FLUORESCENCE AND EXCIMER KINETICS IN MICELLAR DETERGENT SOLUTIONS

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Fluorescence and excimer kinetics of pyrene dissolved in micellar water/detergent solutions are intramicellar phenomena. If the average occupation number is not too small, the concentration dependence is similar to that of ordinary solutions in an organic solvent. In the system pyrene/Na-dodecylsulfate/water, where the average occupation is about one pyrene molecule per micelle, the monomer flourescence comes (to the dominant part) from singly occupied micelles and the excimer fluorescence exclusively from twice occupied micelles. The intramicellar excimer kinetics of the twice occupied micelles is independent of the pyrene (brutto-) concentration, which only determines the distribution of pyrene molecules among the micelles. The number g of detergent molecules per micelle can be calculated from fluorescence intensity measurements by way of statistical considerations. g is strongly increasing with the ionic strength J of the aequous solvent at the expense of the quantity of micelles; hereby a new type of monomer/excimer fluorescence-change is observed. The rate constant n_r of intramicellar excimer formation, not depending on pyrene (brutto-) concentration, varies with g. The dependences $g(J)$ and $n_r(g)$ were measured.

Aromatic hydrocarbons can be dissolved in aequous micellar solutions of detergents. With regard to fluorescence and excimer kinetics such systems behave more or less similarly as ordinary solutions of the aromatic hydrocarbons in organic solvents. Though the micellar systems are to be described partly by other parameters than ordinary solutions, it can be stated that encounters between the micelles and/or inter-micellar transitions of the aromatic molecules exert practically no influence on excimer kinetics[1]. The higher the average occupation of the micelles by aromatic molecules, the more similar is the behaviour to homogenous solutions. In the case of multiple occupation we apparently can describe the concentration dependence of fluorescence and excimer kinetics by the concept of a local concentration [1], as if the micelles were another liquid phase immiscible with the water phase, the aromatic molecules being soluble in the former only. We have investigated a system—pyrene in aequous solution of Na-dodecylsulfate—the maximum occupation of which is about one aromatic molecule per micelle on the average. In order to understand the different behaviour of this system let us briefly rewiev the main features of excimer kinetics in ordinary solutions. According to the

[1] This can hardly be true in general for slower chemical processes.

reaction scheme [2]

$$\begin{array}{ccc} A^* + A & \underset{n_d}{\overset{n_r = n_a \cdot c}{\rightleftharpoons}} & (AA)^* \\ {\scriptstyle n}\downarrow & & \downarrow{\scriptstyle n'} \\ A;\, h\nu & & A + A;\, h\nu' \end{array}$$

this is the bimolecular diffusion-controlled excimer formation process, rate constant $n_r = n_a \cdot c$, where c is the concentration of the unexcited monomer A, which competes with the deactivation processes of the primarily excited monomer A^*. The latter processes such as fluorescence, intersystem crossing, etc. can be described by a common rate constant n. This can also be done with the deactivating processes of the excimer $(AA)^*$, giving the rate constant n' and competing with the excimer dissociation, rate constant n_d. The time dependences of fluorescence of both excited species are given by the concentrations $A^*(t)$ and $(AA)^*(t)$, described by two simultaneous differential equations derived from the reaction scheme. In the photostationary state the fluorescence intensity I of the monomer depends on c in accordance with a Stern—Volmer straight line $I_0/I = 1 + c/c_h$; the excimer fluorescence intensity I' fits another straight line $I'_\infty/I' = 1 + c_h/c$, the half value concentration c_h being the same in both equations, $c_h = n(n' + n_d)/n' \cdot n_a$. If we excite the fluorescence by a light flash of negligible duration (δ-function), then both time dependences or 'decay functions' $I_\delta = C_1 e^{-\lambda 1 t} + C_2 e^{-\lambda 2 t}$ and $I'_\delta = C_3(e^{-\lambda 1 t} - e^{-\lambda 2 t})$ consist of two exponential functions. In order to know all four rate constants of the reaction scheme, it is sufficient to measure λ_1 and λ_2 [2] as functions of c because

$$\lambda_1 + \lambda_2 = n + n' + n_d + n_a \cdot c \tag{1}$$

$$\lambda_1 \cdot \lambda_2 = n(n' + n_d) + n' \cdot n_a \cdot c \tag{2}$$

involve four straight line parameters. — In Fig. 1 one can see experimental decay functions of pyrene in dodecane solution (which should be similar to the aliphatic interior of dodecylsulfate micelles). The monomer fluorescence intensity rises almost as fast as the exciting flash, but the excimer intensity maximum is pronouncedly shifted to later times. The exciting flash is separately shown on the left of the figure. The monomer curves are normalized to constant height of their maxima; the excimer curves are normalized so as to demonstrate that later both fluorescence components obey the same constant — the smaller of the two — because the contribution of the larger one has already approached zero[3]. The concentration of curve b is approximately equal to c_h. — The following figures refer to our micellar system. From Fig. 2 one can see that to a large extent, excimer kinetics, has nothing to do with encounters between the micelles [1]. The dilution of the micellar solution with water can be increased to much more than tenfold without any change in the excimer/monomer fluorescence intensity ratio; according to the reaction scheme one should expect this ratio to be proportional to the pyrene concentration and it should at least be influenced in that sense, if excimer formation

[2] In principle one could use the concentration dependences of C_1, C_2 and C_3 for kinetic analysis too, but this procedure is not recommended for various reasons.

[3] Generally one of the two λ of an excimer system is limited by $n \leqq \lambda \leqq n'$, but the other increases strongly with concentration and may become immeasurable.

were favoured by encounters of the micelles. But the intensity ratio depends only on the concentration ratio of aromat/detergent, as far as the concentration of the micelles c_M remains proportional to the concentration of the detergent c_D. The latter is no longer true if c_D becomes comparable to the critical concentration

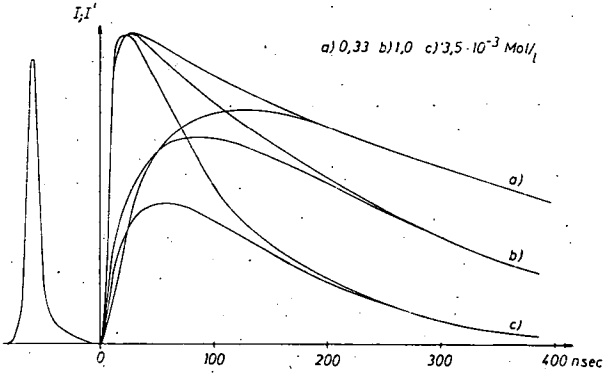

Fig. 1. Time dependence of pyrene fluorescence at various concentrations in dodecane

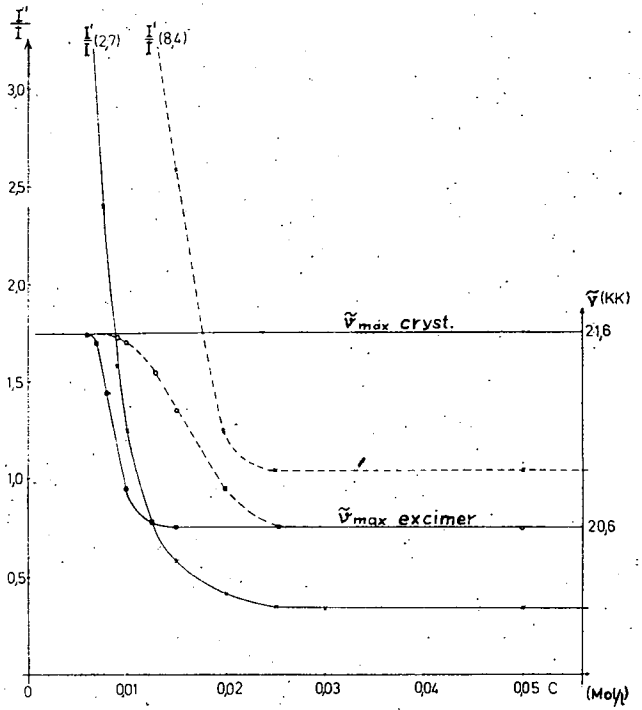

Fig. 2. Excimer/monomer intensity quotients and apparent spectral shifts of excimer maximum depending on detergent concentration at constant pyrene/detergent concentration ratio

c_k of micelle formation in accordance with the equation $c_M \approx (c_D - c_k)/g$, where g is the number of detergent molecules per micelle. With higher and higher dilution more and more micelles are destroyed; pyrene molecules are distributed among the remaining micelles. Excimer formation is favoured according to the rising average occupation and finally pyrene crystallites get segregated, however, sedimentation is very slow and pyrene crystal fluorescence appears to be contributing to a further rise of I'/I. The real increase of excimer intensity can be separated from the misleading rise as one can see from Fig. 3, showing some of the total fluorescence spectra from which the curves of Fig. 2 were evaluted. As soon as pyrene crystallites are segregated, the excimer maximum begins to shift towards the crystal fluorescence maximum. In case of the dashed I'/I curve in Fig. 2 the micelles have been almost saturated and there was little possibility for redistribution of pyrene molecules with

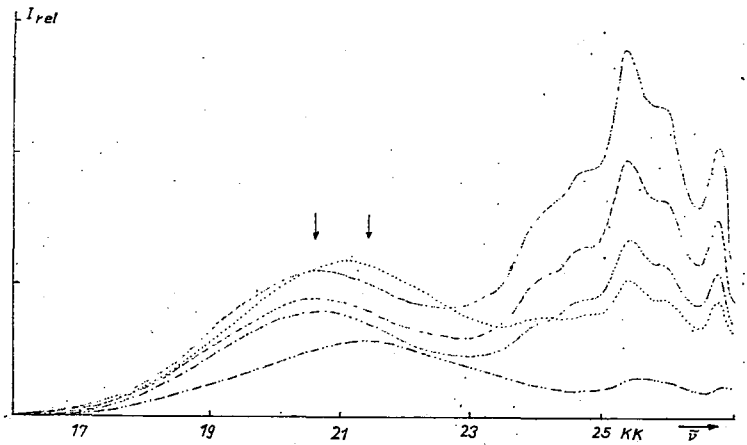

Fig. 3. Total fluorescence spectra from which the dependences in Fig. 2 were evaluated

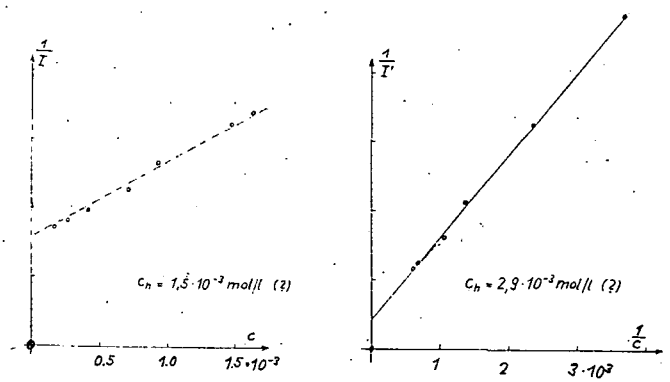

Fig. 4. Reciprocal fluorescence intensities $1/I$ of monomer and $1/I'$ of excimer depending on pyrene concentration at constant detergent concentration $c_D = 0.1$ mol/l

dilution; the apparent rise of the intensity ratio is caused partly by pyrene crystallites from its beginning. We shall not further discuss the behaviour of our system in the vicinity of the critical concentration c_k, but we notice the possibility of measuring critical concentrations by excimer studies.

While the results shown in Figs. 2 and 3 could be explained with the concept of local concentration too, this is hardly possible with the behaviour shown in Fig. 4. The reciprocal fluorescence intensities I/I and I/I' seem to fit straight lines, but the apparent half value concentrations are remarkably different; if we try to calculate the local c within the 'micelle phase' we find a discrepancy of about two orders of magnitude referring to dodecane. Our most striking results [3], can be seen from Figs. 5 and 6. Within the concentration range of Fig. 2 the shape of the excimer time dependence does not change at all; otherwise it can exactly be desribed by the difference of two exponential functions. This behaviour is such as if a certain 'effective concentration' which is quite independent of the real concentration of pyrene (at constant detergent concentration) would determine the excimer kinetics within the micelles. The time dependence of the monomer fluorescence is shown in Fig. 6. If we neglect for a moment the small intensity components which are superimposed at the beginning, we measure at all concentrations the same slowly decaying exponential function with a time constant corresponding to a fluorescence decay time of about 465 nsec; this can be measured in organic solvents too, but at concentration $c \to 0$, where no excimer formation can take place. One cannot detect this slow time constant in the excimer function Fig. 5 (*cf.* Fig. 1), but the small superimposed components in Fig. 6 do contain the time constant λ_1 of Fig. 5; it is only the intensity and not the shape of the superimposed components which is with concentration. We conclude: The greatest part of monomer fluorescence is variable emitted from those micelles which are occupied by one single pyrene molecule. Excimer fluorescence comes from micelles occupied by at least two pyrene molecules. Moreover, micelles containing more than two pyrene molecules must be very seldom

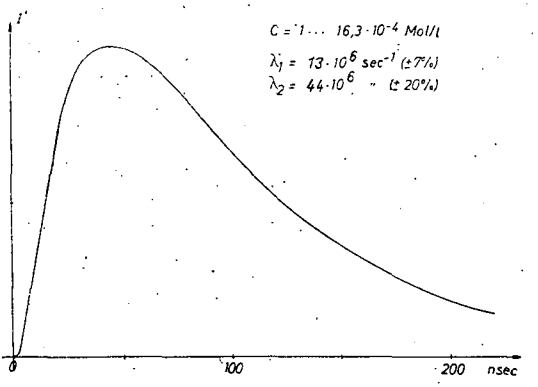

Fig. 5. Time dependence of excimer fluorescence at various pyrene concentrations, $c_D = 0.1$ mol/l

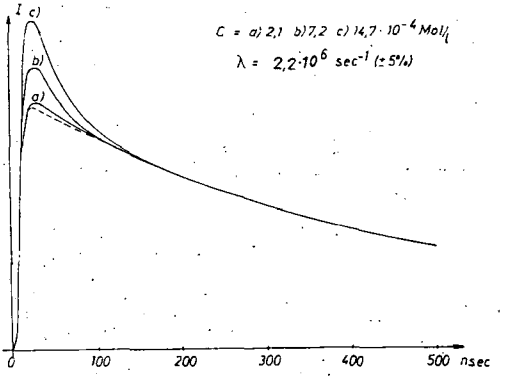

Fig. 6. Time dependence of monomer fluorescence intensity at various pyrene concentrations, $c_D = 0.1$ mol/l

in our system. The latter statement results from the fact that not more than two time constants can be detected in Fig. 5. Suppose there were triply occupied and twice occupied micelles in comparable amounts, then the effective concentration within the former would be twice that of the latter (we have to look at the number of reaction partners of the excited monomer), giving another pair of different time constants; the measured excimer time function would be a superposition of two functions of the type shown in Fig. 5.[4] — Excimer formation within our twice occupied micelles is fast, but not fast enough to totally prevent competing monomer fluorescence. If the excimers were preformed in the ground state as dimers or oligomers then the excimer intensity in Fig. 5 would rise almost as fast as the exciting flash and there would be no competing monomer emission. — How to explain the concentration dependence which we have seen in Fig. 4? It is caused by variation with concentration of the amounts of micelles containing 0, 1 or 2 pyrene molecules. In ordinary homogenous solutions excimer formation is a question of kinetics, but in our system it is primarily a question of distribution. We shall give a convenient statistical model below. But without making use of special statistics we may state from an evaluation of the decay functions, that the three monomolecular rate constants of the reaction scheme have approximately the same values as in organic solvents $n=2$, $n'=13$ and $n_d=7$ times 10^6 sec^{-1} each at room temperature [4]. Together with these we get the bimolecular rate constant of excimer formation $n_r=33\cdot 10^6$ sec^{-1}, but we have to explain what this constant value does mean. In organic solvents n_r describes the concentration dependence of excimer formation $n_r=n_a\cdot c$ with the aid of the rate constant of a diffusion-controlled reaction $n_a\approx 10^{10}$ l/mol · sec, which is inversely proportional to the solvent viscosity. If we formally calculate the concentration within the twice occupied micelles using the volume of a micelle and n_a, then n_r should be at least ten times greater than that measured. It is hardly justified to suppose a very high viscosity within the micelles, because there are experiments indicating that this is not the case. We tend to believe that the formal concentration — that is the number of particles per volume — is not directly suitable to describe reaction rates or even rates of encounters if we have to do with a few particles enclosed in a small volume. — For elucidating the connexion of n_r and micelle volume or whatever may play a role, we started with varying the temperature. But at the present state of knowledge this procedure causes more problems than it solves, because not only various characteristic parameters of the micelles but also all four rate constants of the reaction scheme depend on temperature. — Fig. 7 demonstrates a possibility of influencing micellar systems at constant temperature, where most of the rate constants remain unchanged. Even at constant concentration of pyrene and detergent we get a new type of 'fluorescence change', looking very similiar to well-known figures, but dependent on salt concentration or ionic strength, respectively, of the aequous solvent. There is an isoemissive point indicating that no additional deactivation

[4] There is one special type of distribution which, in principle, could account for only two time constants even though all occupation numbers were realized, namely the Poisson distribution. But if this distribution were valid the time constants would depend on the respective average occupation number or pyrene concentration; we could then use the concept of local concentration. Any other distribution law admitting many different occupation numbers would demand concentration dependent time constants.

process is included. Whether the salt destroys only part of the micelles or whether it influences the intramicellar kinetics can be decided from Fig. 8. Clearly the shape of the excimer time function does change, indicating slower excimer formation at higher salt concentrations. This is not contradictory to the result of Fig. 7, where excimer intensity increases with salt concentration. The decisive answer is given by Fig. 9. Let us keep in mind that the intensity of monomer fluorescence from twice occupied micelles is proportional to the area under the fast decaying component, and the intensity from the singly occupied ones is proportional to the area under the slow decaying component (dashed lines). At higher ionic strengths we get less of the latter and more of the former. Evidently the association number g, and by

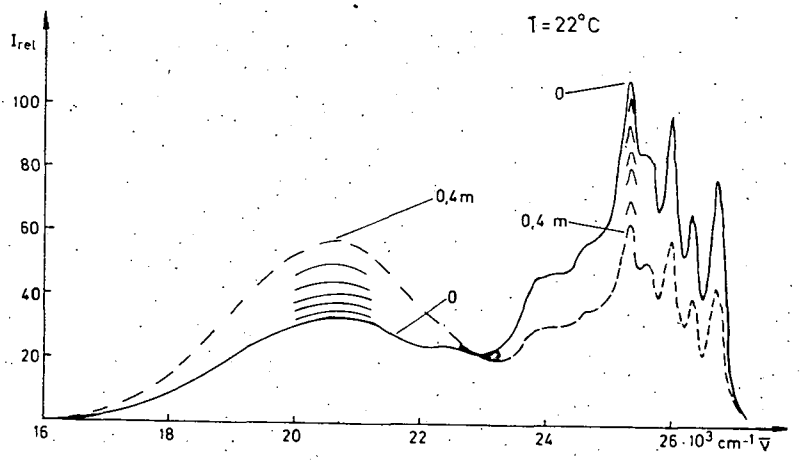

Fig. 7. Fluorescence spectra of pyrene $6.6 \cdot 10^{-4}$ mol/l and $c_D = 0.1$ mol/l depending on concentration of Na_2SO_4 0...0.4 mol/l.

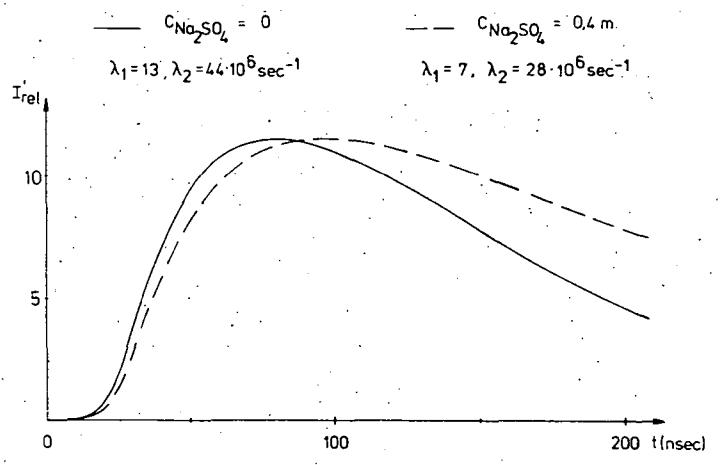

Fig. 8. Time dependence of excimer fluorescence. Concentration of pyrene and detergent *cf.* Fig. 7

this the size of the micelles increases at the expense of their quantity. Though monomer emission from the twice occupied micelles is favoured when the size increases (because the diffusion path of excimer formation becomes longer), this influence is overcompensated by the decreasing amount of singly occupied micelles. Equality of the time constants of superimposed monomer fluorescence with those of the excimer fluorescence is found as before in Figs. 5 and 6, but now the time constants depend on salt concentration, excepted only the slow time constant of the singly

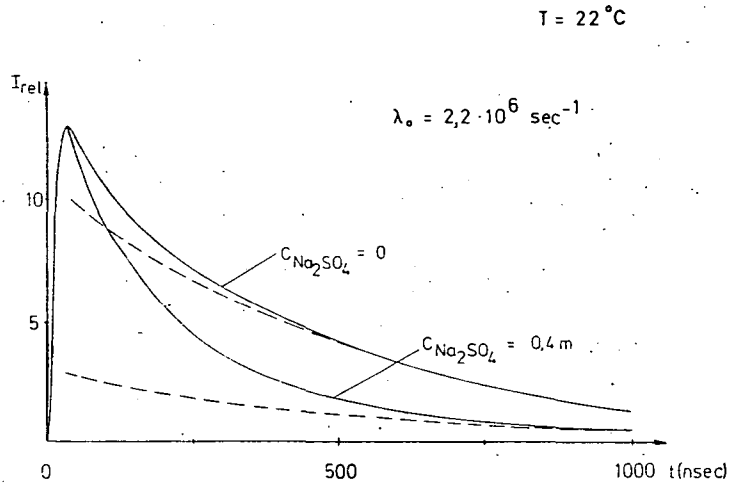

Fig. 9. Time dependence of monomer fluorescence. Concentration of pyrene and detergent *cf.* Fig. 7

occupied micelles. Still there is no indication of more than twice occupied micelles up to the pyrene concentration of Figs. 7—9. The evaluation of the time constants shows that only n_r is reduced up to a factor of almost four by the salt influence, but the three other rate constants remain unchanged. We could give a figure showing the dependence of n_r on the ionic strength now, but because n_r depends on the latter only indirectly, we may delay it.

So far we have been discussing quantitatively only the kinetic aspects and dealing qualitatively with the influence of distribution. However, the concentration dependences of Fig. 4 (pyrene) and Fig. 7 (salt) deserve a statistic explanation. The physical concept of a limited occupation number and no forces between the particles (unexcited pyrene molecules) is compatible with the following simple Bose statistics.

$$K = \frac{Z!}{\prod_{i=0}^{j} z_i!}; \quad Z = \sum_{i=0}^{j} z_i = \text{const}; \quad N = \sum_{i=0}^{j} i \cdot z_i = \text{const}.$$

Let the maximum possible occupation number be j and the number of micelles occupied by i particles be z_i. It results from maximizing K under the conditions of

constant number of micelles Z and particles N that the parameter x

$$x = \frac{z_{i+1}}{z_i} = \text{const.}$$

can be calculated from the average quotient of occupation $\frac{N}{Z}$.

$$\sum_{i=0}^{j} x^i \left(\frac{N}{Z} - i\right) = 0. \tag{3}$$

In our case $j=2$ in Eq. (3) is simply quadratic. We may express $\frac{N}{Z} = \frac{c \cdot g}{c_D}$ by the number of detergent molecules per micelle g, the concentration of pyrene c and of detergent c_0. The only adjustable parameter g has to be determined from experimental data. This can be done because x appears in some equations concerning fluorescence intensity, *e.g.* the monomer/excimer intensity quotient

$$\frac{I}{I'} = \frac{\eta_1}{2x \cdot \eta_2'} + \frac{\eta_2}{\eta_2'}. \tag{4}$$

(Experimental values I/I' follow from Fig. 4). Another convenient equation exists for the monomer fluorescence intensity quotient of twice/singly occupied micelles

$$\frac{I_2}{I_1} = 2x \frac{\eta_2}{\eta_1}. \tag{5}$$

(Experimental values concerning the dependence on pyrene concentration follow from Fig. 6; those depending on salt concentration in addition we get from measurements of the type of Fig. 9.) The various fluorescence quantum efficiencies η appearing in Eqs. (4) and (5) can be derived[5] from measured micellar rate constants and the limiting quantum efficiencies η_0 and η_∞ which can be shown to be the same as in organic solvents. The factors 2 appear in equs. (5) and (4) because a twice occupied micelle absorbs twice the exciting light intensity of a singly occupied one. — At salt concentration equal to zero and room temperature the corresponding experimental dependences fit well to Eqs. (4) and (5) if we postulate $g=55...60$; in the literature we find $g=40...80$.

This most simple version of a new method for determning g is applicable in those cases of micelles, where the excimer time dependence is given by the difference of two exponential functions the two time constants of which do not depend on pyrene concentration. If the maximum occupation number is $j=3$ we must generalize Eqs. (4) and (5); the criterion of concentration-independent time constants is still preserved, but the shape even of the excimer time function will then change with concentration in an analogous manner as does the monomer time function already in the case $j=2$ (and there will be two superimposed components on the

[5] In particular:

$\eta_1 = \eta_0$ (single occupation, monomer fluorescence)
η_2 (twofold occupation, monomer fluorescence)
η_2' (twofold occupation, excimer fluorescence).

We get them all by replacing $n_a \cdot c$ in the Stern—Volmer etc. equations by the appropriate n_r.

monomer time function instead of only one). If $j>3$ it will be increasingly difficult to ascertain the many time constants contained in the experimental curves.

Eqs. (4) and (5) are utilized to investigate the salt influence too. We measure I/I' and I_2/I_1 dependent on pyrene concentration to get g at various salt concentrations. It can be seen from Fig. 10 that the number of detergent molecules per micelle g depends strongly on ionic strength, the type of salt being of no influence[6]. The dependence of the excimer formation rate n_r on g is given in Fig. 11. g is a proportional measure of the micelle volume (at least it should be). From this $1/g$ should be proportional to the efficient concentration in the twice occupied micelles. The question whether the linear, nearly proportional dependence in Fig. 11 holds good in general, deserves further investgations. If we take it as it is, then the concept of an efficient concentration, given by the true (and not the average) number of reaction partner molecules, describes the reaction rate n_r. However, the calculation of the intramicellar concentration with the aid of g, the dodecane density and n_a still gives n_r too large by a factor of ten. — According to Fig. 11 the micelle volume is proportional to g. There are other reasons to assume that the micelle surface is proportional to g too. From both it would result that the micelles cannot be spherical (if need be they should be hollow spheres; a non-spheric shape seems however to be more likely). Perhaps one could use intramicellar radiationless energy migration to decide this question.

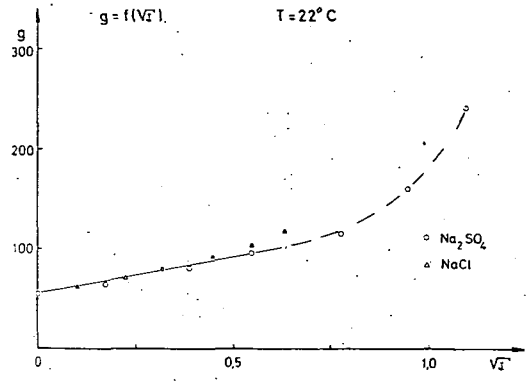

Fig. 10. Number of detergent molecules per micelle, g, depending on ionic strength

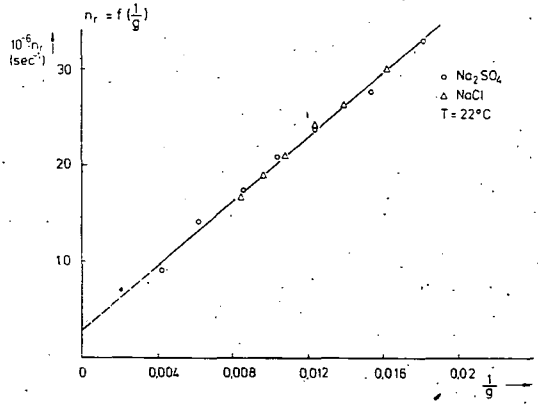

Fig. 11. Rate constant n_r of excimer formation as a function of $1/g$.

On the basis of our knowledge we hope to understand the temperature dependences not only of intramicellar excimer kinetics but also those of g, etc. Our final aim is to know the behaviour of very few molecules which are enclosed in isolated loci. This could be helpful in many fields of research.

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[6] Provided that no quenching ions are involved.

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ФЛУОРЕСЦЕНЦИЯ И ЭКСИМЕРНАЯ КИНЕТИКА В МИЦЕЛЛЯРНЫХ ДЕТЕРГЕНТНЫХ РАСТВОРАХ

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Кинетика эксимера и флуоресценция пирена в мицеллярном растворе вода-детергент представляют собой интермицеллярные явления. Если среднее число населенности пирена не очень мало, концентрационные зависимости подобны нормальным растворам в органических растворителях. В системе пирен (На- додекилсульфат) — вода, где число населенности около одной молекулы в одной мицелле, флуоресценция мономера происходит от однократной населенности мицелл, флуоресценция эксимера — от двухкратной населенности мицелл. Интрамицеллярная эксимера — от двухкратной населенности мицелл. Интрамицеллярная эксимерная кинетика дважди населенных мицелл не зависит от концентрации пирена, от которой зависит только распределение молекул пирена в мицеллах. Число молекул детергента g в мицеллах определяется путём измерения интенсивности флуоресценции на основе статистической обработки. Значение g сильно увеличивается с увеличением силы ионов J водного раствора под действием количества мицелл, вследствие чего наблюдается новый тип изменения флуоресценции мономера — эксимера. Скорость константы образования интрамицеллярных эксимеров n_r, которая не зависит от концентрации пирена, изменяется со значением g. Зависимости $g(J)$ и $n_r(g)$ были измерены.