Rate of Decomposition of Murexide in Mixed Solvents: An Indicator for Proton Activity

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The rate of decomposition of murexide depends strongly on the proton concentration. The observed rate constant correlates well with the relative permittivity of the solvent. This correlation is established by measurements in binary mixtures of water-dioxane and water-ethanol between 20 and 40 °C and may be applied to the estimation of the proton concentration in the aqueous domains of microemulsions.

Microemulsions are used as solvents for reactions involving ions and non-polar molecules, since both are soluble in these media.¹⁻³ Ions and non-polar molecules partition into the aqueous and the oily microdomains, respectively, and the reactions proceed preferentially at the interfaces between those regions. For a detailed understanding of the reaction mechanism the local concentrations of the reacting species have to be known in the different domains. This is especially important for protons, which act as catalysts or are involved in pre-equilibria for many reactions. However, it is difficult to determine their concentration by spectrophotometric methods, since the volume of the aqueous regions and the partitioning of the indicators are not known. Potentiometric methods are also difficult to apply in these structured solvents. Therefore it has been proposed to use the rate of decomposition of murexide (ammonium purpurate), Scheme 1, as proton indicator,⁴ since this reaction depends strongly on the proton activity, and murexide is very polar and partitions quantitatively into the aqueous domains. The reaction proceeds under pseudo-first-order conditions, and therefore only the relaxation time ($\tau = 1/k_{obs}$) has to be measured and concentrations and absorption coefficients do not need to be known.



The decomposition of murexide (Scheme 1) proceeds according to eqn. (I), with Mu^- , MuH, U and A denoting murexide anion, purpuric acid, uramil and alloxan, respectively.⁵

$$Mu^- + H^+ \rightleftharpoons MuH \to U + A$$
 (I)

The rate-determining step for this reaction is the irreversible decomposition of purpuric acid, whereas the protonation of the murexide anion is diffusion controlled.⁶ In this contribution it is assumed that the activity coefficients depend only on the charge of the ions and the ionic strength of the solution. This leads to the rate law, eqn. (1), since in the rate-

determining step all species involved are uncharged (with f = 1).

$$\frac{d[U]}{dt} = k[MuH] \tag{1}$$

$$\frac{1}{\tau} = \frac{kKf^{2}[H^{+}]}{1 + Kf^{2}[H^{+}]}$$
(2)

$$K = \frac{\lfloor MuH \rfloor}{\lfloor Mu^{-} \rfloor [H^{+}] f^{2}}$$
(3)

Under first-order conditions (buffered solutions) the integration of eqn. (1) yields eqn. (2) for the relaxation time, where Kis the association constant of purpuric acid, eqn. (3), and f is the activity coefficient of monovalent ions.

In order to estimate reliably the proton concentration from the decomposition rate, the influence of the solvent on both the equilibrium constant, K, and the rate constant, k, has to be known. In this paper these are determined in binary mixtures of varying composition. Furthermore, some preliminary measurements in microemulsions are reported.

Experimental

Measurements were performed in water-1,4-dioxane and water-ethanol mixtures and in microemulsions composed of Igepal CA 520 water. octane and $[C_9H_{19}-C_6H_4-(O-CH_2-CH_2)_5-OH]$. The composition of the binary solvents is given by the ratio of the volumes of the different compounds mixed together. All chemicals were commercially available and of analytical grade except for Igepal CA 520 (Aldrich). In the binary mixtures the measurements were performed at $(25 \pm 0.1)^{\circ}$ C using 5×10^{-5} mol dm⁻³ murexide, if not indicated otherwise. For microemulsions the temperature of the experiments has to be chosen according to the stability range of the solvent.

The aqueous stock solution of murexide was freshly prepared daily and the reactant solutions were prepared immediately before use. For relaxation times, $\tau > 100$ s, the reaction was started by adding the appropriate amount of the murexide stock solution with a syringe to the solvent, which contained HCl for the adjustment of the proton concentration. The progress of the reaction was observed with a diode array spectrophotometer (HP 8452 A). Faster reactions were studied by the stopped-flow technique mixing equal volumes of a solution containing murexide with a solution containing HCl. In order to avoid disturbances by the Schlieren effect, both solutions had to consist of the same solvent. The reaction was followed by measuring the optical absorption of the murexide anion at $\lambda_{max} = 521$ nm. In all experiments the reaction proceeded under pseudo-first-order conditions, and 638

the absorbance vanished at equilibrium, *i.e.* the change in absorbance was given by eqn. (4).

$$A = A_0 \exp(-t/\tau) \tag{4}$$

The kinetic measurements were evaluated by analogue/digital conversion of the absorbance between t = 0 and $t = 5\tau$, storing 1024 equidistant values of A, and fitting eqn. (4) to the absorbance values by a Marquardt algorithm. No systematic deviation between the experimental points and the fitted curves was observed.

Results

The decomposition of murexide has already been studied in detail in aqueous solutions at 25 °C.⁵ The measurements are extended to other temperatures, to binary mixtures, and to microemulsions. In the binary mixtures the dependence of the reaction rate on the proton concentration is measured at different volume ratios of water to dioxane between 80:20 and 20:80 and of water to ethanol between 60:40 and 20:80. The results are shown in Fig. 1 and 2. The temperature dependence of the relaxation time is measured for different proton concentrations in water and in 50: 50 water-dioxane. For the mixed solvent the results are shown in Fig. 3. For each mixture and temperature eqn. (2) is fitted to the experimentally obtained values of $1/\tau$ in order to evaluate K and k. This is carried out by minimizing the squared relative deviations using a computer program. The values of the constants are summarized in Table 1, and the curves shown in the figures are calculated with those values.

In aqueous solution the absorbance at the time of mixing (A_0) has been determined by re-extrapolating the absorbance according to eqn. (4) at proton concentrations between 10^{-4} and 1.5 mol dm⁻³. A_0 refers to a time, where the murexide anion is in equilibrium with purpuric acid [see Scheme (I)] and the decomposition reaction has not yet started. The plot of A_0 vs. log [H⁺] in Fig. 4 yields a sigmoidal curve characteristic of a dissociation equilibrium. The absorbances at very



Fig. 1 τ^{-1} vs. [H⁺] for water-dioxane mixtures at different volume ratios V_w/V_{di} : (\bigcirc) 80:20, (\bigcirc) 70:30, (\times) 60:40, (+) 50:50, (\bigcirc) 40:60 and (\triangle) 30:70. T = 25 °C. The curves are calculated according to eqn. (2) using the constants given in Table 1.

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Fig. 2 τ^{-1} vs. [H⁺] for water-ethanol mixtures at different volume ratios V_w/V_{et} : (×) 60: 40, (\blacksquare) 40: 60, (\triangle) 30: 70 and (\bigcirc) 20: 80. $T = 25 \,^{\circ}$ C. The curves are calculated as in Fig. 1.

low and at very high proton concentrations are due to the absorption of the murexide anion and of purpuric acid, respectively, and the point of inflexion corresponds to the state where both are of equal concentration. In aqueous solution it is not possible to shift the dissociation equilibrium completely to purpuric acid. Therefore for purpuric acid the wavelength of maximum absorbance and the absorption coefficient are obtained from A_0 in 10:90 water-dioxane at $[H^+] = 0.01 \text{ mol dm}^{-3}$, where the equilibrium is completely shifted to purpuric acid and the rate of decomposition is relatively low. Here we determined $\lambda_{max} = 447 \text{ nm with } \varepsilon = 4200$



Fig. 3 τ^{-1} vs. $[H^+]$ in 50:50 v/v water-dioxane mixtures at (\blacksquare) 288, (\Box) 293, (\blacktriangle) 298, (\bigtriangleup) 303, (\spadesuit) 308 and (\bigcirc) 313 K. The curves are calculated as in Fig. 1.

Table 1 Relative permittivity^{15,16} and rate and equilibrium constants obtained for the decomposition of murexide in binary mixtures of water and organic solvent at different volume ratios

<u>Т</u> /°С	$V_{\mathbf{w}}: V_{\mathrm{org}}$	ê _r	$\frac{Kk}{/\mathrm{dm}^3 \mathrm{mol}^{-1} \mathrm{s}^{-1}}$	log k	log (K/dm ³ mol ⁻¹)
25	100 : 0ª	78.48	0.95	0.05	-0.05
25	80 : 20ª	61.86	1.45	0.05	0.10
25	70 : 30ª	53.28	2.07	0.15	0.15
25	60 : 40ª	44.54	3.15	-0.05	0.55
25	50 : 50ª	35.85	4.80	-0.10	0.80
25	40 : 60ª	27.21	14.8	-0.40	1.55
25	30 : 70ª	19.07	67	-0.60	2.45
25	20:80ª	11.86	1720	-0.90	4.15
25	60 : 40 ^b	59.16	1.26	-0.05	0.15
25	40 : 60 ^b	47.70	1.60	-0.50	0.70
25	30 : 70 ^b	41.76	2.33	-0.45	0.80
25	20 : 80 ^b	35.72	4.2	-0.65	1.30
20	50 : 50ª	36.89	2.91	-0.31	0.77
25	50 : 50 ^a	35.85	4.82	-0.10	0.80
30	50 : 50ª	34.81	6.17	-0.14	0.93
35	50 : 50 ^a	33.88	10.6	0.15	0.88
40	50 : 50ª	32.91	15.6	0.28	0.91
20	100 : 0	80.10	0.55	-0.30	0.04
25	100:0	78.30	0.95	0.05	-0.05
30	100:0	76.55	1.55	0.11	0.08
35	100:0	74.83	2.21	0.28	0.08
40	100 : 0	73.15	3.17	0.46	0.04

" Water-dioxane mixtures; b water-ethanol mixtures.

cm⁻¹ mol⁻¹ dm³. The value for λ_{max} agrees with that for aqueous solutions, as can be seen in Fig. 5, where the spectrum has been recorded with a short delay after mixing 5×10^{-4} mol dm⁻³ murexide with 3 mol dm⁻³ HCl. This spectrum is well described by the superposition of two Gaussian curves with $\lambda_{max} = 521$ nm for murexide and $\lambda_{max} = 447$ nm for purpuric acid. The decomposition rate of murexide has also been deter-

The decomposition rate of murexide has also been determined in a few ternary microemulsions consisting of water, octane, and Igepal CA 520. Owing to the restricted stability range of the microemulsions, the measurements could only be performed at relatively low proton concentrations, where eqn. (2) can be approximated by eqn. (5), and only the product Kk has been evaluated.

$$\frac{1}{\tau} = kKf^{2}[\mathrm{H}^{+}] \tag{5}$$

The composition of microemulsions is given by $\alpha = m_o/(m_o + m_w)$ and $\gamma = m_s/(m_s + m_o + m_w)$; m_o , m_w and m_s are the masses of octane, water and Igepal, respectively. At constant



Fig. 4 Absorbance at time of mixing vs. log [H⁺] in an aqueous solution of murexide (2.5×10^{-4} mol dm⁻³, d = 2 cm), T = 25 °C, $\lambda = 447$ nm. The curve is calculated with K = 0.9 dm³ mol⁻¹.



Fig. 5 Spectrum of an aqueous solution containing 2.5×10^{-4} mol dm⁻³ murexide and 1.5 mol dm⁻³ HCl, 0.52 s after mixing. The dashed curve is calculated by the superposition of two Gaussian curves with $\lambda_1 = 447$ nm (purpuric acid) and $\lambda_2 = 521$ nm (murexide).

surfactant content the oil fraction, α , is varied between 30 and 60% and at constant α the surfactant fraction is varied from 10 to 35%. Since some of the microemulsions separate into two phases at 25 °C, experiments have to be carried out at other temperatures, and the relaxation times are estimated for 25 °C as discussed later.

Discussion

The association constant, K, for the protonation of the murexide anion is very small for solvents of high permittivity. Therefore, in water-rich solvents, K has to be determined at high proton concentrations, where care has to be taken in the estimation of the activity coefficients. We use the extended Debye-Hückel equation, eqn. (6), where α and β are calculated from the relative permittivity constant of the solutions (see Table 1) and a is estimated to be 5 Å. For aqueous solutions and ionic strengths larger than 0.2 mol dm⁻³ activity coefficients for HCl were taken from the literature.⁸

$$\log f = \frac{-\alpha I^{0.5}}{1 + \beta a I^{0.5}} \tag{6}$$

With these values the results shown in Fig. 1–3 are evaluated according to eqn. (2). The limiting slope at low proton concentration yields the product Kk with an accuracy of $\pm 5\%$. The deviation from the linear relation at higher proton concentrations enables the separation of the product into the individual constants, which, however, have a relatively high error of $\pm 25\%$. Table 1 summarizes the rate and equilibrium constants obtained from the fitting of eqn. (2) to the relaxation times for the different solvents and for different temperatures. From the temperature dependence of Kk, apparent activation energies of (58 ± 4) and (62 ± 4) kJ mol⁻¹ are calculated for aqueous solution and 50:50 water : dioxane, respectively. The values of K were independent of temperature within experimental error, which is equivalent to $\Delta H_0 = (0 \pm 7)$ kJ mol⁻¹.

The calculation of K and k from the relaxation times depends strongly on the choice of the equation used to estimate the activity coefficients. This is most critical for aqueous solutions, where K has the smallest value and the highest ionic strength has to be used. Therefore we determined the absorbances, A_0 , immediately after mixing aqueous solutions of murexide and hydrochloric acid. At this time, the presence of purpuric acid is evident, as can be seen in Fig. 4 and 5. The pH dependence of A_0 shows that the concentrations of murexide anion and purpuric acid are equal at $[H^+] = 1.1$ mol dm⁻³. Including activity coefficients yields log K = 0.07.



Fig. 6 Log K [left scale, (\bigcirc) , (\blacktriangle)] and log (Kk) [right scale, (\bigcirc) , (\bigtriangleup) , (\bigtriangleup)] as function of $1/\varepsilon_r$; (\bigtriangleup) , (\bigstar) dioxane; (\bigcirc) , $(\textcircled{\bullet})$ ethanol; (\Box) microemulsions

Within experimental error this value agrees with $\log K$ listed in Table 1, and thus we may trust in our evaluation.

For reactions where both association and dissociation proceed at a diffusion-controlled rate, the association constant can be estimated by eqn. (7) according to Eigen⁹ and Fuoss.¹⁰ *a* is the distance of closest approach and e_0 the elementary charge. For monovalent ions, *K* depends only weakly on the exact choice of the distance *a*. For $z_+z_- = -1$, $\varepsilon_r = 78$, T = 298 K and assuming a = 5 Å, we obtain, for aqueous solutions, K = 1.3 dm³ mol⁻¹ (log K = 0.11). This value agrees well with the experimentally obtained value for the association of Mu⁻ and H⁺ to purpuric acid. Therefore K should depend on the composition of the solvent according to eqn. (7), *i.e.* at constant temperature it should depend only on the relative permittivity.

$$K = \frac{4\pi a^3}{3} N \exp\left(-\frac{z_+ z_- e_0^2}{\varepsilon_r a k T}\right)$$
(7)

In Fig. 6, log K is plotted vs. $1/\varepsilon_r$ and a linear relation is observed. Differentiating eqn. (7) leads to eqn. (8), and inserting the same parameters as used above we calculate $[d \ln K/d(1/\varepsilon_r)] = -110$ in agreement with the value of -130 ± 20 obtained from the slope of the corresponding straight line in Fig. 6. Differentiating ln K with respect to 1/Tyields eqn. (9). Using the same parameters and d ln $\varepsilon_r/d \ln T = -1.5$ we obtain d ln K/d(1/T) = -500 K (equivalent to a reaction enthalpy $\Delta H_0 = 4$ kJ mol⁻¹). In accordance with this small value the temperature dependence of K cannot be observed.

$$\frac{\partial \ln K}{\partial (1/\varepsilon_{\rm r})} = -\frac{z_+ z_- e_0^2}{akT}$$
(8)

$$\frac{\partial \ln K}{\partial (1/T)} = -\frac{z_+ z_- e_0^2}{\epsilon_* ak} (1 + \partial \ln \epsilon_r / \partial \ln T)$$
(9)

Summarizing it may be said that the association constant, K, of purpuric acid can be well estimated from the relative permittivity of the solvent using eqn. (7).

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In comparison with the association constant, the rate constant depends only weakly on the solvent. We observe a slight decrease of k with decreasing water ratio, which may be attributed to the decrease in hydration of purpuric acid. Since, frequently, measurements are restricted to low proton concentrations and thus only the product Kk can be obtained experimentally, this product is also plotted in Fig. 6. Again we observe a linear relation between log(Kk) and $1/\varepsilon_r$, which also allows us to estimate the proton concentration from the decomposition rate of murexide according to eqn. (5), when the relative permittivity of the solvent is known.

Finally, we discuss briefly the results obtained in microemulsions. The values of Kk in Table 2 are calculated with the assumption that the different solvent molecules and ions are homogeneously distributed in the solution, *i.e.* the microstructure of the solvent has not been taken into account. The values are extrapolated to 25 °C using the apparent activation energy 60 kJ mol⁻¹ as obtained both for aqueous solutions and for a 50:50 water-dioxane binary mixture. These values are included in Fig. 6. The relative permittivity has been estimated from data reported for systems of similar composition.¹¹ It turns out that, for microemulsions, Kk is much smaller than the corresponding value for binary mixtures of the same permittivity. This indicates that in the microemulsions both protons and murexide anions partition into the aqueous domains, where the relative permittivity is relatively large, and a uniform distribution of ions and molecules cannot be assumed. However, the data presented in this contribution are not sufficient for a detailed discussion of the decomposition of murexide in microemulsions along the lines of a pseudophase ion-exchange model.¹²⁻¹⁴ A systematic study varying the composition of the microemulsion over a wide range is in progress. Since the dependence of the reaction rate on proton concentration and solvent composition is well understood this simple reaction, may be used to estimate the proton concentration in the aqueous compartments, into which the both the murexide anions and protons partition.

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 Table 2
 Kk for the decomposition of murexide in microemulsions of different compositions

α	γ	T/K	$[H^+]/10^{-3} \text{ mol } dm^{-3}$	ê _r	$(Kk)_T/dm^3 mol^{-1} s^{-1}$	$Kk/dm^3 mol^{-1} s^{-1}$
30	15	293.1	0.86	32	1.63	2.48
40	15	294.7	0.6-8	24	2.17	2.89
50	15	295.0	0.8-20	18	3.15	4.10
60	15	298.3	0.8-6	15	4.09	4.06
50	10	295.4	0.47-2.28	18	3.06	3.85
50	35	302.7	0.23-1.74	12	10.1	7.05

 $[H^+]$ is the range of proton concentration, over which the experiments were carried out. $(Kk)_T$ is calculated from the experimental values by eqn. (5); Kk is calculated for 298.2 K with $E_{a}^{spp} = 60 \text{ kJ mol}^{-1}$.

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