

P-7: Impact of Ultrasound on Some Solute-Solvent Interactions

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Acetonitrile-water mixtures are widely used in many fields such as liquid chromatography, solvent extraction, organic synthesis etc.

Small additions of acetonitrile are frequently used to dissolve practically insoluble substrates in water, e.g. for kinetic measurements. As usual, the fate of the substrate after blending the addition with the solvent system is not much concerned about.

We determined first-order rate constants for the neutral hydrolysis of 4-methoxyphenyl dichloroacetate (4-MPDCA) in the presence of small and very small additions of acetonitrile under ultrasound and without sonication. The results are presented in Figure 1.

Additions of acetonitrile (lower curve on Figure 1) at first enhanced the reaction rate which passed a maximum at 0.04 mole % of acetonitrile (a 2000 times molar excess to the ester) and further decreased similarly to the case of any water-organic reaction medium.

Application of ultrasound demonstrated incomplete dissolution of the ester in the region up to 0.03 mole % of acetonitrile. The first point in Figure 1 corresponds to a 200 times molar excess of acetonitrile. Sonication of this mixture provides the hypothetical silent rate constant for pure water as indicates the extrapolation from aqueous acetonitrile solutions to pure water (see the insertion in Figure 1.). Kinetic sonication effects at further additions of acetonitrile reflect more complicate solvation phenomena.

Results of this work clearly demonstrate usefulness of sonochemical methods for elucidation of solute-solvent interactions. A conclusion, also important for the laboratory practice, affirms that too small additions of acetonitrile may not ensure complete dissolution of the substrate while greater additions can bring about unexpected solvent effects.

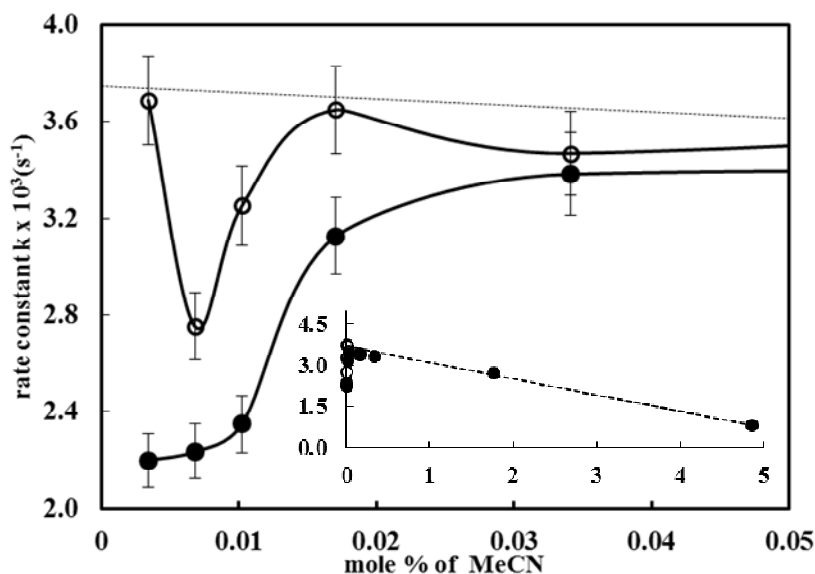


Figure 1. First-order rate constants for the neutral hydrolysis of 4-MPDCA in the presence of small and very small additions of acetonitrile under ultrasound (\circ) and without sonication (\bullet). Dashed line represents extrapolation from aqueous acetonitrile solutions to pure water.

Experimental

Kinetic measurements of the neutral hydrolysis of 4-MPDCA in the presence of acetonitrile were carried out on the ultrasonic on-line spectrophotometric system developed for kinetic measurements of homogeneous polar reactions under ultrasound. The setup consists of an ultrasonic bath, an HPLC UV/Vis detector, an HPLC pump, a refrigerated heating circulator bath, and a data processing unit (Figure 2 (Piiskop, 2012)). An analog-digital

converter was constructed and a data processing program AD_com was written for registration of the detector signal.

All hydrolysis reactions were performed without sonication and under ultrasound. The pH of the solutions was maintained at 3.65 ± 0.05 with hydrochloric acid. Calculated amounts of 4-MPDCA were dissolved in analytical grade acetonitrile. Solutions were injected into 150 mL of the aqueous solution in the reaction cell providing 10^{-5} M initial concentration of the ester. All experiments were performed at 25.0 ± 0.05 °C under argon atmosphere. The formation of 4-methoxyphenol was monitored at 290 nm.

Sonication was performed with Elma TI-H-5 MF2 cleaning bath at 25 kHz. The ultrasonic power was 1.6 ± 0.5 W/150 mL in water according to the calorimetric measurements carried out in the reaction cell.

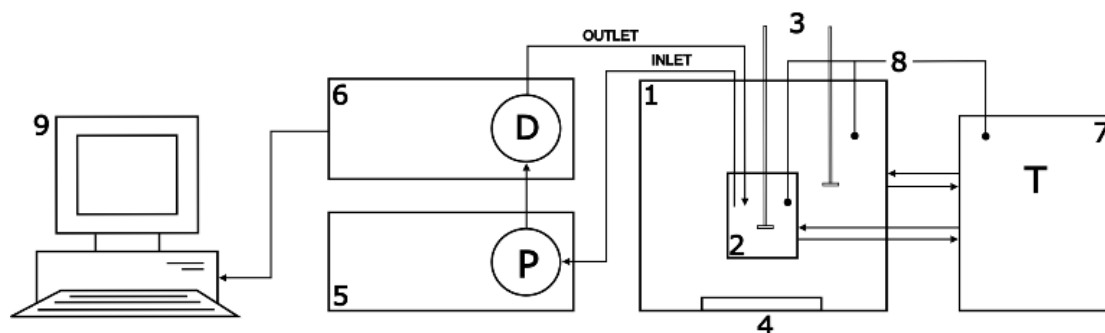


Figure 2. The ultrasonic on-line spectrophotometric system: 1) ultrasonic bath with temperature control 2) reaction cell with temperature control 3) mechanical stirrers 4) ultrasonic transmitter 5) HPLC pump 6) HPLC UV/Vis detector 7) thermostat 8) temperature control 9) data processing unit

Acknowledgement

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References

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