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# EQUILIBRIA IN SOLUTIONS OF METHANOL OR ETHANOL, SULFURIC ACID, AND ALKYL SULFATES

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Summary: Equilibria in reactions of methanol and ethanol with sulfuric acid or in hydrolyses of alkyl sulfates were followed using $^{13}$C NMR, anion-exchange HPLC, and titrations. Variations of equilibrium constant $K = [\text{ester}][H_2O]/[ROH][HSO_4^-]$ with acidity indicate participation of reactions $ROH_2^+ + HSO_4^- \rightleftharpoons ROH^+SO_3^- + H_2O$, accompanied by acid base equilibria involving the alcohol and the ester. For mixtures containing initially 20% (w/w) alcohol, $pK_{MeOH_2^+} = -4.2$, $pK_{EtOH_2^+} = -3.7$, $pK_{MeOH^+SO_3^-} = -3.3$ and $pK_{EtOH^+SO_3^-} = -2.7$.

Even though equilibria between ethanol, sulfuric acid, and ethyl sulfate play a role in the manufacture of ethanol from ethylene and diethyl ether from ethanol, little attention has been paid to equilibrium constants of such reactions[1,2] and in particular to their dependence on sulfuric acid concentration. The reaction is now of interest because of its possible use in the treatment of aqueous solutions of ethanol, resulting from biomass treatment. Proton[3-5] and $^{33}$S NMR[6-8] show limited separation of signals for the alcohol and the sulfuric acid ester, and sulfuric acid and its ester, respectively. Well separated peaks in the $^{13}$C NMR spectra for methanol or ethanol and their esters enabled finding ratios [ester]/[ROH] as well as determining the concentration of dialkyl ethers observed for $[H_2SO_4] > 65\%$ (w/w). Anion-exchange HPLC yielded $[\text{ester}^-]/[HSO_4^-]$ ratios and titrations gave ester concentration. Concentrations of dialkylesters $(RO)_2SO_2$ have been negligible. Equilibrium constant $K = [\text{ester}][H_2O]/[ROH][HSO_4^-]$ describes the system better than $K' = [\text{ester}]/[ROH][HSO_4^-]$, as proved by measurements of equilibrium concentrations at given concentration of sulfuric acid and varying concentration of ethanol. At $[H_2SO_4] < 45\%$ (w/w) the establishment of the equilibrium occurs in several days. Dependence of equilibrium constant K on acidity function $H_0^{Et}$ (obtained[4,9,10] in $H_2SO_4$-$H_2O$ - 20% EtOH) follows the expression $K = K_e\,(1 + K_{SOH}/[H^+])/(1 + K_{ROH}/[H^+])$ corresponding to the system of reactions (1)-(3):

$$ROH_2^+ \rightleftharpoons ROH + H^+ \qquad K_{ROH_2^+} \qquad (1)$$

$$ROH_2^+ + HSO_4^- \rightleftharpoons ROH^+SO_3^- + H_2O \qquad K_e \qquad (2)$$

$$ROH^+SO_3^- \rightleftharpoons ROSO_3^- + H^+ \qquad K_{SOH} \qquad (3)$$

By curve fitting of $K = f(H_o^{Et})$ the following values were obtained for solutions initially containing 20% (w/w) of the alcohol:

| Alcohol | $K_e$ | $pK_{ROH_2^+}$ | $pK_{SOH}$ |
|---|---|---|---|
| MeOH | 4.4 | -4.2 | -3.3 |
| EtOH | 2.1 | -3.7 | -2.7 |

Plots of log I vs. $H_o^{Et}$ are linear with slopes of about 0.7 indicating that anilines are acceptable but not ideal indicators for these systems. Values of $pK_{ROH_2^+}$ are a function of initial alcohol concentration, indicating a solvent effect, which results from high equilibrium concentrations of the alcohol and the ester. Quoted $pK_{ROH_2^+}$ values are thus only approximate, but closer to the values $pK_{EtOH_2^+} = -4.8$ (proton NMR[5]) and $pK_{MeOH_2^+} = -4.86$ (Raman[11]) than to the widely adopted $pK_{MeOH_2^+} = -1.94$ (proton NMR[3], using Bunnett-Olsen[12] treatment).

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