 24.45% O, 13.8% S and 12.5% Cl.

The mol fraction of the cosolvent in the resin particles as a function of the composition of the surrounding liquid (= bulk liquid) and the distribution coefficient of the alkene over the swollen resin and the bulk liquid were determined for resin samples of particle sizes between 0.9×10^{-3} m and 1.0×10^{-3} m for Amberlite IR-120 and between 0.6×10^{-3} m and 0.71×10^{-3} m for XE-307. For Imac C16P, the solvent compositions in the resin phase and the distribution coefficients of the alkene were not determined.

The desired particle size fractions were sieved out from the commercially obtained resins. During the sieving process, the ion exchange resin was kept wet with tap water. The sieve fractions were transferred into a glass column and were cycled two times between the H^+ - and the Na^+ -form using 4 M HCl and NaCl solutions in doubly distilled water. After each exchange step, the resin was washed with doubly distilled water until no Cl^- -ions could be detected in the effluent. The adhering water was removed from the resin by centrifugation at $\sim 3000 \text{ m s}^{-2}$.

For the kinetic experiments, the commercially obtained resins were first treated as described above. To obtain reliable kinetic data, it is important that intraparticle mass transfer limitation of the hydration rate is prevented. Therefore only particles with a very small diameter can be used in the kinetic experiments. These were obtained by powdering the resin in a coffee-mill after removal of the adhering water. Particles smaller than 63×10^{-6} m were sieved out in the air-dried state. Completely dry resins were obtained by evacuating ($P < 2 \text{ kPa}$) the air-dried resin during one day at a temperature of $\sim 100^\circ \text{C}$. Evacuation of the same sample for another 24 h at $\sim 120^\circ \text{C}$ did not result in a further loss of weight.

For the determination of the capacity of the resins, an excess of a 4 M aqueous NaCl solution was added to an accurately weighed amount (about 100 mg) of the resin. The amount of H^+ -ions in the resulting suspension was determined by potentiometric titration using a standard aqueous NaOH solution ($0.100 \text{ mol kg}^{-1}$). Sulfolane (Shell) was purified before use by distillation under reduced pressure. 1,4-Dioxan (Merck, *pro analysi*) was used without further purification.

Determination of the solvent composition inside the ion exchange particles as a function of the bulk liquid composition

An accurately weighed amount of the solvent mixture, W_L , with a known composition was added to an accurately weighed amount of the water-swollen resin, W_{IE} . The system was equilibrated for about 2 h, after which the composition of the free liquid no longer changed. The ion exchange resin particles were then separated from the solvent, and the adhering

liquid was removed by centrifugation for ~ 5 min at $\sim 3000 \text{ m s}^{-2}$. The capacity of the remaining resin was determined. From this capacity (σ_{eq} , expressed in equiv H^+ per kg of the swollen resin), the capacities of the water-swollen and completely dried resins ($\sigma_{\text{H}_2\text{O}}$ and σ_{dry} , respectively) together with the mol fractions of the cosolvent in the bulk liquid before and after equilibration [$x_0(\text{L})$ and $x_{\text{eq}}(\text{L})$, respectively], and the mol fraction of the cosolvent in the equilibrated resin [$x_{\text{eq}}(\text{IE})$] can be calculated from a mass balance:

$$\begin{aligned}
 & x_0(\text{L}) \frac{W_{\text{L}}}{x_0(\text{L}) \cdot M_{\text{c}} + [1 - x_0(\text{L})] \cdot M_{\text{H}_2\text{O}}} \\
 &= x_{\text{eq}}(\text{IE}) \frac{W_{\text{IE}} \left(\frac{1}{\sigma_{\text{eq}}} - \frac{1}{\sigma_{\text{dry}}} \right) \sigma_{\text{H}_2\text{O}}}{x_{\text{eq}}(\text{IE}) \cdot M_{\text{c}} + [1 - x_{\text{eq}}(\text{IE})] \cdot M_{\text{H}_2\text{O}}} \\
 &+ x_{\text{eq}}(\text{L}) \frac{W_{\text{L}} + W_{\text{IE}} \left(1 - \frac{\sigma_{\text{H}_2\text{O}}}{\sigma_{\text{eq}}} \right)}{x_{\text{eq}}(\text{L}) \cdot M_{\text{c}} + [1 - x_{\text{eq}}(\text{L})] \cdot M_{\text{H}_2\text{O}}} \quad (1)
 \end{aligned}$$

where M_{c} and $M_{\text{H}_2\text{O}}$ stand for the molecular weights of the cosolvent and water, respectively.

The composition of the free liquid was determined with a Becker model 419 gas chromatograph equipped with a separating column packed with Porapak Q (80-100 mesh). The length and the internal diameter of the column were 1.0 and $2.1 \times 10^{-3} \text{ m}$, respectively. The column temperature was 180°C for mixtures of 1,4-dioxan and water and 250°C for mixtures of sulfolane and water. Helium was used as carrier gas; the flow rate was $7 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$.

The components of the solvent mixtures were detected by gas-liquid chromatography. The peaks were integrated by a Spectra Physics Auto Lab-IV system. For mixtures of 1,4-dioxan and water, the retention times were 130 and 12 s, respectively. For mixtures of sulfolane and water, the corresponding retention times were 350 and 12 s.

Distribution coefficient of alkenes over the ion exchange particles and the bulk liquid

This distribution coefficient is defined as the ratio of the concentration the alkene in the resin phase to that in the bulk liquid. The concentration ratios were determined in the apparatus described in [10].

For the determination of the solubilities in the resin phase, the procedure followed was almost identical to that for the determination of the solubilities of the alkenes in binary mixtures of water and 1,4-dioxan or sulfolane containing not more than 10 mol% of the organic solvent [10]. The position of the mercury drop at the start of the absorption process

($t = 0$) was calculated by a least squares fit of the positions of the mercury drop, $L(t)$, as a function of time, using from [11]:

$$\frac{L(t) - L(0)}{L(\infty) - L(0)} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_{\text{eff}} \pi^2 n^2 t}{R^2}\right) \quad (2)$$

with $L(0)$ and $L(\infty)$ the positions of the mercury drop at the start and at the end of the sorption process, and D_{eff} and R the effective diffusion coefficient and the radius of the resin particles, respectively. From $L(0)$ and $L(\infty)$, the solubility of the alkene in the resin phase could be calculated assuming ideal gas behaviour of the alkene. The solubilities of the alkene in the bulk around the resin particles were determined as described previously [10].

Kinetic runs

The procedure for the determination of the kinetics of the hydration of 2-methylpropene catalyzed by strong acid ion exchange resins is almost identical to the procedure followed for the reactions catalyzed by *p*-toluenesulfonic acid and poly (styrenesulfonic acid) [10]. In the experiments described in the present paper, ~ 1 g accurately weighed air-dried resin (particle size $d_p < 63 \times 10^{-6}$ m) was brought into the reaction cell. An accurately weighed amount of solvent (between 15 and 25 g) with a known composition was added to the resin. The rate of reaction was followed by measuring the rate of absorption of the alkene in a slurry of catalyst particles from the displacement of a drop of mercury in a horizontal calibrated glass tube, see [10]. For Amberlite IR-120 and XE-307, the composition of the free liquid in the reaction mixture was calculated using the solvent distribution between the resin particles and the bulk liquid. For Imac C16P, the composition of the bulk liquid was assumed to be equal to the composition of the solvent added. The deviations were always less than 2 mol%. This appeared from the corrections calculated for Amberlite IR-120 and XE-307. The amount of the product, 2-methyl-2-propanol, which is formed during an experiment, is so low ($< 6 \times 10^{-4}$ mol) that it is reasonable to assume that the phase equilibria do not change noticeably during the course of an experiment.

Results and discussion

The rate of reaction, R_{eq} , defined as the number of moles of the alkene converted per equivalent of acid groups and per second, is calculated from the steady state molar absorption rate, $\psi_{\text{mol}, \infty}$ of the alkene by the reaction mixture according to (3):

$$R_{\text{eq}} = \frac{\psi_{\text{mol}, \infty}}{\text{CAP}} \quad (\text{mol equiv}^{-1} \text{ s}^{-1}) \quad (3)$$

Here CAP represents the total number of equiv of acid groups present in the slurry. The values of R_{eq} turned out to be independent of the amount of resin used, indicating that the mass transfer resistance between gas and liquid phase was negligible. Also intraparticle mass transfer limitations were negligible at the experimental conditions used (see Appendix). The hydration reaction obeys a pseudo-first order rate law:

$$R_{eq} = k[\text{alkene}] = kS \quad (4)$$

with k the pseudo-first order rate constant ($\text{kg}_L \text{ eq}_{\text{acid}}^{-1} \text{ s}^{-1}$) and S the solubility of the alkene in the solvent used (mol kg_L^{-1}) as a measure of the concentration. Equation 4 was obtained by mechanistic studies on the acid-catalyzed hydration of alkenes [13, 14]. Since the equilibrium constant K , defined in terms of liquid phase concentrations:

$$K = ([\text{t-butanol}]/[\text{2-methylpropene}])_{\text{chem. eq}} \quad (5)$$

is equal to 1.6×10^5 at 298 K and water as solvent [12], the hydration reaction may be considered irreversible. This conclusion is not affected by the use of cosolvents [10]. In Table 1, the reaction rates R_{eq} and the pseudo-first order rate constants are presented for the reactions in pure water as solvent, catalyzed by Amberlite IR-120, XE-307 or Imac C16P. The results for Amberlite IR-120 and XE-307 show a reasonable agreement with the values determined by Petrus [12]. Table 1 shows that the rates in pure water as solvent increase in the order Amberlite IR-120 < XE-307 < Imac C16P. This result is in agreement with the results of Gates *et al.* [15], who investigated the dehydration of pure 2-methyl-2-propanol catalyzed by resins with different amounts of divinylbenzene and found that the reaction rate increases with increasing degree of crosslinking.

Since swelling of the resins is increasingly hampered at higher degrees of crosslinking, the local concentration of acid groups increases with more crosslinking. As a result an increase in R_{eq} may be expected [10].

In Figs. 1, 2 and 3, the ratio of the values of R_{eq} determined in co-solvent-water and in water, $R_{eq}^{\text{H}_2\text{O}}$, are plotted as a function of the mol

TABLE 1

Reaction rates ($R_{eq}^{\text{H}_2\text{O}}$) and rate constants ($k_{\text{H}_2\text{O}}$) of the hydration of 2-methylpropene in water catalyzed by some strong acid ion exchange resins at 0.1 MPa partial pressure of 2-methylpropene and 25.0 °C

Resin	$10^3 S_{\text{H}_2\text{O}}^a$ (mol kg _L ⁻¹)	$10^6 R_{eq}^{\text{H}_2\text{O}}$ (mol equiv ⁻¹ s ⁻¹)	$10^3 k_{\text{H}_2\text{O}}$ kg _{H₂O} equiv ⁻¹ s ⁻¹
Amberlite	5.0	10.3	2.06
XE-307	5.0	16.0	3.20
Imac C16P	5.0	18.9	3.78

^a S is the solubility of the alkene at 0.1 MPa and 25.0 °C.

Fig. 1. Ratio of the rates R_{eq} and $R_{eq}^{H_2O}$ for the hydration of 2-methylpropene in cosolvent-water mixtures and in pure water, respectively, catalyzed by Amberlite IR-120 at 0.1 MPa partial pressure of 2-methylpropene and 25.0 °C; (○) 1,4-dioxan-water; (●) sulfolane-water.

fraction of the cosolvent for the resins Amberlite IR-120, XE-307 and Imac C16P, respectively.

The variations of the solubility of 2-methylpropene as a function of the mol fraction of 1,4-dioxan or sulfolane are visualized in a plot of the ratio of the solubilities in cosolvent-water mixtures and in water (S_L/S_{H_2O}) as shown in Fig. 4. This Figure is derived from the solubility data presented in [10]. It is remarkable that the variations of $R_{eq}/R_{eq}^{H_2O}$ (Figs. 1, 2 and 3) are considerably smaller than those of S_L/S_{H_2O} (Fig. 4) for each of the resins investigated. For 60 mol% 1,4-dioxan, the values of $R_{eq}/R_{eq}^{H_2O}$ lie between 1.1 and 1.3, whereas the solubility ratio S_L/S_{H_2O} is about 180 for the same solvent composition. For 70 mol% sulfolane, the values of $R_{eq}/R_{eq}^{H_2O}$ and S_L/S_{H_2O} are about 4 and 35, respectively. For both cosolvents, the values of $R_{eq}/R_{eq}^{H_2O}$ for Amberlite IR-120, XE-307 and Imac C16P show approximately the same dependency of the mol fraction of the cosolvent. This can be visualized very clearly by plotting the ratio of the rate constants in cosolvent-water mixtures and in water (k/k_{H_2O}) as a function of the mol fraction of the cosolvent. Figures 5 and 6 show the dependence of this ratio for the resins studied as a function of the mol fraction of 1,4-dioxan and sulfolane, respectively.

Fig. 2. Ratio of the rates R_{eq} and $R_{eq}^{H_2O}$ for the hydration of 2-methylpropene in cosolvent-water mixtures and in pure water, respectively, catalyzed by XE-307 at 0.1 MPa partial pressure of 2-methylpropene and 25.0 °C; (○) 1,4-dioxan-water; (●) sulfolane-water.

Fig. 3. Ratio of the rates R_{eq} and $R_{eq}^{H_2O}$ for the hydration of 2-methylpropene in cosolvent-water mixtures and in pure water, respectively, catalyzed by Imac C16P at 0.1 MPa partial pressure of 2-methylpropene and 25.0 °C; (○) 1,4-dioxan-water; (●) sulfolane-water.

Fig. 4. Ratio of the solubilities S and S_{H_2O} [10] of 2-methylpropene in cosolvent-water mixtures and in pure water, respectively, at 0.1 MPa partial pressure of 2-methylpropene and 25.0 °C; (—) 1,4-dioxan-water; (- · -) sulfolane-water; $S_{H_2O} = 5.0 \times 10^{-3}$ mol $\text{kg}_{H_2O}^{-1}$.

The rate constants needed for the Figs. 5 and 6 were calculated with eqn. (4), using the experimental values of R_{eq} and the solubilities which were graphically derived from those presented in [10].

Figure 5 shows that the value of k/k_{H_2O} decreases continuously with increasing 1,4-dioxan concentration for all resins studied. The rate constant decreases by a factor of $\sim 10^2$ on going from water to a solvent mixture containing about 60 mol% 1,4-dioxan. However, Fig. 6 shows that for mixtures of sulfolane and water with about 50 mol% sulfolane, k/k_{H_2O} passes through a minimum. To gain insight into the behaviour of the rate constants as a function of the solvent composition, it is necessary to realize that the hydration reaction only takes place in the resin phase. From this it may be clear that:

$$R_{eq} = kS_L = k_{IE}S_{IE} \quad (6)$$

where k_{IE} is the rate constant based on the concentration of the alkene in the resin phase, and S_{IE} the solubility of the alkene in the resin phase expressed in mol per kg of the swollen resin.

Fig. 5. Ratio of the rate constants k and k_{H_2O} for the hydration of 2-methylpropene in water-1,4-dioxan mixtures and pure water, respectively, catalyzed by the resins Amberlite IR-120 ($-\triangle-$), XE-307 ($-\circ-$) and Imac C16P ($-\cdot-\nabla-\cdot-$).

Fig. 6. Ratio of the rate constants k and k_{H_2O} for the hydration of 2-methylpropene in water-sulfolane mixtures and pure water, respectively, catalyzed by the resins Amberlite IR-120 ($-\triangle-$), XE-307 ($-\circ-$) and Imac C16P ($-\cdot-\nabla-\cdot-$).

Introduction of a distribution coefficient:

$$\lambda = \left(\frac{S_{IE}}{S_L} \right)_{eq} \quad (\text{kg}_L/\text{kg}_{IE}) \quad (7)$$

of the alkene over the resin phase and the surrounding liquid results in the following relation between k and k_{IE} :

$$k = k_{IE} \lambda \quad (8)$$

Because k_{IE} and λ are both dependent on the solvent composition in the resin phase, this solvent composition was determined as a function of the composition of the liquid around the resin particles for both cosolvents and the resins Amberlite IR-120 and XE-307. The results are collected in Fig. 7, which shows that the mol fraction of the cosolvent in the resin is higher for sulfolane than for 1,4-dioxane for cosolvent concentrations in the free liquid above 40 mol%. This is in agreement with the differences in the sorption behaviour of strong acid ion exchange resins towards solvents with different polarities as reported by Moody and Thomas [16]. The cosolvent concentrations in Amberlite IR-120 are smaller than those in XE-307 for almost all

Fig. 7. Mol fractions of the cosolvent in strong acid ion exchange resins equilibrated with cosolvent-water mixtures at 25.0 °C; (●) 1,4-dioxan-water and Amberlite IR-120; (▲) sulfolane-water and Amberlite IR-120; (○) 1,4-dioxan-water and XE-307; (△) sulfolane-water and XE-307.

compositions of the liquid around the resin particles. This agrees with the results of Blasius and Schmitt [17], who observed that the amounts of organic solvent taken up by the resins are much greater for resins with a permanent porosity than for gel-type resins. In the intermediate and macroreticular resins, a very large part of the cosolvent taken up is present in the permanent pores of these resins. These macropores contain only a small part of the acid groups, however. The main part of these groups is present in the domains built up from a homogeneous polymer network. The gel-type resins like Amberlite IR-120 consist mainly of such homogeneous polymer lattices. From these considerations, it may be assumed that the influence of the composition of the bulk liquid on k_{IE} for Amberlite IR-120 is comparable with that for XE-307 and Imac C16P. The solvent effects on k must therefore mainly be ascribed to variations of the distribution coefficient λ with the solvent composition. From the rather low cosolvent concentrations in Amberlite IR-120 and the solvent effects on the hydration rates of 2-methylpropene in solutions of *p*-toluene sulfonic acid or poly(styrene sulfonic acid) [10], it can be concluded that the variation of k_{IE} plays only a minor role in the observed solvent effect on k . Unfortunately, the determination of λ for 2-methylpropene is strongly hampered by its relatively high reactivity towards water in strong acidic media. Distribution coefficients for the inert sodium forms of the resins give no reliable values for the acidic forms of the resins, because the solvent composition inside the resin is strongly dependent on the exchangeable cation [17, 18]. In order to obtain reliable data on the

Fig. 8. Ratio of the distribution coefficients λ and λ_{H_2O} for *cis*-2-butene at 0.1 MPa partial pressure of the alkene and 25.0 °C; (∇) 1,4-dioxan-water and Amberlite IR-120; ($\circ$) 1,4-dioxan-water and XE-307; (Δ) sulfolane-water and XE-307; λ_{H_2O} (Amberlite IR-120) = 2.3 kg_L kg_{IE}⁻¹ and λ_{H_2O} (XE-307) = 1.7 kg_L kg_{IE}⁻¹ [19].

influence of the solvent on the distribution coefficient λ , this parameter was determined for the much less reactive *cis*-2-butene. For XE-307, λ was determined for a number of different mol fractions of both cosolvents. For Amberlite IR-120 only one 1,4-dioxan-water mixture was investigated. For water, the λ values are calculated from solubility data of Petrus [19] and the densities of the water-swollen resins. The results are collected in Fig. 8, where the ratio of the distribution coefficients for the cosolvent-water mixtures and for pure water are plotted as a function of the mol fraction of the cosolvent in the bulk liquid. It is remarkable that for mixtures of 1,4-dioxan and water the solvent effects on k/k_{H_2O} (Fig. 5) on the one side, and those on λ/λ_{H_2O} on the other side are quite similar. For mixtures of sulfolane and water, a similarity between Figs. 6 and 8 is also present, but less pronounced. These observations support the already mentioned conclusion that the influence of the solvent composition on the rates of heterogeneously catalyzed hydration of alkenes by strong acid ion exchange resins is mainly governed by the distribution of the alkene over the resin and the surrounding liquid. This distribution is strongly dependent on the solvent composition inside the particles. Unfortunately, the resin phase favours the more polar component of the solvent mixture, however. Nevertheless the overall effect on the rate is very positive in the case where sulfolane is used as a cosolvent, particularly at mol fractions above 50% (Figs. 1 - 3).

Conclusions

The rate of the heterogeneous catalyzed hydration of 2-methylpropene by strong acid ion exchange resins in 1,4-dioxan-water and sulfolane-water mixtures is, especially in the latter case, considerably dependent on the mol fractions of the organic solvent. The observed solvent effects are only slightly different for the resins Amberlite IR-120, XE-307 and Imac C16P. The rate of hydration in the solvent mixtures investigated is influenced by the acidity of the sulfonic acid groups in the resins, the composition of the solvent inside the particles (which is different from that of the bulk liquid), the solubility of the alkene in the bulk liquid, and the distribution of the alkene over resin phase and surrounding liquid.

Applying a mixture of 80 mol% sulfolane in water as a solvent results in an enhancement of the hydration rate of 2-methyl propene by a factor of more than 10 relative to the rate obtained with pure water.

Symbols

$c_{IE,i}$	concentration of alkene in catalyst at interface of resin and liquid $\text{mol m}_{IE}^{-3} \text{ s}^{-1}$
CAP	total number of equivalents of acid —
D_{eff}	effective diffusion coefficient of alkene in ion exchange resin $\text{m}^2 \text{ s}^{-1}$
d_p	diameter of the resin particles m
K	equilibrium constant of the reaction 2-methylpropene $\rightarrow$ t-butanol —
k	(pseudo) first order rate constant $\text{kg}_L \text{ equiv}^{-1} \text{ s}^{-1}$
$L(0)$	starting position of mercury drop —
$L(t)$	distance mercury drop from $L(0)$ at time t m
$L(\infty)$	final distance mercury drop from $L(0)$ m
M_c	molecular weight of cosolvent kg kmol^{-1}
M_{H_2O}	molecular weight of water kg kmol^{-1}
M_w	Weisz-Prater number —
P	pressure kPa
R_{eq}	hydration rate per equivalent acid $\text{mol equiv}^{-1} \text{ s}^{-1}$
R_v	hydration rate per m^3 ion exchanger $\text{mol m}_{IE}^{-1} \text{ s}^{-1}$
S	solubility of the alkene in solvent indicated or ion exchanger mol kg^{-1}
t	time s
$x_0(L)$	mol fraction of cosolvent added to slurry —
$x_{eq}(L)$	mol fraction of cosolvent in slurry after equilibrium —
x_{IE}	mol fraction of cosolvent in resin after equilibrium —
η	effectiveness factor of ion exchanger —
$\psi_{mol, \infty}$	steady state molar absorption rate of alkene in slurry $\text{mol equiv}^{-1} \text{ s}^{-1}$
ρ_{IE}	density of ion exchanger kg m_{IE}^{-3}
σ_{dry}	acidic capacity of ion exchanger (dry) $\text{equiv H}^+ \text{ kg}^{-1}$

σ_{eq}	acidic capacity of ion exchanger in solvent swollen state equiv H^+ kg^{-1}
σ_{H_2O}	acidic capacity of ion exchanger in water equiv H^+ kg^{-1}
λ	distribution coefficient $kg_L kg_{IE}^{-1}$

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Appendix

Intraparticle mass transfer limitation of hydration rates

Whether intraparticle mass transfer limitation plays a significant role can be established with the well-known Weisz-Prater criterion [20]. For Weisz-Prater numbers, $M_w > 0.7$, the effectiveness factor, η , is significantly lower than one. For (pseudo)first order reactions, M_w can be calculated from observed reaction rates by:

$$M_w = \left(\frac{d_p}{6} \right)^2 \frac{R_v}{c_{IE,i} D_{eff}} \quad (A1)$$

The reaction rate, R_v , can be calculated from R_{eq} by:

$$R_v = R_{eq} \rho_{IE} \sigma_{eq} \text{ mol m}_{IE}^{-3} \text{ s}^{-1} \quad (A2)$$

When the mass transfer resistance between the bulk liquid and the external surface of the resin is assumed to be negligible, the values of $c_{IE,i}$ for our experiments can be obtained from the solubilities, S_L , of the alkene in the cosolvent-water mixtures (Fig. 4) and the distribution coefficient of the alkene between the resin phase and the bulk liquid:

$$c_{IE,i} = \lambda S_L \rho_{IE} \text{ mol m}_{IE}^{-3} \quad (\text{A3})$$

Substitution of eqns. (A2) and (A3) into (A1) gives:

$$M_w = \left(\frac{d_p}{6} \right)^2 \frac{R_{eq} \sigma_{eq}}{\lambda S_L D_{eff}} \quad (\text{A4})$$

For XE-307 in pure water, M_w becomes 6×10^{-3} , ($d_p = 63 \times 10^{-6}$ m, $R_{eq} = 16.0 \times 10^{-6}$ mol equiv $^{-1}$ s $^{-1}$, see Table 1; $\sigma_{eq} = 1.83$ equiv kg $_{IE}^{-1}$ as was experimentally determined, $\lambda = 1.7$ kg $_L$ kg $_{IE}^{-1}$ [19], $S_L = 5.0 \times 10^{-3}$ mol kg $_L^{-1}$ and $D_{eff} = 60 \times 10^{-12}$ m 2 s $^{-1}$ [19]). For XE-307 in 69.0 mol% sulfolane, M_w becomes 5×10^{-3} , ($R_{eq} = 67.3 \times 10^{-6}$ mol equiv $^{-1}$ s $^{-1}$, see Fig. 2; $\sigma_{eq} = 1.94$ equiv kg $_{IE}^{-1}$, as was experimentally determined, $\lambda = 0.27$ kg $_L$ kg $_{IE}^{-1}$, see Fig. 8, $S_L = 0.18$ mol kg $_L^{-1}$, see Fig. 4, and $D_{eff} = 60 \times 10^{-12}$ m 2 s $^{-1}$ [19]). From these values of M_w , it can be concluded that the effectiveness factor $\eta = 1$.