Effects of urea, Na$^+$ and Li$^+$ ions on the kinetics and mechanism of intramolecular general base-catalyzed glycolysm of ionized phenyl salicylate in ethane-1,2-diol–acetonitrile solvents at a constant water concentration

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ABSTRACT: Pseudo-first-order rate constants (k_1) for the reaction of ethane-1,2-diol (DOL) with ionized phenyl salicylate (PS$^-$), obtained in mixed DOL–CH$_3$CN solvent at constant [H$_2$O] and [NaOH], obey the relationship $k_1 = \alpha[\text{DOL}]_T/(1 + 2K_A[\text{DOL}]_T)$, where α is the apparent second-order rate constant, K_A is the association constant for the dimerization of DOL and [DOL]$_T$ is the total concentration of DOL. The values of K_A, in the presence of Na$^+$ ions, decrease with increase in [H$_2$O]. Lithium ions cause almost complete depolymerization of polymeric DOL (i.e. $K_A \approx 0$) under the experimental conditions imposed. The effect of 0.5 M urea on the structural behavior of the mixed solvent is kinetically insignificant. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: phenyl salicylate; ethane-1,2-diol; urea; sodium salt; lithium salt; transesterification; kinetics; intramolecular general base catalysis

INTRODUCTION

Intramolecular general acid (GA) and general base (GB) catalysis appear to be the ubiquitous feature of many enzymatic catalyses.[1] It is widely believed that the dielectric constant of the microenvironment of the active site where enzyme-catalyzed reactions occur is significantly lower than that of a pure aqueous solvent.[2] It is therefore of interest to study the effects of solvents with low dielectric constants on intramolecular GA and GB catalysis.

Intramolecular GB catalysis is considered to involve the alkanolysis of ionized phenyl salicylate (PS$^-$).[3] The structural behavior of mixed aqueous–alkanol solvents has been elucidated by studies on the alkanolysis of PS$^-$ where the change in the content of the alkanol changes both the concentration of alkanol and the dielectric constant of the reaction medium. Ethane-1,2-diolysis of PS$^-$ in mixed HOCH$_2$CH$_2$OH (DOL)–H$_2$O [containing ≤2% (v/v) CH$_3$CN, 0.01 M NaOH and 0.01 M KOH] and DOL–CH$_3$CN [containing 5% (v/v) H$_2$O and 0.01 M NaOH] revealed characteristically different [DOL]–rate profiles.[4] Lithium ions as compared with other alkali metal cations produced a different effect on [CH$_3$OH]–rate profiles for the methanolysis of PS$^-$ in a reaction medium of nearly isodielectric constant.[5] Many solution properties of CH$_3$OH–H$_2$O solvent are different from those of DOL–H$_2$O solvent.[6] It was therefore decided to study the effects of Li$^+$ and Na$^+$ ions on the rate of ethane-1,2-diolysis of PS$^-$ in DOL–CH$_3$CN solvent containing a constant content of H$_2$O. The results and the probable explanations are presented in this paper.

EXPERIMENTAL

Materials. Reagent-grade chemicals obtained commercially were used throughout the kinetic study. A stock solution of phenyl salicylate was prepared in acetonitrile.
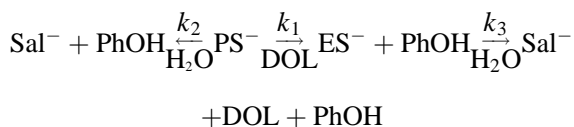
Kinetic measurements. The rate of reaction of-ethane-1,2-diol (DOL) with ionized phenyl salicylate (PS$^-$) in mixed DOL–CH$_3$CN–H$_2$O solvent was studied spectrophotometrically by monitoring the appearance of product (phenolate ion) at 290 nm. Details of the experimental procedure are described elsewhere.[7]

The general reaction scheme for the cleavage of PS$^-$ in DOL–CH$_3$CN–H$_2$O solvent is as follows:

$$\text{Sal}^- + \text{PhOH} \underset{H_2O}{\overset{k_2}{\longleftarrow}} \text{PS}^- \underset{DOL}{\overset{k_1}{\longrightarrow}} \text{ES}^- + \text{PhOH} \underset{H_2O}{\overset{k_3}{\longrightarrow}} \text{Sal}^-$$

$$+ \text{DOL} + \text{PhOH}$$

where Sal$^-$, ES$^-$ and PhOH represent salicylate ion, ionized 2-hydroxyethylsalicylate and phenol, respectively, and k_1, k_2 and k_3 are pseudo-first-order rate constants for the reaction of DOL with PS$^-$, hydrolysis of PS$^-$ and hydrolysis of ES$^-$, respectively. Under the present experimental conditions, $k_1/k_2 > 10$ (Ref. 7) and $(k_1 + k_2)/k_3 > 50$ (Ref. 8), hence these results show that k_2 and k_3 are negligible compared with k_1.

All the kinetic runs were carried out for a period of more than three half-lives of the reactions and the observed data (observed absorbance versus time) obeyed a first-order rate raw. Details of the data analysis are described elsewhere.[9]

A product analysis study has been described in an earlier paper.[10]

RESULTS

Effects of varying the content of DOL at constant [H$_2$O] and [urea]

The rate of reaction of PS$^-$ with DOL was studied at 35 °C with 4% (v/v) H$_2$O and 0.01 M NaOH and within the DOL concentration range 5–90% (v/v) in mixed DOL–CH$_3$CN solvents. The reaction rates were also studied at 8 and 18% (v/v) H$_2$O and within the DOL concentration range 5–70% (v/v) in the absence and presence of 0.5 M urea. A few kinetic runs were carried out within the DOL concentration range 5–70% (v/v) at 28% (v/v) H$_2$O. The results are shown graphically in Figure 1.

In order to establish the effect of Li$^+$ ions on the rate of reaction of DOL with PS$^-$, several kinetic runs were carried out at 8, 18 and 28% (v/v) H$_2$O and in the absence and presence of 0.5 M urea with different concentrations of DOL in DOL–CH$_3$CN solvents containing 0.01 M LiOH. The results are shown as the plots of pseudo-first-order rate constants (k_1) versus [DOL] in Figure 2.

It may be noted that the reaction mixtures at 8% (v/v) H$_2$O with ≤25% (v/v) DOL and 18% (v/v) H$_2$O with ≤15% (v/v) DOL were initially colourless but became turbid as the reaction progressed. The reaction half-life at which this turbidity appeared decreased with decrease in the content of DOL. The presence of 0.5 M urea decreased this turbidity. For example, in the absence of urea at 18% (v/v) H$_2$O and 15% (v/v) DOL the turbidity appeared at 2.2 half-lives, whereas such turbidity did not appear until 3.4 half-lives in the presence of 0.5 M urea.
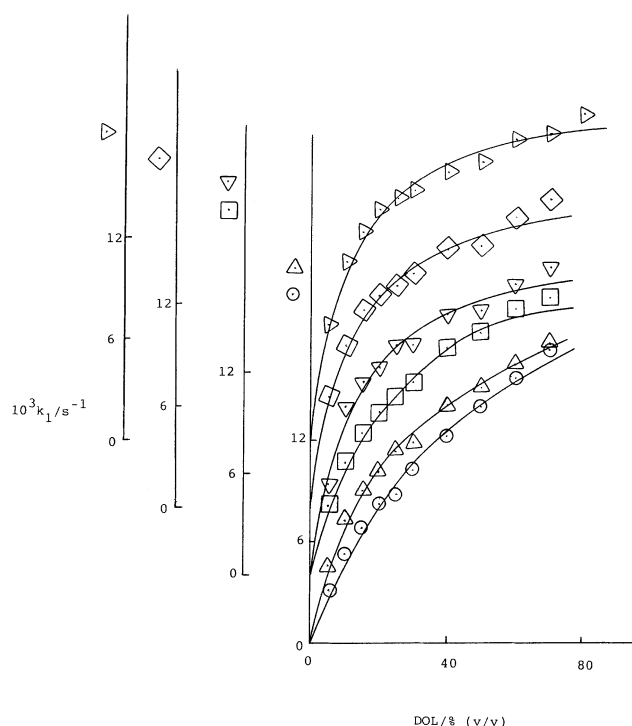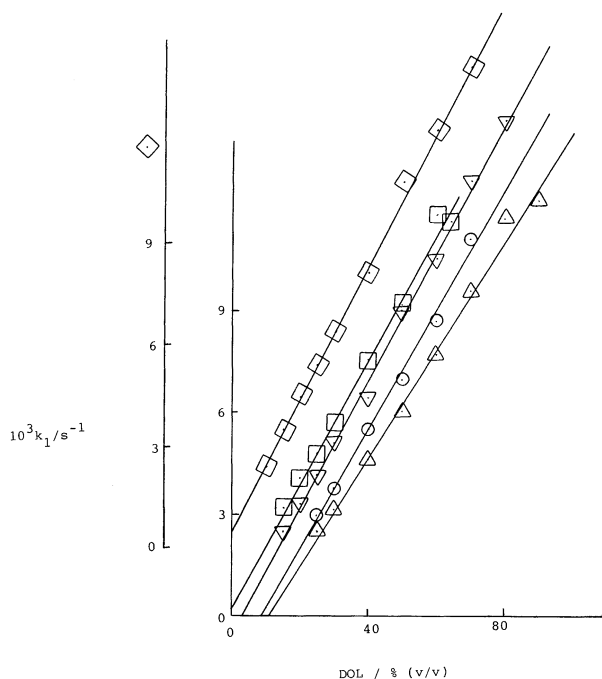

Figure 1. Plots showing the dependence of pseudo-first-order rate constants (k_1) for the reaction of DOL with PS$^-$ on the content of DOL in the reaction mixtures containing mixed DOL–CH$_3$CN solvents, 2.0×10^{-4} M PS$^-$, 0.01 M NaOH and 4% (v/v) H$_2$O (▷), 8% (v/v) H$_2$O + 0.5 M urea (◊), 8% (v/v) H$_2$O (▽), 18% (v/v) H$_2$O + 0.5 M urea (□), 18% (v/v) H$_2$O (△) and 28% (v/v) H$_2$O (○). The solid lines are drawn through the least-squares calculated points

DISCUSSION

Pseudo-first-order rate constants (k_1) for the reaction of DOL with phenyl salicylate obtained within the DOL concentration range 10–90% (v/v) were found to be independent of [HO$^-$] within the range 0.01–0.05 M.[10] Hence the rate of ethane-1,2-diolysis of phenyl salicylate under the present experimental conditions should be independent of pH. The pH-independent hydrolysis[11–13] and alkanolysis[3] of phenyl salicylate have been shown to involve intramolecular GB catalysis. The occurrence of kinetically indistinguishable intramolecular GA catalysis in these reactions has been ruled out. The mechanism of alkanolysis of ionized phenyl salicylate (PS$^-$) has been discussed elsewhere.[3]

The dielectric constant (ε) of CH$_3$CN ($\varepsilon = 37.0$ at 25 °C[14]) is similar to that of DOL ($\varepsilon = 37.7$ at 25 °C[15]). Therefore, ε of mixed DOL–CH$_3$CN solvents containing a constant [H$_2$O] and different ratios of [DOL] and [CH$_3$CN] may be considered to be constant. Hence the change in k_1 values with the change in the content of DOL in DOL–CH$_3$CN solvents containing a constant [H$_2$O] cannot be attributed to the effect of ε of the

Figure 2. Plots showing the dependence of pseudo-first-order rate constants (k_1) for the reaction of DOL with PS^- on the content of DOL in the reaction mixtures containing mixed DOL–CH_3CN solvents, 2.0×10^{-4} M PS^-, 0.01 M LiOH and 8% (v/v) H_2O (△), 8% (v/v) H_2O + 0.5 M urea (○) 18% (v/v) H_2O (▽), 18% (v/v) H_2O + 0.5 M urea (□) and 28% (v/v) H_2O (◊)

reaction medium. The rate law for the overall reaction of DOL with PS^- may be given as

$$\text{rate} = k[\text{DOL}][\text{PS}^-] \qquad (1)$$

where k is the apparent second-order rate constant for ethane-1,2-diolysis of PS^-. Equation (1) predicts that the plot of pseudo-first-order rate constants (k_1, where $k_1 = k[\text{DOL}]_T$) versus total concentration of DOL ($[\text{DOL}]_T$) should be linear with zero intercept provided that $[\text{DOL}] = [\text{DOL}]_T$, i.e. all the DOL molecules exist in monomeric form, (DOL). This appears to be true only at very low contents of DOL in the presence of 0.01 M NaOH (Figure 1). Pseudo-first-order rate constants show negative deviations from linearity at high contents of DOL (Figure 1). Causes such as self-association of PS^- molecules only and association of DOL and PS^- molecules, of the non-linear nature of such a plot have been ruled out.[10] The most probable cause for the non-linear variation of k_1 against [DOL] may be ascribed to the self-association of DOL molecules.
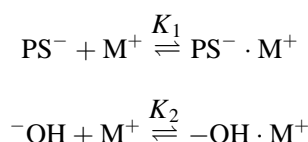
The concept of self-association of alkanol molecules in mixed aqueous solvents has been used to explain the rate–[alkanol] profiles in the alkanolysis of PS^-.[3–5,7,16,17] The characteristics of self-association of DOL molecules

may provide the relationship between [(DOL)] and $[\text{DOL}]_T$ as given by the equation[18]

$$[(\text{DOL})] = \frac{[\text{DOL}]_T}{1 + 2K_A[\text{DOL}]_T} \qquad (2)$$

where $K_A = [(\text{DOL})_2]/[(\text{DOL})]^2 = [(\text{DOL})_3]/[(\text{DOL})_2]\cdot[(\text{DOL})] = \ldots[(\text{DOL})_n]/[(\text{DOL})_{n-1}][(\text{DOL})]$[19] and $[(\text{DOL})]$ is the concentration of monomeric DOL.

In mixed DOL–CH_3CN–H_2O solvents with H_2O contents of $\leq 28\%$ (v/v), the following ion-pair formation between cations and anions:

$$\text{PS}^- + \text{M}^+ \overset{K_1}{\rightleftharpoons} \text{PS}^- \cdot \text{M}^+$$

$$^-\text{OH} + \text{M}^+ \overset{K_2}{\rightleftharpoons} {}^-\text{OH} \cdot \text{M}^+$$

cannot be completely ruled out. These reactions can lead to the equation provided that $1 << K_2[\text{M}^+]$ or $K_2[\text{HO}^-]$,

$$[\text{PS}^-] = \frac{[\text{PS}]_T}{1 + \beta[\text{M}^+]_T^{1/2}} \qquad (3)$$

where $[\text{PS}]_T$ and $[\text{M}^+]_T$ represent the total concentration of phenyl salicylate and cation, respectively, and $\beta = K_1 K_2^{-1/2}$.

The enhanced reactivity of PS^- towards a nucleophile with hydrogen attached to the nucleophilic site is the consequence of intramolecular GB catalysis due to the ionized o-phenolic group.[11–13] The ion-pair ($PS^-.M^+$) formation is expected to decrease the efficiency of intramolecular GB catalysis. The rate of reaction of DOL with $PS^-.M^+$ is therefore ignored compared with that with the free form (PS^-) of ionized phenyl salicylate.

The observed rate law, rate $= k_1[\text{PS}]_T$, and equation (1) with $[(\text{DOL})]$ and $[\text{PS}^-]$ obtained from equations (2) and (3) can yield the equation

$$k_1 = \frac{k[\text{DOL}]_T}{(1 + \beta[\text{M}^+]_T^{1/2})(1 + 2K_A[\text{DOL}]_T)} \qquad (4)$$

At constant $[\text{M}^+]_T$, equation (4) is reduced to equation (5) provided that β remains constant with changes in the ratio of mixed solvent components, where $\alpha = k/(1 + \beta[\text{M}^+]_T^{1/2})$.

$$k_1 = \frac{\alpha[\text{DOL}]_T}{1 + 2K_A[\text{DOL}]_T} \qquad (5)$$

where $\alpha = k/(1 + \beta[\text{M}^+]_T^{1/2})$.
Pseudo-first-order rate constants (k_1) obtained in the presence of 0.01 M NaOH obeyed equation (5). The unknown parameters, α and K_A, were calculated from

Table 1. Values of α and K_A calculated from equation (5)[a]

[MOH] (M)	[H$_2$O] (%, v/v)	[Urea] (M)	$10^3\alpha$ (M^{-1} s^{-1})	$10^3 K_A$ (M^{-1})	[DOL]range (%, v/v)	No. of runs
0.01[b]	4	0.0	10.9 ± 0.6[c]	266 ± 20[c]	5–90	11
	8	0.0	9.09 ± 0.76	223 ± 25	5–70	10
	8	0.5	9.72 ± 0.90	245 ± 30	5–70	10
	18	0.0	5.36 ± 0.42	119 ± 15	5–70	10
	18	0.5	4.89 ± 0.29	112 ± 11	5–64	10
	28	0.0	3.06 ± 0.18	51.8 ± 6.7	5–70	10
0.01[d]	8	0.0[e]	0.885 ± 0.032		25–90	8
	8	0.5	0.979 ± 0.041		25–70	6
	18	0.0	1.05 ± 0.02		15–80	9
	18	0.5	1.01 ± 0.04		15–64	8
	28	0.0	1.10 ± 0.02		10–70	9

[a] $[PS]_0 = 2 \times 10^{-4}$ M, 35°C, $\lambda = 290$ nm, organic co-solvent CH$_3$CN.
[b] MOH = NaOH.
[c] Error limits are standard deviations.
[d] MOH = LiOH.
[e] The values of α were calculated from the equation: $k_1 = \Psi + \alpha$ [DOL]$_T$.

equation (5) using the non-linear least-squares technique. The calculated values of α and K_A at different [H$_2$O] and in the absence and presence (0.5 M) of urea are summarized in Table 1. The fitting of the observed data to equation (5) is evident from the standard deviations associated with α and K_A (Table 1) and from the plots in Figure 1 where the solid lines are drawn through the least-squares calculated points.

An increase in water content from 4 to 28% (v/v) decreased α from 10.9×10^{-3} to 3.06×10^{-3} M^{-1} s^{-1} and K_A from 0.266 to 0.052 M^{-1}. The decrease in K_A due to the increase in [H$_2$O] is due to the water molecules acting as the depolymerizing agents for the DOL structure in DOL–CH$_3$CN solvent. Nearly 1.5- and 2.5-fold decreases in α and K_A, respectively, were obtained in the methanolysis of PS$^-$ under essentially similar experimental conditions.[5] The value of k (2.10×10^{-3} M^{-1} s^{-1})[17] for the methanolysis of PS$^-$ in CH$_3$OH–H$_2$O solvent is slightly larger than k (1.52×10^{-3} M^{-1} s^{-1})[4] for ethane-1,2-diolysis of PS$^-$ in DOL–H$_2$O solvent. However, the value of α (10.9×10^{-3} M^{-1} s^{-1}) for DOL is nearly three times larger than α (3.15×10^{-3} M^{-1} s^{-1}) for methanol[5] at 4% (v/v) H$_2$O in mixed alkanol–acetonitrile solvents. It seems to be unlikely that $K_1 K_2^{-1/2}$ in DOL–CH$_3$CN is smaller than that in CH$_3$OH–CH$_3$CN at 4% (v/v) H$_2$O and therefore k should be significantly larger at 4% (v/v) H$_2$O than k at >28% (v/v) H$_2$O in DOL–CH$_3$CN solvent. The value of k has been shown to be nearly 30 times larger at 10% (v/v) H$_2$O than at 30% (v/v) H$_2$O in the presence of Na$^+$ ion for methanolysis of PS$^-$.[5]

The increase in k with decrease in the content of H$_2$O in mixed DOL–CH$_3$CN solvents may be attributed to the following reasons. (i) The decrease in the content of H$_2$O in mixed DOL–CH$_3$CN–H$_2$O solvents is expected to decrease the number of H$_2$O molecules in the solvation shells of monomeric DOL and free PS$^-$ molecules. This characteristic, in turn, decreases the solvation energy of (DOL) and free PS$^-$ because water molecules are much better solvating molecule than acetonitrile molecules. The decrease in the solvation energy of (DOL) and free PS$^-$ should decrease the apparent activation energy for the reaction of DOL with PS$^-$. (ii) The mechanism of the reaction of DOL with PS$^-$ involves a transient intramolecular intimate ion pair (**I$_1$**). The stability of such an intermediate should increase with decrease in the dielectric constant of the reaction medium. Hence the decrease in the content of H$_2$O in DOL–CH$_3$CN–H$_2$O solvent should stabilize the apparent transition state and consequently increase the rate constant, k. Significantly larger values of α for DOL (Table 1) compared with the corresponding values of α for CH$_3$OH[5] may be partially attributed to the stabilization of the intramolecular intimate ion pair due to internal hydrogen bonding as shown by **I$_2$** in a solvent of low dielectric constant and containing low content of water.

R = CH$_2$CH$_2$OH

I$_1$

I$_2$
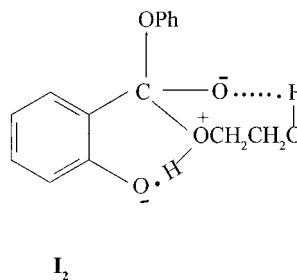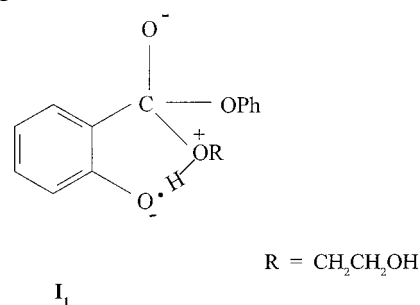
The plots of k_1 versus [DOL] obtained in mixed DOL–CH$_3$CN solvents containing 0.01 M LiOH and a constant content of H$_2$O turned out to be linear (Figure 2). Similar results were obtained in the methanolysis of PS$^-$ under similar experimental conditions.[5] The linearity of these plots indicates that $K_A \approx 0$ under the experimental conditions of these obervations. Lithium ions break the alkanol structure owing to their high surface charge density. Hence for the mixed DOL–CH$_3$CN–H$_2$O solvents containing $\leq 28\%$ (v/v) H$_2$O, 0.01 M LiOH and 2×10^{-4} M phenyl salicylate, $K_A \approx 0$. Equation (4) is reduced to

$$k_1 = \frac{k[DOL]_T}{1 + \beta[Li^+]_T^{1/2}} \quad (6)$$

if $K_A = 0$.

Equation (6) predicts that the plot of k_1 versus $[DOL]_T$ should be linear with essentially zero intercept if β remains constant with change in the content of CH$_3$CN in DOL–CH$_3$CN solvents with a constant [H$_2$O]. This seems to be true at $\geq 18\%$ (v/v) H$_2$O. The linear plots at 8% (v/v) H$_2$O revealed negative intercepts. The large negative intercepts reveal the change in β with the change in the content of CH$_3$CN at low content of DOL in DOL–CH$_3$CN solvents containing a constant $[Li^+]_T$ and [H$_2$O].[5]

The slopes $\{\alpha = k/(1 + \beta[Li^+]_T^{1/2})\}$ of the linear plots of k_1 versus $[DOL]_T$ were calculated by the linear least-squares technique and the results obtained are summarized in Table 1. The values of α slightly increased (ca 20%) with increase in the content of H$_2$O from 8 to 28% (v/v). Similar observations were made in the methanolysis of PS$^-$ at 0.01 M LiOH.[5] The value of α at a constant [H$_2$O] is significantly larger at 0.01 M Na$^+$ than at 0.01 M Li$^+$ (Table 1). The value of k may not be expected to change with change in cation from Li$^+$ to Na$^+$ ion.[17] Hence the lower α values in the presence of Li$^+$ ions are the consequence of the larger β values in the presence of Li$^+$ ions compared with Na$^+$ ions.

The proposal that $K_A \approx 0$ in the presence of Li$^+$ does not necessarily mean that k_1 should be larger in the presence of Li$^+$ than Na$^+$ where $K_A \neq 0$. The rate of ethane-1,2-diolysis of ionized phenyl salicylate is proportional to the concentration of both monomeric DOL, [(DOL)], and free ionized phenyl salicylate, [PS$^-$] [equation (1)]. In terms of equation (4), the decrease in K_A should increase k_1 provided that β remains unchanged with the change from Li$^+$ to Na$^+$. Significantly lower values of α in the presence of Li$^+$ compared with Na$^+$ indicate that β values are larger in the presence of Li$^+$ than Na$^+$. Hence although $K_A \approx 0$ in the presence of Li$^+$, the values of k_1 are smaller for Li$^+$ than for Na$^+$ simply because the α values are smaller for Li$^+$ than for Na$^+$ (Table 1). Similar results were obtained in the methanolysis of PS$^-$ where the respective values of k, β and K_A are 2.18×10^{-3} M^{-1} s^{-1}, 0.94 M$^{-1/2}$ and 20.5 M^{-1} for

K$^+$, 2.42×10^{-3} M^{-1} s^{-1}, 2.70 M$^{-1/2}$ and 19.2 M^{-1} for Na$^+$ and 1.80×10^{-3} M^{-1} s^{-1}, 11.5 M$^{-1/2}$ and 0.0 M^{-1} for Li$^+$ at 30% (v/v) H$_2$O and 30 °C.[5]

Urea molecules are known to reduce hydrophobic interactions.[20] Urea molecules are expected to be preferentially solvated by water molecules in DOL–CH$_3$CN–H$_2$O solvent. Hence the presence of urea should increase both α and K_A owing to entrapment of water molecules by the solvation shells of the urea molecules. However, the presence of 0.5 M urea at 8 and 18% (v/v) H$_2$O did not produce a detectable effect on α and K_A at 0.01 M NaOH and on α at 0.01 M LiOH (Table 1). This shows that under such conditions, the concentration of urea was not sufficient to cause a significant decrease in the number of water molecules in the solvation shells of DOL and CH$_3$CN molecules. The values of α and K_A are not appreciably different at 4 and 8% (v/v) H$_2$O (Table 1). The use of higher concentrations of urea (>0.5 M) was restricted owing to relatively low solubility of urea in CH$_3$CN.

Many solution properties of polyhydric alcohols and mixed aqueous polyhydric alcohols are very different from those of monohydric alcohols and mixed aqueous monohydric alcohols.[6,21] However, the effects of [Li$^+$] and [Na$^+$] on rates of intramolecular general base-catalyzed methanolysis[5] and ethane-1,2-diolysis of PS$^-$ in mixed alkanol–acetonitrile solvents containing a constant [H$_2$O] appeared to be insensitive to the different solution properties of these mixed solvents.

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