THE INFLUENCE OF SELECTIVE SOLVATION ON THE KINETICS OF REACTION BETWEEN MALACHITE GREEN AND HYDROXIDE ION

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abstract: The kinetics of the reaction between malachite green and hidroxide ion was studied in several binary mixtures of water with alcohols (methanol, ethanol, 1-propanol, ethylene glycol and glycerol) and aprotic solvents (DMSO). In all solvents, the selective (preferential) solvation is present. A method for estimating the dielectric constant in the solvation shell and the constant of preferential solvation was proposed. The results indicate that the composition of solvent in the solvation shell depends on the nature of nonaqueous component; in solvents containing ethanol, 1-propanol and glycerol, the water is preponderant in the solvation shell, while in solvents containing methanol, ethylene glyol and DMSO, the nonaqueous component is in greater proportion than in bulk solution.

Introduction

The solvent effect on the reaction rates can be studied using either a series of solvents with different discontinuous properties or binary solvent mixtures. Using binary solvent mixtures has the advantage of the continuous variation of solvation properties, accompanied however by an increase of the solvation complexity due to the occurrence of preferential (or selective) solvation, induced by the differences in the specificity of solvate-solvent interactions. This differences lead to significant changes in the composition of the solvation shell as compared with the bulk composition.

The preferential solvation can be explained quantitatively by several theoretical models. Some simple models consider that the equilibrium constant for preferential solvation depends on the distribution of solvents in the solvation shell and the bulk solution [1,2] or that it is a competition between solvent molecules in the process of solvation, depending on the geometric and electronic affinity [3]. These models can be improved by considering the demixing energy or the corresponding excess free energy [4].

For the study of preferential solvation, a simple ion-ion reaction (reaction of malachite green with hydroxyl ion) was chosen, because for reactions between charged species the electrostatic effects have the greatest weight. Binary mixtures of water with hydroxylic

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components (methanol, ethanol, 1-propanol, 2-propanol, ethylene glycol and glycerol) or aprotic solvents (acetone, dioxane, tetrahydrofurane and dimethylsulfoxide) were used.

The reaction of malachite green (4-[(4-dimethylaminophenyl)-phenyl-methyl]-N, N-dimethyl-aniline) with hydroxide ions in aqueous media follows a first order kinetics in excess of HO-. The reaction can be followed spectrophotometrically at λ=630 nm [5].

Experimental

The fading of malachite green was followed at λ = 630 nm using a Pye-Unicam spectrophotometer until no change of absorbance was observed. The initial concentration of malachite green was [MG] = 1.54 10^{-4} M and of sodium hydroxide $[HO^-] = 1.07 \cdot 10^{-3}$ M. Several kinetic measurements were made for different quantities of nonaqueous component. For mixtures containing a very small amount of 2-propanole, acetone and THF, a shift in absorption maximum of malachite green was observed; for DMSO the shift was observed at concentrations of solvent exceeding 10%(in volume), and in the case of ethyleneglycole at concentrations greater than 50%. In all other mixtures no significant shifts were observed. Since the hydroxide is in large excess in all data sets, the reaction is apparently of a pseudo-first order and the integral kinetic equation has the form:

$$A_t / A_0 = \exp(-k_1 t) \tag{1}$$

where A_t and A_0 stand for absorbance at the time t, and 0 respectively, k_1 is the pseudo-first order constant and t is the time. The kinetic constants k_1 were estimated by nonlinear regression, fitting equation (1) on the experimental data $A = f(t)$ and the kinetic constants for the second order reaction were calculated as $k_2 = k/[HO^-]$, where $[HO^-] = 1.07\ 10^{-3}$M. The dielectric constants of the media were taken from literature [6, 7, and 8].

Results and discussions

The integral kinetic curves absorbance *vs*. time, for different solvent compositions, is presented in Fig. 1 for methanol-water mixtures.

The pseudo-first order rate constants k_1 were estimated by nonlinear regression; for all data runs the correlation coefficient was greater than 0.995, indicating that the reaction can be safely approximated as being of first order. The values of k_1 increase with the nonaqueous component concentration for methanol, ethanol, 1-propanol and DMSO and present a maximum for ethyleneglycole and glycerol-water mixtures.

For ion-ion reactions, where the dielectric solvation is the most important, a linear dependence of the logharithm of kinetic constant on the reciprocal of dielectric constant of the media is expected. For the reaction between malachite green and hydroxide ion, it can be observed in Fig. 2 that the plots are not linear. This pattern can be attributed to the preferential solvation of ions in the binary mixtures.

For a quantitative analysis of the preferential solvation, a very simple model was proposed. It is assumed that the solvent is distributed between two phases: the bulk solvent mixture and the solvate solvation shell [1]. The equilibrium constant for the preferential solvation depends on the molar ratio of the mixture components within the two phases. Due to the selective interactions between the ions and solvents molecules, in the solvation shell the mixture composition is different from those in the bulk solution.

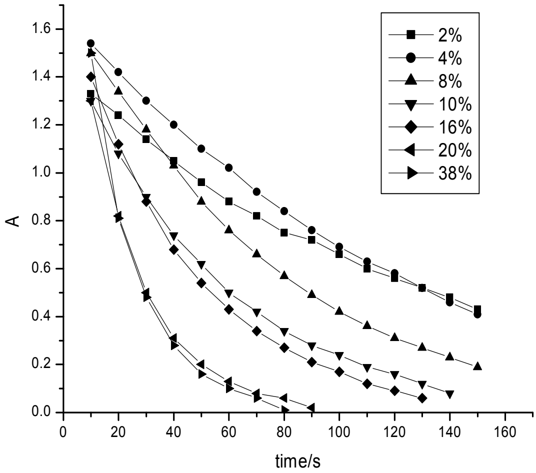

Fig. 1 *Kinetic data for malachite green fading in water-methanol mixtures*

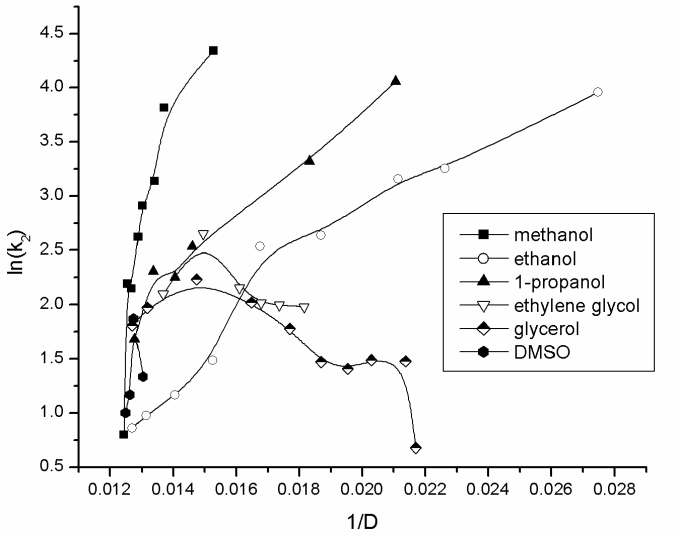

Fig. 2 *Variation of the rate constants with the dielectric constant in mixed solvents*

For regular solutions, a linear relation between the ratio of molar ratios of the components in the solvation shell and in bulk solution should be obtained. For other real solutions, deviations from linearity appear, due to the preferential solvation. This phenomenon was also observed for other reactions of dye fading [9]. The equilibrium constant for preferential solvation was calculated as the ratio between the mole number of solvent components in the solvation shell (n_w^*/n_s^*) and those in the bulk solution (n_w/n_s), where n_w is the number of moles of water and n_s the numbers of moles of nonaqueous component:

$$K_{ps} = (n_w^*/n_s^*)/(n_w/n_s) \tag{2}$$

A new method for estimating the constant of preferential solvation (K_{ps}) was proposed. For an ion-ion reaction between ions A and B with charges z_A and z_B, respectively:

$$\mathrm{A}^{z_A} + \mathrm{B}^{z_B} \leftrightarrow \mathrm{X}^{\neq(z_A+z_B)} \rightarrow \text{products}$$

where $\mathrm{X}^{\neq(z_A+z_B)}$ is the corresponding transition state, the rate constant depends on the activity coefficients of reactants and transition state according to Brönsted-Bjerrum equation : $ln\, k = ln\, k_0 + ln\, \gamma_A + ln\, \gamma_B - ln\, \gamma_{X^{\neq}}$ where the activity coefficients are given by:

$$\ln \gamma_i = -\frac{N_A e^2}{8\pi\varepsilon_0 RT}\frac{z_i^2}{r_i}\left(1-\frac{1}{D}\right) + \text{nonelectrostatic term}$$

In the absence of preferential solvation, the rate constant can be calculated as:

$$ln\, k = ln\, k_0 - B \cdot F + B \cdot F/D \tag{3}$$

where:

$$B = \frac{N_A e^2}{8\pi\varepsilon_0 RT} \quad \text{and} \quad F = \frac{z_A^2}{r_A} + \frac{z_B^2}{r_B} - \frac{z_{X^{\neq}}^2}{r_{\neq}} \tag{4}$$

For the reaction between malachite green and HO^- in mixed solvents, a deviation from linearity exists for all mixtures. The deviation is:

$$d(ln\, k)/d(1/D) = B \cdot F/\varphi \tag{5}$$

where φ is a correction factor which includes the change of dielectric constant due to the selective solvation of reactants by the components of mixture. If the correction factor φ is known, the dielectric constant in the solvation shell (D^*) can be calculated as:

$$D^* = \varphi \cdot D \tag{6}$$

Since for all studied mixtures the macroscopic dielectric constant can be conveniently expressed as a function of the molar ratios of components according to an empirical equation of the form:

$$D = a_0 + a_1\left(n_w/n_s\right) + a_2\left(n_w/n_s\right)^2 + a_3\left(n_w/n_s\right)^3 + a_4\left(n_w/n_s\right)^4 \tag{7}$$

where a_i are parameters depending on the concerned solvent, a similar equation, with the same coefficients is assumed to be valid for the dependence of the dielectric constant within the solvation shell on the molar ratios of components:

$$D^* = a_0 + a_1\left(n_w^*/n_s^*\right) + a_2\left(n_w^*/n_s^*\right)^2 + a_3\left(n_w^*/n_s^*\right)^3 + a_4\left(n_w^*/n_s^*\right)^4 \tag{8}$$

For estimation of molar ratios in the solvation shell, the electrostatic factor ($B \cdot F$) in the absence of preferential solvation was calculated as the first degree coefficient (b_1) of the best polynomial fit on the $ln\ k = b_0 + b_1(1/D) + b_2(1/D)^2 + b_3(1/D)^3$ curve; the derivatives $d(ln\ k)/d(1/D)$ were estimated from the best fit function on the $ln\ k = f(1/D)$. The estimated value of B was compared with the one obtained from electrostatic model of dielectric solvation (4); the values are of the same order of magnitude. After the calculation of the correction factor, φ, according to equation (5), the dielectric constant in the solvation shell was calculated using the equation (6). The coefficients of the 4th order polynomial of equation (7) were estimated by linear regression on $D = f((n_w/n_s))$ data, and the molar ratio in the solvation shell was estimated by numerical solving of equation (8); the constant of preferential solvation was estimated from the relation (2). If $K_{ps} < 1$, in the solvation shell the nonaqueous component is in greater proportion, while if $K_{ps} > 1$, the water is predominant in the solvation shell; if $K_{ps} = 1$, there is no selective solvation by none of the components.

For the reaction between malachite green and sodium hydroxide the values of dielectric constants in the solvation shell is smaller than the macroscopic one in all mixtures, except for the DMSO-water mixture, when greater values were obtained. The variation of the preferential equilibrium constant with the molar ratio of the nonaqueous component is given in Fig. 3.

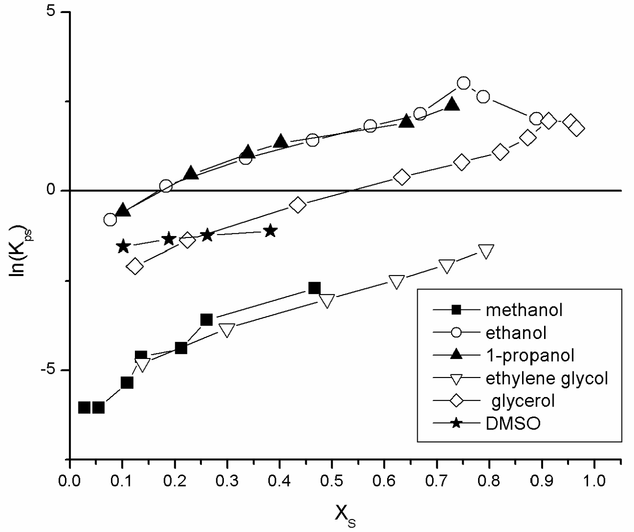

Fig. 3 *Variation of preferential solvation constant with the molar ratios of nonaqueous component*

From Fig. 3 it can be observed that the preferential solvation constant is smaller than unity in water - methanol, water – ethylene glycol and water – DMSO mixtures, indicating that in the solvation shell the nonaqueous component is in greater proportion that in the bulk solution. In water-ethanol, water – 1-propanol and water-glycerol mixtures, the values of preferential solvation constant are both over and below unity; in the solvation shell the water is preponderant at a molar ratio greater than 0.15 for ethanol 0.16 for 1-propanol and 0.5 for glycerol. The results can be attributed to the properties of concerned mixtures, so that the differences (ΔD) between the measured dielectric constants and the calculated ones (assuming that the mixtures are ideal [10]) were estimated. For water –ethanol and water-glycerol mixtures, the change of sign of preferential solvation constant coincides with the extreme point of the variation $\Delta D=f(X_S)$; in the other mixtures, no correlation was observed.

The interpretation of these results meets with difficulties due to the complexity of interactions of both reactants and transition state. The hydroxide ion keeps in the solvation shell mostly the water molecules, while the malachite green, due to benzene rings can interact also with the hydrophobic residues of the nonaqueous components.

In all mixtures the reaction was faster than in water, so that the interactions between malachite green and the nonaqueous component from the solvation shell have a crucial role in the increasing of the rate constant.

Conclusions

The reaction between malachite green and sodium hydroxide was studied in several aqueous binary solvent mixtures with nonaqueous solvents (methanol, ethanol, 1-propanol, ethyleneglycol, glycerol and DMSO). The rate constants were estimated by nonlinear regression. The variation of the rate constants with the dielectric constant is nonlinear due to preferential solvation of reactants by the mixture components. Starting from Brönsted-Bjerrum equation and the expression of activity coefficients of ions as a function of the dielectric constant of the medium, a method for estimating the dielectric constant in the solvation shell and the constant of preferential solvation was proposed. The results indicate that for mixtures of water with methanol, ethylene glycol and DMSO, in the solvation shell the nonaqueous component is in greater proportion than in bulk solution, while in mixtures of water with ethanol, 1-propanol and glycerol, in the solvation shell the water is preponderant.

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