

Effect of water on sulfuric acid catalyzed esterification

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Abstract

This paper reports on an investigation into the impact of water on liquid-phase sulfuric acid catalyzed esterification of acetic acid with methanol at 60 °C. In order to diminish the effect of water on the catalysis as a result of the reverse reaction, initial reaction kinetics were measured using a low concentration of sulfuric acid (1×10^{-3} M) and different initial water concentrations. It was found that the catalytic activity of sulfuric acid was strongly inhibited by water. The catalysts lost up to 90% activity as the amount of water present increased. The order of water effect on reaction rate was determined to be -0.83 . The deactivating effect of water also manifested itself by changes in the activation energy and the pre-exponential kinetic factor. The decreased activity of the catalytic protons is suggested to be caused by preferential solvation of them by water over methanol. A proposed model successfully predicts esterification rate as reaction progresses. The results indicate that, as esterification progresses and byproduct water is produced, deactivation of the sulfuric acid catalyst occurs. Autocatalysis, however, was found to be hardly impacted by the presence of water, probably due to compensation effects of water on the catalytic activity of acetic acid, a weak acid.
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1. Introduction

Esterification of carboxylic acids with alcohols represents a well-known category of liquid-phase reactions of considerable industrial interest due to the enormous practical importance of organic ester products. These ester products include environmentally friendly solvents, flavors, pharmaceuticals, plasticizers, polymerization monomers and emulsifiers in the food, cosmetic and chemical industries [1–3]. Recently, a growing interest in ester synthesis has been further stimulated due to the great promise shown by long chain mono alkyl esters as fuels for diesel engines [4,5].

Esterification can take place without adding catalysts due to the weak acidity of carboxylic acids themselves. But the reaction is extremely slow and requires several days to reach equilibrium at typical reaction conditions. Either homogenous mineral acids, such as H_2SO_4 , HCl or HI , or heterogeneous solid acids, such as various sulfonic resins, have been shown to be able to effectively catalyze the reaction. The catalysts essentially promote the protonation of the carbonyl oxygen on the carboxylic group,

thereby activating nucleophilic attack by an alcohol to form a tetrahedral intermediate [5]. Disproportionation of this intermediate complex ultimately yields the ester (refer to Fig. 1).

In spite of the long history of esterification and the large amount of literature concerning the performances of various catalysts and the kinetics of different ester syntheses, there are still many fundamental issues that remain poorly understood. For instance, an important subject that needs to be better understood is the effect that water produced from esterification may have on the acid catalysis. Pronounced inhibition effects of water on homogenous acid catalyzed esterification have been reported by different researchers [4,6–8]. For example, Aafaqi et al. [4] showed that, when esterification was carried out using homogenous *para*-toluene sulfonic acid (*p*-TSA) with an initial 15 vol% water, the conversion of carboxylic acids was decreased by around 40% (after 4 h of reaction). Similarly, Hu et al. [7] found that homogenous $\text{H}_3\text{PW}_{12}\text{O}_{40}$ lost about 30% of its catalytic activity when only 7.5 mol% water was introduced into the esterification of propionic acid with isobutyl alcohol at 70 °C.

Few studies, however, have ever focused on how water actually affects reaction activity. The decrease in esterification kinetics in the presence of water has generally been attributed to reverse hydrolysis [4,6]. The water retardation effect on ester formation, however, is not limited to esterification. Acid catalyzed

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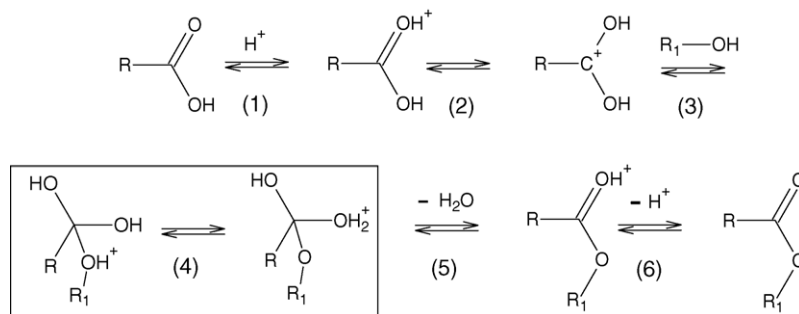


Fig. 1. Mechanistic route of acid catalyzed esterification.

transesterification has also been found to be inhibited in the presence of water [6,7,9,10]. Moreover, when carried out in an alcoholic medium, acid catalyzed hydrolysis has been found to be faster than in an aqueous medium [11,12]. Obviously, these observations suggest that the effect of water on esterification is more than just simple reverse hydrolysis. Smith [13], based on the assumption that the interaction between protonated methanol and carboxylic acid was the rate-determining step, ascribed the effect of water on esterification to the competition for protons between water and methanol. More recently, it has been suggested that the hindered catalyst performance is due to the reduced acid strength of the catalyst caused by the coordination of water to protons [7].

Currently, knowledge regarding how water affects the efficiency of acid catalysts for esterification is quite limited and mostly qualitative. Thus, the focus of the present study was to increase the quantitative and conceptual understanding of the deactivating effect of water on acid catalyzed esterification. Here, the esterification of acetic acid with methanol using sulfuric acid was investigated with different initial water concentrations.

2. Experimental

2.1. Material

Reagents including methanol (99.9%, Acros Organics), acetic acid (99.7%, Aldrich) and water (HPLC, Acros Organics) were used without further purification. Because both methanol and acetic acid are hygroscopic, the moisture contents of the reagents were determined by Galbraith Laboratory using Karl Fischer titration. The analysis showed water contents of 160 ppm for methanol and 961 ppm for acetic acid. These moisture contents were able to be ignored since they were very small compared to the amount of water produced during the initial reaction period.

2.2. Reaction procedure

Kinetic measurements were carried out in a Parr 4590 batch reactor that consisted of a stainless steel chamber of 50 ml, a three-blade impeller and a thermocouple. The temperature was maintained within $\pm 0.5^\circ\text{C}$. Prior to reaction, a predetermined amount of reagent mixture was loaded into the reactor

and heated to the desirable temperature while being stirred at 850 rpm. This mixing speed was determined to be sufficient to eliminate any mass transfer limitations. No change in reaction rate was detected when the stirrer speed was varied from 567 to 1417 rpm. The catalyst, concentrated sulfuric acid alone or diluted in a small amount of methanol, was charged into the reactor to initiate reaction. Although esterification occurs during the heating period due to autocatalysis, this starting method of reaction was the best way to ensure good control of temperature, which is particularly important for accurate determination of initial reaction kinetics (below 10% conversion of the limiting reagent). A microscale syringe was used for sampling at definite time intervals. A sample was always taken right before catalyst charging as the zero point for every run. Samples from the reaction mixture were immediately diluted in cold 2-propanol, and reaction stopped because of cooling and dilution.

A Hewlett-Packard 6890 gas chromatograph equipped with a DB-1 column (0.32 mm \times 30 m \times 0.53 μm) and a FID detector was used for sample analysis with toluene as an internal standard. The concentrations of all species (except water) were accurately quantified and found to obey well the stoichiometry of the reaction, which along with the nonappearance of unknown peaks as detected by GC analysis indicated the absence of side reactions under the experimental conditions used.

2.3. Experimental design

In order to better observe the effect of water on reaction and to minimize the contribution of reverse hydrolysis, a small amount of catalyst ($C_C = 1 \times 10^{-3} \text{ M}$) was used and attention was focused particularly on the initial period of reaction. A series of experiments with varying amounts of initial water addition were carried out at 60°C with a fixed catalyst concentration. Table 1 shows initial concentrations of reagents and the concentrations of water initially added. The initial water concentrations used corresponded to the amounts of water that could have been produced by esterification at different conversions. The idea behind this approach was to observe how catalyst activity is affected with increasing concentration of water, as occurs during esterification.

Because the molar ratio of methanol-to-acetic acid was kept constant and no solvent was used, kinetic comparisons are based on reaction constants instead of reaction rates. As mentioned earlier, esterification can be autocatalyzed by acetic acid itself.

Table 1

Concentrations of initial water added ($C_{W,0}$) and equivalent acetic acid conversion based on the initial acetic acid concentration ($C_{A,0}$) and the amount of water initially added

Initial water added (M) ^a	0	0.5	1.3	2.6	9.0
$C_{A,0}$ (M) ^a	7.32	7.26	7.20	7.07	6.27
$C_{M,0}$ (M) ^a	14.6	14.5	14.4	14.1	12.5
Equivalent acetic acid conversion based on $C_{A,0}$ and initial amount of water added (%)	0.0	6.3	14.9	27.0	58.8

^a Experimental error: $\pm 1\%$.

At 60 °C, the rate of autocatalysis was about a seventh of the overall catalysis rate when only 1×10^{-3} M sulfuric acid was employed. Therefore, esterification occurred as a combination of two catalytic routes. As has been reported [14–18], homogenous acid catalyzed and autocatalyzed esterification follows second-order and third-order kinetics, respectively. Thus, the overall esterification rate can be written as:

$$-\frac{dC_A}{dt} = (k_C C_C + k_{\text{Auto}} C_A) C_A C_M - (k_{-C} C_C + k_{-\text{Auto}} C_A) C_E C_W \quad (1)$$

where k_C and k_{Auto} represent the observed acid catalyzed and autocatalyzed esterification constants, respectively, and k_{-C} and $k_{-\text{Auto}}$ are related to reverse hydrolysis; C_C , C_A , C_M , C_E and C_W denote the concentrations of sulfuric acid, acetic acid, methanol, methyl acetate ester and water, respectively. For initial kinetic measurements, because reverse hydrolysis is negligible and $k_C C_C + k_{\text{Auto}} C_A \approx k_C C_C + k_{\text{Auto}} C_{A,0}$, Eq. (1) can be reduced, in terms of acetic acid conversion ($x = \frac{C_{A,0} - C_A}{C_{A,0}}$), to

$$\frac{dx}{dt} = [k_C C_C C_{A,0} + k_{\text{Auto}} C_{A,0}^2] (1-x) \left(\frac{C_{M,0}}{C_{A,0}} - x \right) \quad (2)$$

Integrating Eq. (2) and letting $k_1 = k_C C_C + k_{\text{Auto}} C_{A,0}$, at $C_{M,0}/C_{A,0} = 2$, we have:

$$\ln \left(\frac{2-x_t}{1-x_t} \right) - \ln \left(\frac{2-x_0}{1-x_0} \right) = k_1 C_{A,0} t \quad (3)$$

where x_0 and x_t represent the conversion of acetic acid at time = 0 and t , respectively. Thus, k_1 can be determined by applying Eq. (3) to experimental data. Typical plots of $\ln[(2-x)/(1-x)]$ versus t are shown in Fig. 2, and k_1 values were calculated from the slopes of these plots. In a similar way, the autocatalytic reaction constant k_{Auto} was able to be obtained using Eq. (2), setting $C_C = 0$, and integrating:

$$\left[\frac{1}{1-x} - \ln \left(\frac{2-x}{1-x} \right) \right] \Big|_{x_0}^x = k_{\text{Auto}} C_{A,0}^2 t \quad (4)$$

Note, reaction constants calculated this way are actually average values for the initial reaction period. Because water is produced by esterification, the water concentration used must account for both the initial water added and the average amount of water

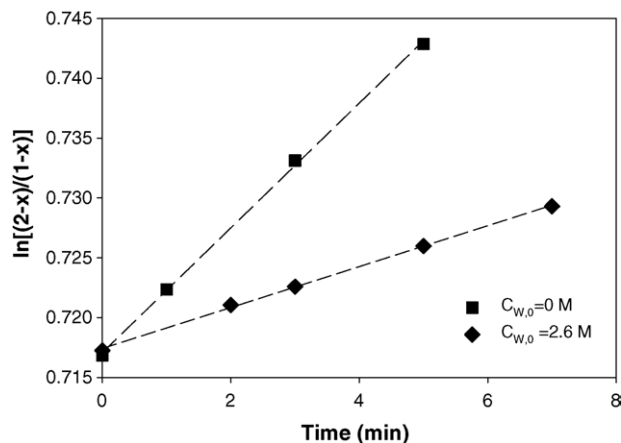


Fig. 2. Suitability of Eq. (3) to experimental data collected in initial period of reaction catalyzed by 1×10^{-3} M H_2SO_4 .

formed during the reaction period:

$$C_W = C_{A,0}(w + \bar{x}) \quad (5)$$

where w is the molar ratio of water initially added to the acetic acid, $C_{W,0}/C_{A,0}$, and \bar{x} is the average conversion of acetic acid from $t = 0$ to t .

3. Results and discussion

The reaction constants for autocatalysis, k_{Auto} , at 60 °C and at different initial water concentrations are summarized in Table 2. The autocatalytic activity was almost unchanged when water content varied from 0.4 to 9.3 M. The small fluctuation in k_{Auto} can be ascribed to experimental errors. However, the multiple roles of water in autocatalysis could also account for some of this small variance. This will be discussed in more detail later. Since the water concentration range used covered the equivalent conversions of acetic acid from about 5 to 60%, it is clear that autocatalysis is hardly affected by the increasing concentration of water produced as esterification progresses. Hence, the k_C can be determined by using the average k_A value of 12.4×10^{-6} ($\text{M}^{-2} \text{min}^{-1}$), $k_C = (k_1 - 12.4 \times 10^{-6} C_{A,0})/C_C$.

Table 2

Dependence of autocatalytic reaction constant (k_A) on water content ($T = 60$ °C, $C_{M,0}/C_{A,0} = 2$)

C_W (M) ^{a,b}	0.4	1.6	3.0	9.3
$C_{A,0}$ (M) ^c	7.3	7.2	7.1	6.3
Equivalent acetic acid conversion based on $C_{A,0}$ and initial amount of water added (%)	4.9	18.0	29.8	59.6
k_{Auto} ($\text{M}^{-2} \text{min}^{-1} \times 10^6$)	13.7	11.2	11.6	13.0

^a Water concentration includes both the initial amount of water added and the average amount formed during the initial period of esterification: $C_W = C_{A,0}(w + \bar{x})$, $w = C_{W,0}/C_{A,0}$.

^b Experimental error: $\pm 3\%$.

^c Experimental error: $\pm 1\%$.

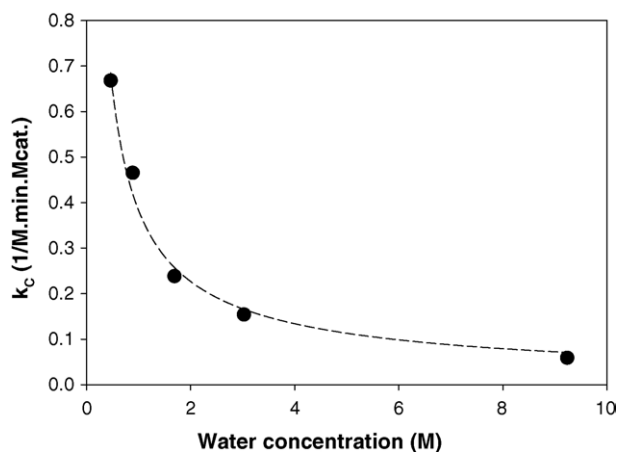


Fig. 3. Dependence of k_C on water concentration ($T=60^\circ\text{C}$; $C_{M,0}/C_{A,0}=2$). The dotted line represents the fitted power law model $k_C = 0.38C_W^{-0.83}$ ($\text{M}^{-1} \text{min}^{-1} \text{Mcat}^{-1}$).

By plotting k_C versus C_W , the impact of water on sulfuric acid catalyzed esterification was able to be determined (Fig. 3). In contrast to autocatalysis, the catalytic activity of sulfuric acid was significantly decreased by water; the greatest decrease was manifested at low water concentrations. The rate constant appeared to approach a limiting value as water concentration increased to above 6 M with the concentration of catalyst used in our experiments. Using a power law model, the effect of water concentration on the rate constant was found to be -0.83 order:

$$k_C = 0.38C_W^{-0.83} (\text{M}^{-1} \text{min}^{-1} \text{Mcat}^{-1}) \quad (6)$$

To confirm the absence of contributions from reverse hydrolysis even for very high initial water concentrations, a series of experiments with initial methyl acetate introduction instead of water were carried out and results are shown in Table 3. Interestingly, larger rate constants for product formation were observed with ester addition rather than being decreased by reverse hydrolysis. However, the addition of an inert (tetrahydrofuran, THF) yielded an identical kinetic enhancement. Here, it should be noted that the ester/THF introduction actually replaced a partial amount of reactants due to the absence of a solvent. Consequently, less water was able to be produced during the initial reaction period of acetic acid (<10% conversion). Therefore, the apparent positive effect exhibited by ester/THF was proba-

Table 3
Variation of k_C with the ester concentration (C_E) and predicted $k_{C,\text{calc}}$ from Eq. (6) ($T=60^\circ\text{C}$, $C_{M,0}/C_{A,0}=2$)

C_E (M) ^{a,b}	0.5	2.6	5.9	0
C_{THF} (M) ^c	0	0	0	5.7
C_W (M) ^b	0.4	0.3	0.2	0.2
k_C ($\text{M}^{-1} \text{min}^{-1} \text{Mcat}^{-1}$) ^d	0.67	0.99	1.28	1.23
$k_{C,\text{calc}}$ ($\text{M}^{-1} \text{min}^{-1} \text{Mcat}^{-1}$)	0.71	0.99	1.30	1.33

^a Ester concentration includes both the initial amount of ester added and the average amount formed during the initial period of esterification: $C_E = C_{A,0}(e + \bar{x})$, $e = C_{E,0}/C_{A,0}$.

^b Experimental error: $\pm 3\%$.

^c Experimental error: $\pm 1\%$.

^d Experimental error: $\pm 5\%$.

Table 4

Impact of initial molar ratio of methanol-to-acetic acid on the effect of water on sulfuric acid catalysis ($T=60^\circ\text{C}$, $C_W=3.0\text{M}$)

$C_{M,0}/C_{A,0}$	2	5	10	20
$C_{M,0}$ (M) ^a	14.6	18.5	20.8	22.0
$C_{A,0}$ (M) ^a	7.3	3.7	2.1	1.1
k_C ($\text{M}^{-1} \text{min}^{-1} \text{Mcat}^{-1}$) ^b	0.15	0.14	0.15	0.14

^a Experimental error: $\pm 1\%$.

^b Experimental error: $\pm 5\%$.

bly due to this decreased water concentration. This possibility was then confirmed by estimation of the respective reaction constant (k'_C) from Eq. (6) (Table 3). The good agreement between estimated and experimental values supports the earlier hypothesis. The primary role of methyl acetate present during initial reaction period was then that of a dilution agent just like THF. Therefore, the variance of k_C as determined in the present study is little affected by any contribution of reverse hydrolysis.

The impact of molar ratio on the inhibition effect of water on acid catalysis was also inspected by fixing the water concentration while varying the molar ratio of alcohol-to-carboxylic acid (Table 4). It was found that as the methanol-to-acetic acid molar ratio was increased from 2:1 to 20:1, the reaction rate constant remained unchanged at a fixed water concentration of 3.0 M. This result points to a conclusion that the impact of water on the catalytic activity of sulfuric acid is not affected by the methanol or acetic acid concentration at the C_W of 3.0 M.

In addition to molar ratio, temperature is another crucial operational parameter. The sensitivity of acid catalysis to water was also examined at 40°C . The apparent order of water effect on reaction rate was found to be almost identical to that at 60°C , as evidenced by the parallel lines in Fig. 4. The apparent activation energies and pre-exponential factors were determined at different water concentrations using the Arrhenius relationship (Fig. 5):

$$\ln k = -\frac{\Delta E^\ddagger}{R} \cdot \frac{1}{T} + \ln A$$

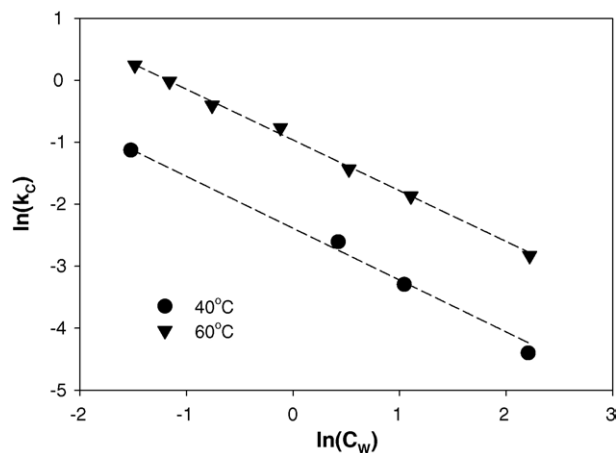


Fig. 4. Determination of apparent reaction order of water at different temperatures ($C_{M,0}/C_{A,0}=2$).

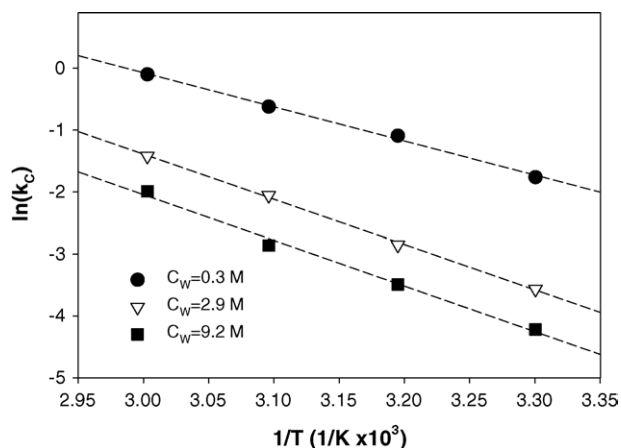


Fig. 5. Arrhenius plots of esterification at different water concentrations ($T = 30\text{--}60^\circ\text{C}$; $C_{M,0}/C_{A,0} = 2$).

Results are tabulated in Table 5. The increase in water concentration from 0.3 to 2.9 M, resulted in a 15 kJ increase in ΔE^\ddagger . However, the enhanced energy barrier was partially compensated for by a simultaneously increase in the pre-exponential factor of around 2 orders of magnitude. If compared to the “transition state theory” represented by the Eyring equation:

$$\ln \frac{k}{T} = -\frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} + \left(\ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} \right)$$

where k is rate constant, ΔH^\ddagger the activation enthalpy, ΔS^\ddagger the activation entropy and k_B and h are Boltzmann and Planck constants, respectively, our results actually indicate a rise in activation enthalpy and entropy caused by water. On the other hand, neither the enthalpy nor entropy term change linearly with water concentration. With a further even larger increase in water concentration from 2.9 to 9.2 M, only very small changes were found for in E^\ddagger and A .

As shown by the initial kinetic measurements, water has a distinct inhibition effect on sulfuric acid catalysis. However, in many kinetic studies of esterification with either homogenous catalysts [1,14] or pseudo-homogenous resin catalysts [19,20], constant catalytic activity independent of reaction progress has been assumed. Few efforts have been made to address the deactivating effect of water on acid catalysis and elucidate the phenomena in a quantitative and conceptual way. In a kinetics study of sulfuric acid catalyzed esterification of palmitic acid by Goto et al. [8], the inhibition effect of water was included in their rate expression. However, their mechanistic scheme was based

Table 5
Variation of apparent activation energy and pre-exponential constant at different concentrations of water (30–60 °C)

C_w (M) ^{a,b}	0.3	2.9	9.2
ΔE^\ddagger (kJ/mol) ^c	46	61	61
A ($\times 10^{-7}$) ^c	1.46	80.7	53.6
$\ln A$	16.5	20.5	20.1

^a $C_w = C_{A,0}(w + \bar{x})$, $w = C_{W,0}/C_{A,0}$.

^b Experimental error: $\pm 3\%$.

^c Experimental error: $\pm 5\%$.

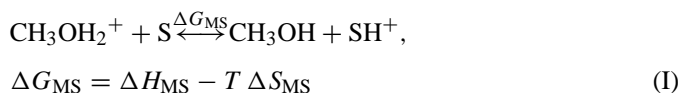
on the assumption that the protonation of carboxylic is the rate-determining step. Nowadays, studies using modern techniques have shown that the protonation of carbonyl oxygen is fast and occurs in a quasi-equilibrium step in the presence of strong acids [21]. The accepted mechanism regards the formation of a tetrahedral intermediate from the nucleophilic attack of alcohol on the protonated carboxylic acid as the rate-limiting step [5,15,22] (refer to Fig. 1). In an aqueous medium, sulfuric acid dissociates into hydronium ions and bisulfate ions. H_3O^+ ions are strong acidic species, so it is unlikely that the increasing amount of water could change the rate-limiting step. Otherwise, ester/ether hydrolysis would not have a symmetric/analogic mechanistic route as esterification as suggested by kinetic studies [21,23–25].

Two main possibilities exist for the deactivating effect of water on sulfuric acid catalysis: (1) decreased acid strength and/or (2) loss of catalyst accessibility. In terms of Bronsted acidity, Sadek et al. [11] have suggested that ROH_2^+ is more acidic than H_3O^+ to explain the enhanced ester hydrolysis in the presence of glycol and glycerol. Indeed, according to the solvation chemistry of protons, the strength of strong acids like sulfuric acid is determined by the solvation state of protons rather than the extent of dissociation. The more strongly solvated a proton is, the lower the chemical and catalytic activity of the proton [26]. If the acid strengths of methoxonium and hydroxonium ions are examined without accounting for the interactions among solvating molecules, such as comparing single MeOH_2^+ and H_3O^+ in vacuum, one would expect MeOH_2^+ to be a weaker acid than H_3O^+ , given the greater inductive effect of the methyl group in methanol. This means that gaseous methanol molecules would have a higher proton affinity [26,27]. Consequently, the higher intrinsic basicity of methanol with respect to water would give rise to a weaker conjugated acid (MeOH_2^+). This is contrary to the suggestion by Sadek et al. [11] of more acidic ROH_2^+ with respect to H_3O^+ .

On the other hand, in condensed phase where molecular interactions must be accounted for, the solvation state of protons is determined by the overall contributions of all solvating molecules. Multiple water molecules are known to form strong hydrogen bond networks through which a charged species can be delocalized and therefore stabilized [28]. Methanol, compared to water, with one hydrogen atom replaced by a $-\text{CH}_3$ group, has less ability to form hydrogen bonds [28]. As indicated by a higher Gutmann’s Donor Number ($\text{DN} = 33$), water is a better electron pair donor and can establish a stronger interaction with cationic species, stabilizing them better than methanol ($\text{DN} = 19$) [29,30]. Therefore, in line with the higher electron donating capacity, a larger enthalpy release would be expected for the proton solvation process in water making the enthalpic state of the H_3O^+ less positive than MeOH_2^+ . On the other hand, water can preferentially self-orient to oppose the external field created by cations due to its high polarity. In turn, water has been described as a proton “sponge” [31] where protons can be easily accommodated inside the “self-assemble” water network with an associated lower entropic state. Methanol molecules, however, having a smaller orientational polarizability than water and being less symmetric due to the $-\text{CH}_3$ group, can only accommodate

protons in their hydrogen bond network in a less ordered way than water does.

Accordingly, in acid–base reactions with a given substrate,

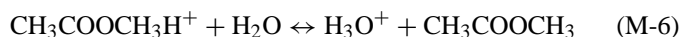
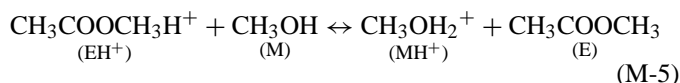
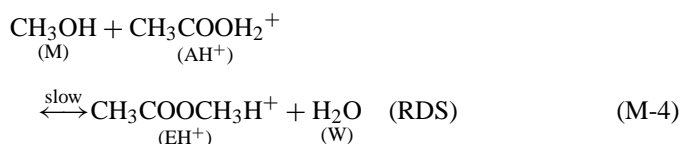
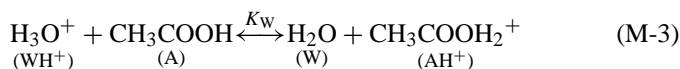
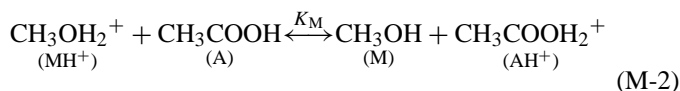
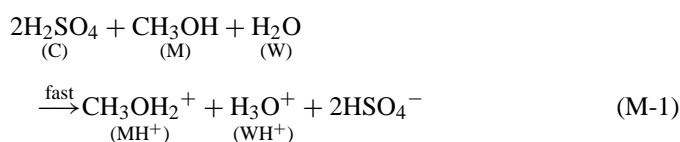


the hydroxonium reaction would require more energy than its methoxonium counterpart. That is, $0 < \Delta H_{\text{MS}} < \Delta H_{\text{WS}}$, which translates to weaker acid strength for protons inside the solvation sphere of water. But deprotonation of hydroxonium has a larger entropic force due to its lower entropic state, $0 < \Delta S_{\text{MS}} < \Delta S_{\text{WS}}$. Thus, when the higher enthalpy demand in reaction (II) is not compensated for by its entropy gradient at temperature T , formation of SH^+ is more favorable via reaction (I) due to $\Delta G_{\text{MS}} < \Delta G_{\text{WS}}$. In esterification, where S is the carboxylic acid and the reaction rate is determined by the nucleophilic attack of the alcohol on a protonated acetic acid molecule, lower concentrations of $\text{CH}_3\text{COOH}_2^+$ will certainly result in hindered kinetics. Thus, we conclude that the diminished catalytic activity observed as the concentration of water increases is likely a consequence of acid strength decline due to strong solvation of protons by water molecules.

As shown in Table 5, our measurements of reaction thermodynamics agree well with the above thermodynamic interpretation. Thus, as proton solvation by water takes over, higher energy is required for the protonation of the C=O moiety in acetic acid by H_3O^+ proton carriers. On the other hand, larger entropy release accompanying protonation of substrates contributes more geometric configurations for the subsequent nucleophilic attack by alcohol and increases the collision efficiency. In addition, this variation of proton activity with water concentration (Fig. 3) is in good agreement with other observations of proton-related characteristics, proton dissociation rate and acid–base equilibrium constant in water–organic mixtures [31]. Water was found to produce the greatest decrease in activity for esterification at low water concentrations ($C_{\text{W}}=0\text{--}3\text{ M}$) where it constituted 0–10% of the total amount of ($\text{H}_2\text{O} + \text{MeOH}$) present. This is almost identical to the results of Pines and Fleming [31] for the impact of water on proton dissociation lifetimes in a $\text{H}_2\text{O} + \text{MeOH}$ mixture (Fig. 1; ref. [31]) and for the acid–base equilibrium constant of protonated aniline in a $\text{H}_2\text{O} + \text{MeOH}$ mixture (Fig. 4; ref. [31]), where the greatest impact was seen for $C_{\text{W}}=0\text{--}4.5\text{ M}$ (also 0–10% of the total amount of ($\text{H}_2\text{O} + \text{MeOH}$) present). This narrow range has been explained in terms of the great preference of water as proton acceptor over methanol by Pines and Fleming [31]. Beyond this range, water seems to dominate the solvation sphere of protons, resulting in the protons behaving fairly constantly with increasing water concentration.

The strong correlation between the competitive proton solvation of water and methanol and the observed esterification kinetic and thermodynamic data can be accounted for by the

following set of chemical equations describing a mechanistic path:



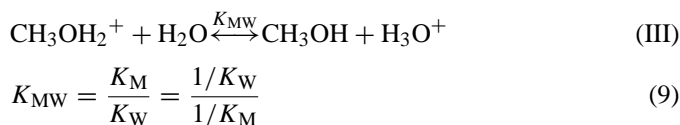
First, let us consider what applies during the initial reaction period where reverse hydrolysis is not important. For (M-4) being the RDS, the forward rate expression can be written as:

$$r = kC_{\text{AH}^+}C_{\text{M}} \quad (7)$$

With the assumption of fast protonation steps (M-2) and (M-3) occurring in quasi-equilibrium and the consideration of the charge balance in the reaction mixture while neglecting the contribution of AH^+ , EH^+ and the second proton dissociation of sulfuric acid, the rate expression becomes:

$$r_1 = \frac{kC_{\text{C}}}{\frac{C_{\text{M}}}{K_{\text{M}}} + \frac{C_{\text{W}}}{K_{\text{W}}}} C_{\text{A}}C_{\text{M}} \quad (8)$$

As defined by reactions (M-2) and (M-3), K_{M} and K_{W} are the equilibrium constants for the protonation of acetic acid from methanol and water, respectively. These constants represent the extent of proton exchange in reactions (M-2) and (M-3) and are related to the acid strength of MH^+ and WH^+ . By subtracting reaction (M-3) from (M-2), K_{M} is connected to K_{W} by the proton exchange constant in methanol–water mixtures:



When the reaction mixture is anhydrous or the concentration of water is significantly low, Eq. (8) can be reduced to:

$$r_1 = \frac{k}{C_{\text{M}}/K_{\text{M}}} C_{\text{C}}C_{\text{A}}C_{\text{M}} \quad (10)$$

$$k_{C,1} = \frac{kK_M}{C_M} \quad (11)$$

where r_1 represents reaction rate of esterification at low (l) water concentration and $k_{C,1}$ is the reaction constant. Therefore, according to Eq. (11), the temperature dependency of $k_{C,1}$ (apparent activation energy) is a result of the combination of the RDS and (M-2) steps:

$$\frac{\partial \ln k_{C,1}}{\partial(1/T)} = \frac{\partial \ln k}{\partial(1/T)} + \frac{\partial \ln K_M}{\partial(1/T)} \sim \frac{-\Delta E_1^\#}{R} \quad (12)$$

where $E_1^\#$ is the activation energy of esterification at low water concentrations. On the other hand, as esterification proceeds, alcohol is consumed while water is produced. When the methanol term becomes less important and may be considered negligible at high water concentration, we have:

$$r_h = \frac{k}{C_W/K_W} C_C C_A C_M \quad (13)$$

$$\frac{\partial \ln k_{C,h}}{\partial(1/T)} = \frac{\partial \ln k}{\partial(1/T)} + \frac{\partial \ln K_W}{\partial(1/T)} \sim \frac{-\Delta E_h^\#}{R} \quad (14)$$

where r_h , $k_{C,h}$ and $E_h^\#$ represent reaction rate, reaction constant and activation energy of esterification at the high (h) water concentrations, respectively. From Eqs. (9), (12) and (14), the difference in apparent activation energy between low and high water concentrations can be expressed as:

$$\frac{\Delta E_h^\# - \Delta E_l^\#}{R} \sim \frac{\partial(\ln K_{MW})}{\partial(1/T)} \quad (15)$$

Using the Van't Hoff equation, the increase in apparent activation energy caused by an increase in C_W can be related to the reaction enthalpy of proton exchange between water and methanol:

$$\frac{\Delta E_h^\# - \Delta E_l^\#}{R} = \frac{-\Delta H_{MW}}{R} \quad (16)$$

Similarly, the difference in pre-exponential factor at high and low water content regimes can be related to the entropy term of the same reaction:

$$\ln A_h - \ln A_l = \frac{-\Delta S_{MW}}{R} \quad (17)$$

The thermodynamic characteristics of proton exchange between water and methanol have been studied at 25 °C by Zhurenko et al. [33]. Since ΔS and ΔH are usually weakly dependent on temperature, the data from Zhurenko et al. may be used to check the validity of Eqs. (16) and (17). From Table 5, the determined difference in $\Delta E^\#$ and $\ln A$ between high ($C_W = 2.9$ M) and low ($C_W = 0.3$ M) water concentrations are 15 and 4.0 kJ, respectively. Both of these values are in fairly good agreement with Zhurenko, but somewhat higher: $-\Delta H_{MW} = 9.1$ kJ/mol, $-\Delta S_{MW}/R = 2.26$. Although the difference may be partially accounted for by the differences in methodology for data acquisition and the deviation of components from ideality in our reaction mixtures, the possible reduced accessibility of acetic acids to protons due to a heavy hydrophilic hydration sphere

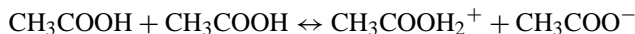
may have also played a role. In addition, for nucleophilic substitution, the different sensitivities of transition state and ground state to the change in solvent medium may be another cause for the increase in apparent activation energy [34].

From Eq. (8), the sulfuric acid catalysis constant can be written as:

$$k_C = \frac{k}{\frac{C_M}{K_M} + \frac{C_W}{K_W}} \quad (18)$$

Comparing Eq. (18) to Eq. (6) (experimental correlation between C_W and k_C), the -0.83 apparent order, while not -1 , can be explained by the presence of the methanol term in the denominator of Eq. (18). Moreover, the comparison supports the predominant impact of water as previously shown, which almost covers the entire esterification process unless a large excess methanol is used. Eq. (18) also agrees with the experimental determination of the apparent reaction order of alcohol being 1 at low alcohol-to-carboxylic acid molar ratios [14,15], while 0 at high molar ratios with simultaneous water removal [35,36].

It is worthwhile to recall that the acid strength of strong acids is determined by solvation state of protons, while for weak acids, the overall acidity depends on both proton dissociation extent and solvation energy [26]. During autocatalysis, esterification is catalyzed by acetic acid which is well known as a weak organic acid. In principle, both acetic acid molecules and dissociated protons can activate the C=O group, catalyzing esterification:



but second-order kinetics with respect to acetic acid indicates that undissociated acid protolysis dominates over the proton catalyzed route [16]. This is probably due to the low availability of protons from the weakly dissociated parent acid ($\text{p}K_a = 9.72$, in pure methanol [37]). Water, on the other hand, is able to promote the dissociation extent of weak acids due to its ability to stabilize carboxylate anions and protons electrostatically [28,37,38]. Thus, with increasing water content, more protons would be released to solution through acetic acid dissociation; however, the catalytic activity of these newly available protons would be diminished due to the same water characteristics that promote acetic acid dissociation. In addition, water is also believed to promote protolysis between carboxylic acid molecules by interacting with acetic acid molecules in such a way that provides a low-energy pathway for proton transfer [40]. Thus, the weak sensitivity of autocatalysis to water should be a result of these multiple balancing effects, higher acetic acid dissociation, intermolecular proton transfer, and proton deactivation.

Finally, a mathematical model has been developed to account for the deactivating effect of water on acid catalysis during the course of esterification. Although Eq. (6) is relatively less general compared to Eq. (18), which is derived mechanistically, the absence of accurate determinations of K_M and K_W makes more difficult the application of Eq. (18). Therefore, using Eq. (6) and

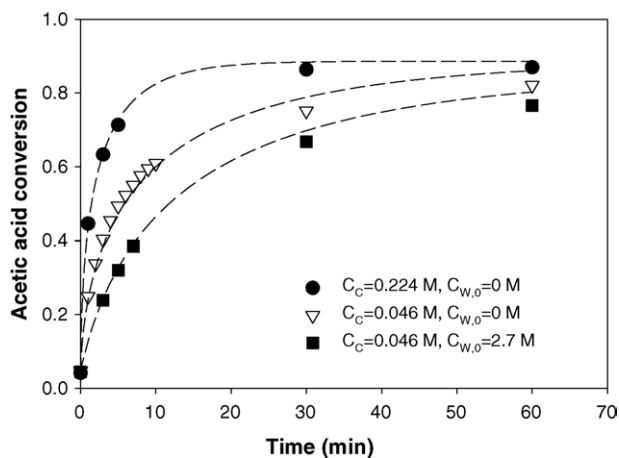


Fig. 6. Comparison of experimental data with values predicted by Eq. (21) for esterification of acetic acid with methanol at 60 °C and $C_{M,0}/C_{A,0} = 2$ (symbol is experimental data; dashed line is model prediction).

inserting it into Eq. (1), we obtain:

$$-\frac{dC_A}{dt} = C_C \cdot \left(\frac{0.38}{C_W^{0.83}} \right) \cdot \left(C_A C_M - \frac{C_E C_W}{K} \right) + k_A C_A \left(C_A C_M - \frac{C_E C_W}{K} \right) \quad (19)$$

where K is the equilibrium constant for esterification at reaction temperature ($K = 6.22$ at 60 °C). Autocatalysis can be neglected when using high catalyst concentrations, thus Eq. (19) reduces to

$$-\frac{dC_A}{dt} = C_C \cdot \left(\frac{0.38}{C_W^{0.83}} \right) \cdot \left(C_A C_M - \frac{C_E C_W}{K} \right) \quad (20)$$

For a molar ratio of $C_{M,0}/C_{A,0} = 2$, when expressed in terms of acetic acid conversion, Eq. (20) becomes:

$$\frac{dx}{dt} = C_C \cdot \left(\frac{0.38}{[C_{A,0}(w+x)]^{0.83}} \right) \cdot C_{A,0} \times \left[(1-x)(2-x) - \frac{x(x+w)}{K} \right] \quad (21)$$

By using numerical integration (Runge–Kutta), the acetic acid conversion at a given time can be predicted from Eq. (21). To check the applicability of Eq. (21), experiments using higher catalyst concentrations, 0.5 and 2 wt% ($C_C = 0.046$ and 0.224 M), with and without initial water addition were conducted. As shown in Fig. 6, experimental results are successfully predicted using Eq. (21) for all cases. The good agreement between predicted and experimental data further supports applicability of Eq. (6) and the validity of initial kinetic measurements as an approach to help build a practical reaction model.

4. Conclusions

The effect of water on liquid-phase sulfuric acid catalyzed esterification of acetic acid with methanol was studied by initial water addition. The decrease in initial reaction kinetics

with increasing concentration of water indicated that catalysis is impaired as esterification proceeds and water is continuously produced from the condensation of carboxylic acids and alcohols. The negative impact of water on catalysis was found to be essentially independent of temperature or molar ratio of methanol-to-acetic acid under the experimental conditions used. The thermodynamic concordance between proton solvation in binary mixtures of methanol/water and esterification indicates a strong correlation between preferential proton solvation by water and the observed deactivating effect of water. It would appear that the loss in acid strength of catalytic protons due to water solvation leads to a decrease in the concentration of protonated carboxylic acid, thus inhibiting the formation of esters. Not only esterification but also other reactions may also suffer such a deactivating effect of water when catalyzed by strong protonic acids. Thus, the simultaneous water removal during reaction should not only inhibit the reverse hydrolysis reaction, but also preserve high activity of the catalytic protons throughout reaction.

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