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Kinetic Measurements on Alkylammonium Halides*

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Chemical relaxation measurements are reported on alkylammonium halides having carbon atoms in the alkyl chain from 10 to 16. Two relaxation times were observed for most of the studied systems. Data are interpreted on the basis of a theory recently developed by G. Aniansson and S. Wall. According to this theory, the fast process is due to a shift of the micellar distribution curve. The residence time of a detergent molecule in the micelle and the half width of the micellar distribution curve are obtained from the fast process. The slow relaxation process is characteristic for the change of the concentration of micelles and permits the evaluation of the concentration of the micellar nuclei and their thermodynamic properties. The obtained results are compared with available data on alkylpyridinium halides.

INTRODUCTION

It is known that the critical micelle concentration and the mean aggregation number depend on the pressure and temperature of the solution.[1] Consequently, if a micellar system is perturbed by a sudden change in pressure or temperature, the system responds by changing the monomer and micellar concentration until a new equilibrium state is reached. While for a number of years it was assumed that the new equilibrium is reached in a single relaxation process,[2] it was observed recently that the new state is approached in two distinct steps, having well separated relaxation times.[3] At the time of the experimental observation of two relaxation times, G. Aniansson and S. Wall proposed a theoretical model to explain quantitatively the two relaxation processes.[4] According to this model, the fast relaxation process is due to a shift of the mean aggregation number of micelles to smaller or larger values. The number of micelles remains constant during this process. The reciprocal relaxation time for this step is given by equation (1)

$$\frac{1}{\tau_1} = \frac{k^-}{\sigma^2} + \frac{k^-}{n} \cdot \frac{c_0 - cmc}{cmc} \tag{1}$$

where k^- is the dissociation rate constant of a monomer leaving the micelle, n the mean aggregation number, σ the half width of the distribution curve,

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c_0 the total detergent concentration and *cmc* the monomer detergent concentration. The fast process is indicated by arrow »1« in Figure 1. In a second step the micelle concentration changes to a new equilibrium value, indicated by arrow »2« in Figure 1. The relative long time for this process is due to very small concentrations of aggregates around the distribution minimum. The rate for the process is mainly governed by the product of these concentrations with their corresponding dissociation rate constants.

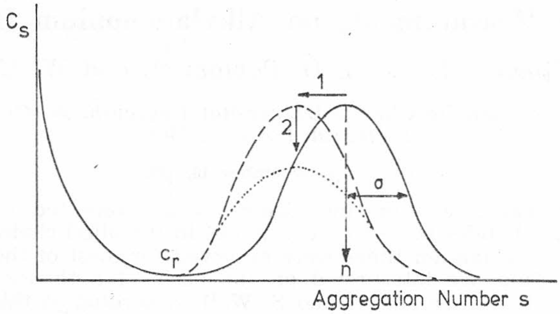

Figure 1. Sketch of a micellar distribution curve and the two relaxation processes in a plot of the concentration of the aggregates against the aggregation number s.

The reciprocal relaxation time for this process is given by equation (2)

$$\frac{1}{\tau_1} = \frac{1}{R \cdot c_3} \cdot \frac{cmc + n^2 c_3}{cmc + \sigma^2 c_3}\,; \qquad R = \Sigma \frac{1}{k_r^- \cdot c_r} \tag{2}$$

where $c_3 = (c_0 - \text{cmc})/n$ is the total micelle concentration, c_r the concentration of aggregates at the distribution minimum and k_r^- the dissociation rate constant of a monomer leaving these aggregates.

These equations permit the evaluation of parameters on micellar systems which have not been accessible from other investigations[5]. As seen from equations (1) and (2) relaxation measurements can be used to obtain residence times for the detergent molecules in the micelles and the rate constants for the incorporation of detergent molecules into the micelle. In addition, these data can be used to obtain information on the thermodynamics of the micellar nucleus and the half width of the distribution curve. Data from chemical relaxation measurements thus lead to a much better and more detailed understanding of the thermodynamics and dynamics of micellar systems.

Kinetic measurements on two homologous detergent systems have been analysed before. The first complete investigation was done on sodium alkyl sulfates[6], the second on alkylpyridinium halides[7].

In the present study, the measurements were extended to the alkylammonium halides. These systems have been of particular interest in many investigations[8]. They have been noted for their special features like the increase of the aggregation number with the increase of ionic strength or total detergent concentration[9].

Alkylammonium halides are ionic detergents possessing the smallest possible headgroup and the head charge is also most closely located to the first CH_2-group. The importance of these conditions was of particular interest in a paper by D. Stigter[10].

One of the objectives of the present investigation was to find out how these specific features on the alkylammonium halides affect the dynamics of micellar equilibria. As a reference state for the new data, the results on alkylpyridinium halides will be used.

EXPERIMENTAL

The alkylammonium chlorides and -bromides were prepared by dissolving the alkylamins in ether and bubbling HBr or HCl through it. The precipitated crystalline compounds were recrystallized twice from aqueous solutions. The alkylammonium iodides were prepared from chlorides by passing the chloride solution through an ion-exchange column charged with iodide.

The relaxation measurements were carried out with a pressure jump apparatus[11] and a shockwave method[12]. Both techniques have been used before. In some of the solutions, relaxation measurements were also carried out with a temperature-jump apparatus. The pressure-jump and shockwave apparatus were equipped with a conductivity readout while the temperature jump apparatus used an optical detection system. Dye indicators were therefore used to monitor relaxation times. In all measurements eosin was used as an indicator. This indicator had been used in previous studies and was found to give results that were identical with those obtained without the indicator with conductivity read out[13]. The cmc-measurements were carried out using a Wayne-Kerr bridge.

Data are summarized in Tables I to IV. Table I presents the *cmc*-values that have been obtained by conductivity measurements. For some systems, values were available in the literature also. They are included in Table I. Also α-values are given:

TABLE I

cmc- *and* α-*Values for Alkylammonium halides and the Corresponding Alkylpyridinium halides at 25* °*C*

Surfactant	*cmc* (Lit.) (mol/dm³)	*cmc* (mol/dm³)	α	*cmc* (RPyX) (mol/dm³)	α (RPyX)
ONH_3Cl	1.8×10^{-1}	—	—	—	—
$DeNH_3Cl$	5.4×10^{-2}	6.08×10^{-2}	0.41	—	—
$DeNH_3Br$	—	4.9×10^{-2}	—	—	—
$DeNH_3I$	—	4.1×10^{-2}	—	2.25×10^{-2}	0.28
DNH_3Cl	1.46×10^{-2}	1.45×10^{-2}	0.42	1.48×10^{-2}	—
DNH_3Br	1.2×10^{-2}	1.2×10^{-2}	0.32	1.16×10^{-2}	0.32
DNH_3I	—	1.05×10^{-2}	0.21	5.25×10^{-3}	0.20
TNH_3Cl	2.8×10^{-3}	3.65×10^{-3}	—	3.98×10^{-3}	0.43
TNH_3Br	—	2.95×10^{-3}	—	2.55×10^{-3}	0.36
TNH_3I	—	—	—	1.52×10^{-3}	0.4
HNH_3Cl	1.07×10^{-3}	1.03×10^{-3}	0.43	9.0×10^{-4}	—

TABLE II

Values for the Slow Relaxation Time τ_2 for Several Alkylammonium Halides as a Function of the Total Concentration c_0 at Various Temperatures

Decylammonium

	Chloride				Bromide				Iodide		
	$\tau_2/\mu s$				$\tau_2/\mu s$				$\tau_2/\mu s$		
$t/^0C$	10	15	20	25	10	15	20	25	10	15	20
c_0 (mol/dm^3)											
4.0×10^{-2}	—	—	—	—	—	—	—	—	5000	—	—
5.0×10^{-2}	—	—	—	—	1000	370	165	80	3300	1500	630
6.0×10^{-2}	—	—	—	—	1050	—	—	—	2300	1200	500
6.5×10^{-2}	170	69	34	15	—	—	—	—	—	—	—
7.0×10^{-2}	150	67	30	15	—	—	—	—	1700	910	370
7.5×10^{-2}	170	75	30	14	1250	500	180	88	—	—	—
8.0×10^{-2}	160	64	29	14	—	—	—	—	1400	680	310
8.5×10^{-2}	150	73	28	13	—	—	—	—	—	—	—
9.0×10^{-2}	200	74	25	12	—	—	—	—	—	—	—
1.0×10^{-1}	—	63	—	—	1300	520	210	95	—	—	—

Dodecylammonium

	Chloride				Bromide				
	τ_2/ms				τ_2/ms				
$t/^0C$	10	15	20	25	25	30	35	40	45
c_0 (mol/dm^3)									
1.3×10^{-2}	—	—	—	—	407	130	62	38	22
1.4×10^{-2}	—	—	—	—	510	143	60	31	15
1.5×10^{-2}	—	111	34	11	—	140	48	22	11
1.6×10^{-2}	—	112	32	11	490	142	53	20	10
1.8×10^{-2}	430	116	32	11	—	112	—	15	8
2.0×10^{-2}	416	123	33	12	—	73	35	12	—
2.2×10^{-2}	—	—	—	—	—	52	25	11	—
2.3×10^{-2}	—	125	37	13	—	40	22	9	—
2.6×10^{-2}	—	135	40	16	—	—	—	—	—

Tetradecylammonium Chloride

	τ_2/ms				
$t/^0C$	25	30	35	40	45
c_0 (mol/dm^3)					
4.0×10^{-3}	—	1400	300	70	—
4.5×10^{-3}	4100	1200	210	61	15
5.0×10^{-3}	4000	1100	220	45	14,5
5.5×10^{-3}	—	1000	238	59	15,2
6.0×10^{-3}	—	—	247	57	15,7

TABLE III

Values for the Fast Relaxation Time τ_1 *for Several Alkylammonium halides as a Function of the Total Concentration* c_0 *at Various Temperatures*

	Dodecylammonium iodide $\tau_1/\mu s$			
$t/^0C$	5	10	15	20
c_0 (mol/dm^3)				
1.2×10^{-2}	120	100	75	62
1.3×10^{-2}	88	73	62	47
1.4×10^{-2}	69	58	43	30
1.6×10^{-2}	45	33	25	20
2.0×10^{-2}	27	19	14	—
2.4×10^{-2}	15	11	—	—
2.8×10^{-2}	12	8	—	—

	Tetradecylammonium Chloride $\tau_1/\mu s$			
$t/^0C$	25	30	35	40
c_0 (mol/dm^3)				
4.0×10^{-3}	153	115	77	55
4.5×10^{-3}	125	90	68	50
5.0×10^{-3}	102	78	62	37
5.5×10^{-3}	96	57	42	32
6.0×10^{-3}	75	50	38	23
6.5×10^{-3}	80	45	30	21
7.5×10^{-3}	57	34	26	15
8.5×10^{-3}	52	30	19	10
1.0×10^{-2}	37	23	14	7

	Hexadecylammonium Chloride $\tau_1/\mu s$	
$t/^0C$	40	45
c_0 (mol/dm^3)		
1.15×10^{-3}	480	390
1.5×10^{-3}	410	330
2.0×10^{-3}	260	200
3.0×10^{-3}	124	94
4.0×10^{-3}	80	63
5.0×10^{-3}	69	45

TABLE IV

Values for the Slow Relaxation Time τ_2 for Several Alkylammonium Halides at Various Total Concentrations as a Function of the Concentration of Added Sodium Halide at Various Temperatures

	Dodecylammonium Chloride + NaCl τ_2/ms										
t/°C	$c_0 = 1.2 \times 10^{-2}$ mol/dm^3 c_{NaCl} (mol %)		$c_0 = 1.4 \times 10^{-2}$ mol/dm^3 c_{NaCl} (mol %)				$c_0 = 1.6 \times 10^{-2}$ mol/dm^3 c_{NaCl} (mol %)			$c_0 = 2.0 \times 10^{-2}$ mol/dm^3 c_{NaCl} (mol %)	
	75	100	25	50	75	100	25	50	75	25	50
15	—	—	181	333	—	—	—	—	—	—	—
20	117	192	56	100	134	322	62	118	—	77	142
25	39	63	25	33	59	85	32	43	77	31	57

they are apparent dissociation degrees of the micelles. They were obtained as the ratio of the slope of the straight lines from the $\varkappa - c_0$ plot after and before the *cmc*. Table II lists the values of relaxation times for the slow process, while values for the fast process are given in Table III. Finally Table IV contains τ_2-values obtained for a given detergent concentration when excess salt was added to the solution. Typical plots of τ-values are given in Figure 2. for τ_2 and in Figure 3. for τ_1.

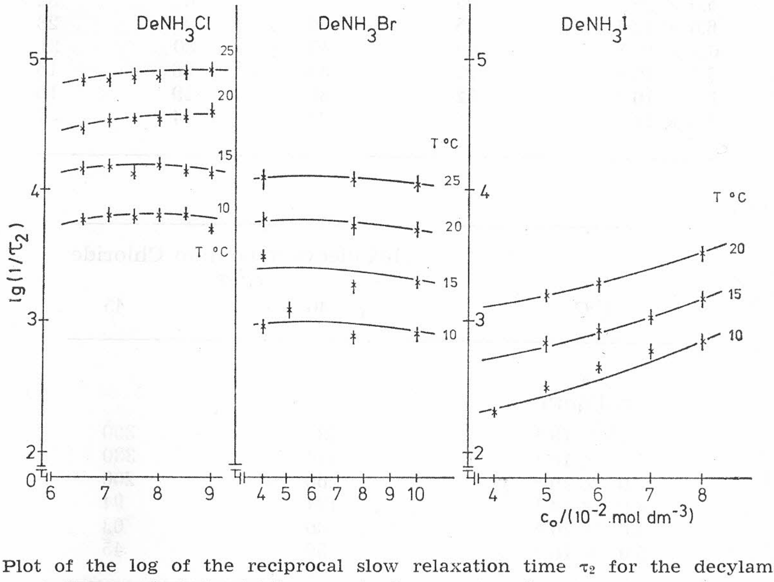

Figure 2. Plot of the log of the reciprocal slow relaxation time τ_2 for the decylammonium halides against the total concentration c_0 at various temperatures.

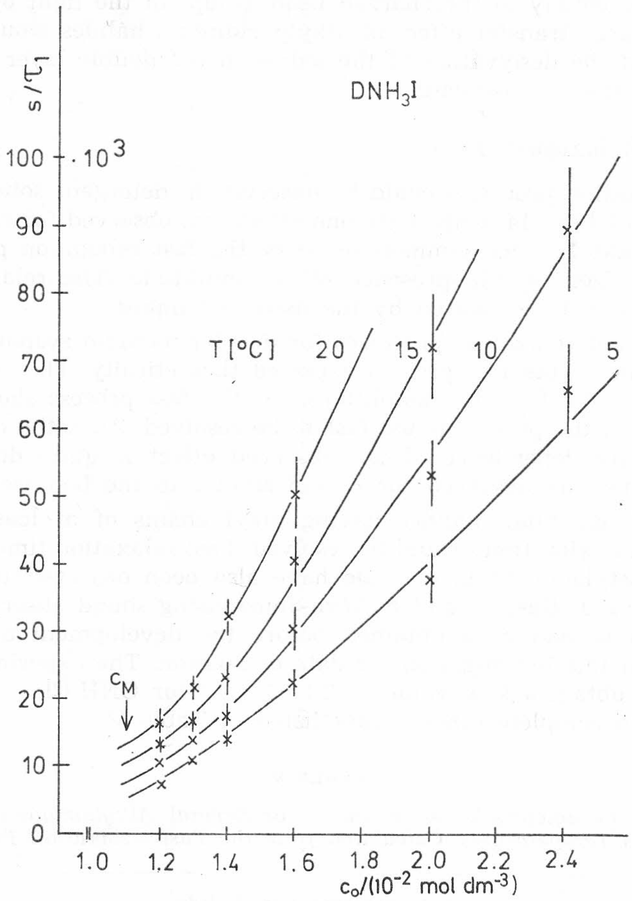

Figure 3. Plot of the reciprocal fast relaxation time τ_1 for dodecylammonium iodide against the total concentration c_0 at various temperatures.

DISCUSSION

1. Cmc-*values*

For a given chain length, the *cmc* values decrease from chloride to iodide. The change of *cmc*-values is accompanied by a change of dissociation degrees of the micelles. It is interesting to note that such a behaviour is also observed for the alkylpyridinium halides. However, in these systems charge transfer effects are usually thought responsible for varying *cmc*-values[14]. This explanation can not be valid for present systems which show the same tendency and have no charge transfer bands. For present systems it is more likely that the different *cmc*-values are due to different degrees of hydration of the counter-ions.

The chloride ion is certainly the most strongly hydrated ion. If we assume that this ion retains its coordination sphere in the double layer of the micelle, it is clear that it is a less effective shielder of the micellar charge than the iodide ion which might have lost part of its hydration sphere and can therefore approach more closely to the charged head group. In the light of this explanation, the charge transfer effect of alkylpyridinium halides would be only a consequence of the desolvation of the iodide in the double layer and not the main cause of the *cmc* decrease.

2. *The fast Relaxation Times*

Two relaxation processes could be observed in detergent solutions having chain lengths of 10 to 14, while only one effect was observed for hexadecylammonium chloride. For decylammonium salts, the fast relaxation process could only be recognized by the presence of its amplitude. The relaxation times were too short to be measured by the used techniques.

The observed relaxation processes for decylammonium systems can certainly not be due to the fast process expected theoretically. This can easily be concluded from the fact that amplitudes for the fast process show up in the experiments but the process is too fast to be resolved. Also, the concentration and temperature dependence of the observed effect is quite different from the behavior usually observed for τ_1 and similar to the behavior of τ_2.

For alkylammonium halides having alkyl chains of at least 12 carbon atoms, fast relaxation times could be resolved. Fast relaxation times of micellar solutions of octylammonium chloride have also been observed in a previous investigation by J. Rassing and E. Wyn-Jones using sound absorption techniques. Their data had been obtained before the development of the theory that is used in this investigation for data evaluation. The experimental points were used to obtain a k^-/n value of $2.1 \cdot 10^7$ s^{-1} for ONH_3Cl at 25 ^{0}C, which can be used to complete other values listed in Table V.

TABLE V

Values for the Parameters k^+, k^-, n *and* σ *for Several Alkylammonium Halides at Various Temperatures, Calculated from the Fast Relaxation Time* τ_1

Dodecylammonium Iodide

t / ^{0}C	k^-/σ^2 / s^{-1}	k^-/n / s^{-1}	k^+ / dm^3/mol · s	k^- / s^{-1}	n	σ	*cmc* / mol/dm^3
5	5.0×10^3	4.9×10^4	9.8×10^8	1.0×10^7	217	45	1.1×10^{-2}
10	7.0×10^3	6.7×10^4	1.4×10^9	1.5×10^7	230	46	1.1×10^{-2}
15	1.1×10^4	8.6×10^4	1.9×10^9	2.1×10^7	243	44	1.1×10^{-2}
20	1.4×10^4	1.1×10^5	2.5×10^9	2.7×10^7	250	44	1.1×10^{-2}

Tetradecylammonium Chloride

t / ^{0}C	k^-/σ^2 / s^{-1}	k^-/n / s^{-1}	k^+ / dm^3/mol · s	k^- / s^{-1}	n	σ	*cmc* / mol/dm^3
25	6.5×10^3	1.3×10^4	2.5×10^9	9.8×10^6	750	39	4.0×10^{-3}
30	8.7×10^3	2.3×10^4	3.9×10^9	1.5×10^7	670	42	4.0×10^{-3}
35	1.3×10^4	3.3×10^4	5.4×10^9	2.1×10^7	650	40	4.0×10^{-3}
40	1.8×10^4	5.0×10^4	8.0×10^9	3.1×10^7	615	41	4.0×10^{-3}

Hexadecylammonium Chloride

t ^{0}C	k^-/σ^2 s^{-1}	k^-/n s^{-1}	k^+ dm^3/mol · s	k^- s^{-1}	n	σ	cmc mol/dm^3
40	2.1×10^3	4.9×10^3	9.4×10^8	1.0×10^6	220	22	1.2×10^{-3}
45	2.5×10^3	6.6×10^3	1.1×10^9	1.3×10^6	190	23	1.2×10^{-3}

Tetradecylpyridinium Chloride

t ^{0}C	k^-/σ^2 s^{-1}	k^-/n s^{-1}	k^+ dm^3/mol · s	k^- s^{-1}	n	σ	cmc mol/dm^3
25	9.7×10^4	2.4×10^5	4.5×10^9	1.9×10^7	80	14	4.2×10^{-3}

In comparison to the alkylpyridinium halides, the relaxation times are almost one order of magnitude longer for corresponding alkylammonium systems with similar *cmc*-values. Longer relaxation times result in unusually small k^-/n *and* k^-/σ^2-values. The evaluated parameters are given in Table V. The system TNH_3Cl for instance has k^-/n values that are even more than an order of magnitude smaller than the value for alkylpyridinium halide[7]. The reason for this behaviour is not yet clear. From electrostatic principles just the opposite effect would have been expected because for the ammonium systems the positive charge is located on a small head group close to the first C-atom of the alkyl group, while for pyridinium detergents, the charge is assumed to be smeared out over the pyridinium ring. The repulsion between the head groups should therefore be higher for the ammonium detergent. One reason for the different behaviour might lie in the micelle packing. It is likely that the bulky pyridinium ring on the alkylpyridinium halides acts as a restraint on the tight packing of the alkyl groups and that therefore alkyl groups can not be as closely packed as alkylammonium halides where the ammonium groups are small and are not a hindrance for the packing in the micelle. As a consequence the hydrophobic interaction could become larger for ammonium detergents than for the pyridinium detergents resulting with smaller k^-/n--values.

In this case, the viscosity of the micellar interior should vary considerably for the two systems. The low values for k^-/σ^2 can be a result of large n and σ-values. All parameters determined from data are given in the Table V. In order to obtain σ and n-values from experimentally determined k^-/n and k^-/σ^2 values, it is necessary to make some further assumptions.

For systems where only τ_1 is known, a data evaluation can be done in the following way. In previous studies, it was observed that the rate constants k^+ are in the range of rate constants for diffusion controlled reactions. It is likely that this occurs also in systems studied by this investigation. We can therefore assume either theoretical rate constants for k^+ or take the values obtained for micellar systems of similar *cmc* and dissociation degree. With these values and the experimental *cmc* values we may determine k^--values from the equation $k^- = k^+ \cdot cmc$.

With these k^--values and experimental values for k^-/n and k^-/σ^2 we can finally calculate σ and n values. The data thus obtained show that the mean aggregation numbers are fairly large and the σ-values are of considerable width. These values may be compared with values evaluated directly for the system TNH_3Cl for which both relaxation times are known. In such a case, enough information is available to calculate k^-, σ, k^+ and n separately from experimental results. The only assumption that has to be made concerns the shape of the distribution curve between the maximum and the minimum of the micellar distribution curve. In previous studies it was shown that reasonable values are obtained if a Gaussian distribution is used for this purpose.

The evaluated parameters are given in Table VI. Regarding the accuracy of the n and σ-values in Table V it should be noted that these values are only rough estimates because exact k^+-values for these systems were not available.

TABLE VI

Values for the Parameters k^+, k^-, n *and* σ *for Tetradecylammonium Chloride at Various Temperatures, Calculated from the Fast Relaxation Time* τ_1 *and the Slow Relaxation Time* τ_2

t / ⁰C	k^-/σ^2 / s^{-1}	k^-/n / s^{-1}	k^+ / $dm^3/mol \cdot s$	k^- / s^{-1}	n	σ	cmc / mol/dm^3
25	6.5×10^3	1.3×10^4	3.5×10^8	1.3×10^6	99	14.1	3.65×10^{-3}
30	8.7×10^3	2.3×10^4	7.1×10^8	2.6×10^6	115	17.4	3.75×10^{-3}
35	1.3×10^4	3.3×10^4	9.1×10^8	3.5×10^6	105	16.3	3.80×10^{-3}
40	1.8×10^4	5.0×10^4	1.3×10^9	5.3×10^6	106	17.2	3.95×10^{-3}

3. *Residence Times of Detergent Molecules Inside the Micelle*

For broad distribution curves it is obvious that the equilibrium constants $K_s = k^+/k^-$ are practically the same for different aggregated species near the maximum of the distribution curve. Furthermore, it is likely that rate constants k^+ are independent of the aggregation number because k^+ has the size of a diffusion controlled rate constant. It follows then that the rate constant k^- should also be independent of the aggregation number s; the residence times t_s become n/k_s^-, increasing linearly with the aggregation number.

Residence times vary strongly with the length of the alkyl chain of the detergent molecule. Figure 4. shows a plot of the log of the reciprocal residence times against the number of carbon atoms in the chain. As for other homologous detergent systems, log k^-/n varies linearly with the number of carbon atoms. This result may be understood by the equation (3)

$$k^-/n = \frac{D}{l^2} \cdot e^{-\varepsilon/kT} \tag{3}$$

where D is the diffusion coefficient of a detergent molecule, l the length of a CH_2-group and ε the total free energy to bring a detergent molecule from its equilibrium position in the micelle to a position where only the last CH_2-group is inside the micelle and the remaining part of the molecule is already in the aqueous phase. The total free energy is composed from a hydrophobic and an electrostatic contribution. If the electrostatic contribution is assumed to be the same for all alkylammonium systems and the hydrophobic part varies linearly with the chain length, we can write: $\varepsilon = m \cdot \varepsilon_0 + \varepsilon_{ele}$. The slope of the plot in Figure 4 should therefore give ε_0 which is the hydrophobic energy for the transfer of a CH_2-group from the aqueous into the micellar phase. The slope leads to a value of $\varepsilon_0 = 1.13 \cdot kT$. This result is in good agreement with values that have been obtained from thermodynamic studies on neutral micellar systems.[5]

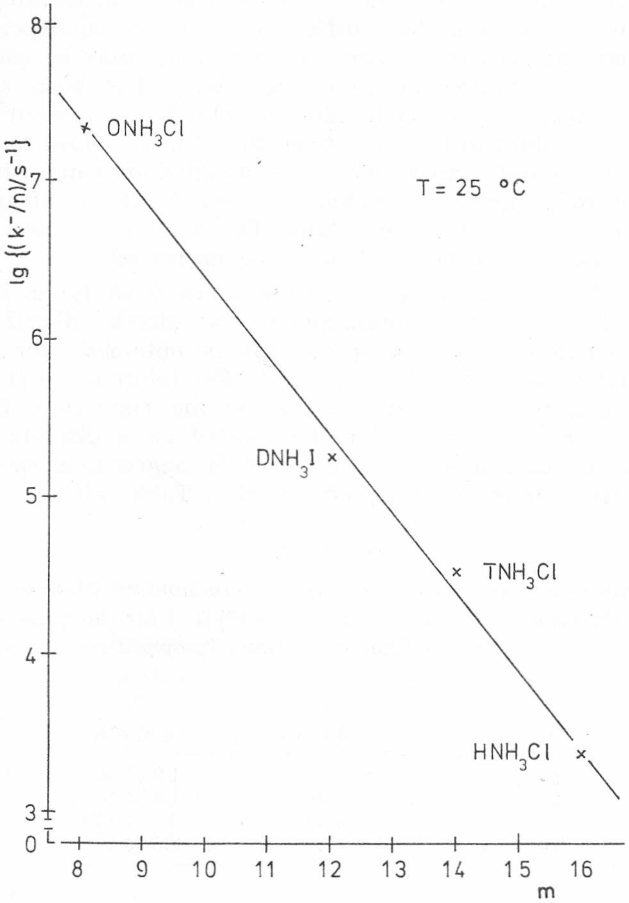

Figure 4. Plot of the log of the k^-/n-values for alkylammonium halides against the number of C-atoms in the alkyl chain at 25 °C.

4. *Slow Relaxation Process*

Slow relaxation process could be observed for the decyl-, dodecyl- and tetradecylammonium halides.

a) Micellar Nucleus. — τ_2-Values are for several orders of magnitude longer than values obtained on other systems having similar *cmc*-values but different head groups. The only two systems where τ_2 has been observed before for an ionic detergent with a decyl group were the decylpyridinium iodide and sodium decyl sulfate. For these two systems, τ_2 was of the order of 10—50 μs. But these two systems have considerable lower *cmc*-values than the alkylammonium salts. Even based on relaxation times of these systems much shorter times were expected for alkylammonium halides. With respect to their τ_2-values it may therefore be said, that the alkylammonium salts behave very uniquely.

It is known that τ_2 depends very much on impurities.[3a] A few tenths of a percent of impurities such as higher homologs or other hydrophobic compounds, are known to lengthen the relaxation times considerably. However, in such cases impurities lead to a different concentration dependence of τ_2 with c_0 than that observed for present systems and it may be concluded that long times were not caused by impurities. What has been said for the τ_2-values for the decylammonium halides can also be said about the dodecyl salts. Again the τ_2-values are much longer than the τ_2-values for other ionic detergent systems having similar *cmc*-values as alkylammonium halides. Both the τ_2-values for dodecylpyridinium chloride and bromide are about 1000 times shorter than for dodecylammonium halides. The relaxation time for the dodecylammonium iodide was even too long to be measured.

The reason for unusual long relaxation times must lie in extreme low concentrations of species at the minimum of the micellar distribution curve. Values for concentrations of these species can be obtained from equation (2) using the evaluated parameters from Table V. For relative rough estimates of c_r, k_r may be assumed to be equal to k^- on the maximum. Furthermore, for the minimum can be assumed to be located on a discrete aggregation number instead of extending over a range of aggregated species. Values resulting from these approximations are listed in Table VII.

TABLE VII

Values of Nuclei Concentration c_r *for Tetradecylammonium Chloride, Calculated from the Gauss' Function* (c_{r_1}) *and from Equation (2)* (c_{r_2}) *for the Total Concentration* $c_0 = 5 \times 10^{-3}$ *mol/dm*^{3} *at Various Temperatures*

t / ^{0}C	c_{r_1} / (mol/dm^3)	c_{r_2} / (mol/dm^3)
25	3.9×10^{-14}	1.2×10^{-13}
30	6.1×10^{-14}	1.8×10^{-13}
35	2.5×10^{-14}	4.7×10^{-13}
40	6.4×10^{-13}	2.5×10^{-12}

b) Aggregation Number of Nuclei. — It has previously been pointed out that the concentration dependence of τ_2 on the total detergent concentration can be used to determine whether aggregates forming the micellar nucleus have counterions bound to them or not. For both decyl- and dodecylammonium chloride the concentration dependence is similar to the one observed for many other systems, which has been recognized as indicative of no bound counterions. At the smallest temperatures for which measurements could be carried out, the $1/\tau_2$-values are relatively insensitive to the total concentration and decrease with increasing concentration. This behaviour is a strong evidence for the fact that counterions are not bound to nuclei. In the case of bound counterions, the rate determining species would have to increase with the total concentration, because the counterion concentration is certainly increasing with the total detergent concentration. In agreement with this conclusion is the change of the $1/\tau_2$-values when NaCl is added to the solution. As observed previously for DPyCl and SDS, $1/\tau_2$ decreases with the salt concentration (Figure 5.). The effect is believed to be due to the lowering of the *cmc* that is caused by the added counterion concentration. The equilibrium of the micellar nucleus with the monomer concentration can be used to derive values for the micellar nucleus aggregation number, when *cmc*-values for different NaCl-concentrations are known. Finally, for the DeNH$_3$I-system $1/\tau_2$ increases with the total detergent concentration. This is also the case for the $1/\tau_2$-values for the DNH$_3$Br-system at high temperatures. For these systems, it is likely therefore that counterions are involved in the formation of the micellar nuclei. However, close to the *cmc*, the influence of the counterions on the nucleus seems still to be very small, if not insignificant. This can be concluded from the fact that the temperature dependence of τ_2 for the concentrations close to the *cmc* for three decylammonium halides is the same (Figure 6.). The species involved in the rate determining step for

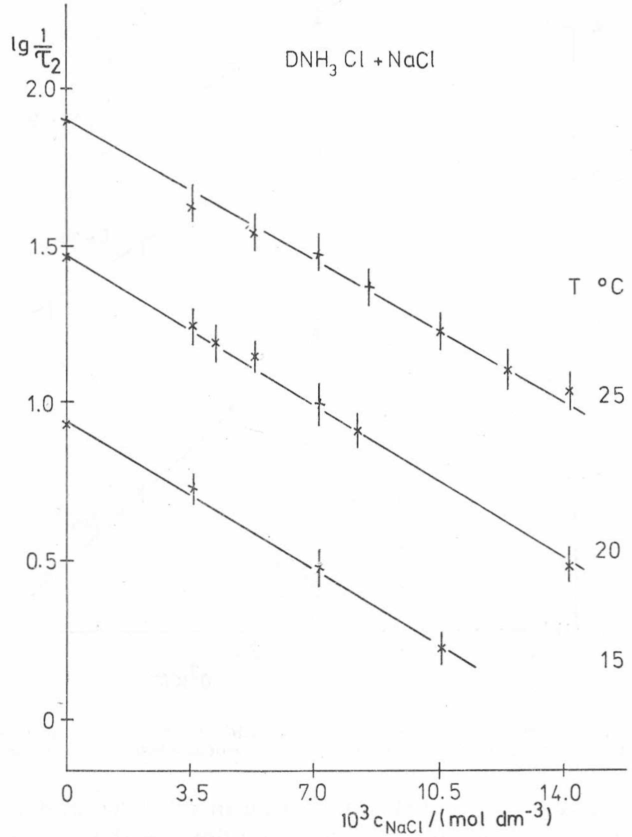

Figure 5. Plot of the log of the reciprocal slow relaxation time τ_2 for dodecylammonium chloride at $c_0 = 1.5 \times 10^{-2}$ mol/dm^3 against the concentration of added NaCl at various temperatures.

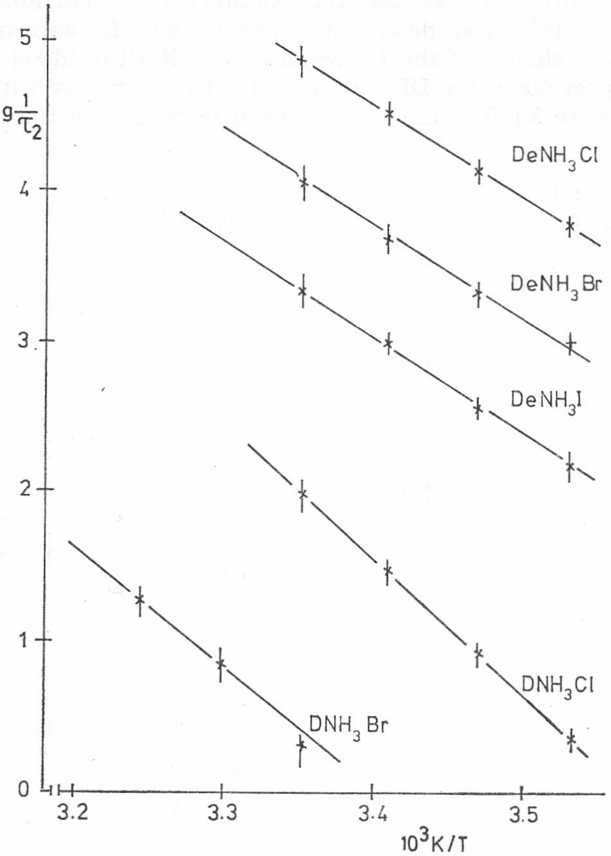

Figure 6. Plot of the log of the reciprocal slow relaxation time τ_2 near the cmc for decyl- and dodecylammonium halides against the reciprocal absolute temperature.

the micelle formation are probably the same in all three systems. Systems of the same detergent ion, having different counterions that do not bind to the nuclei, should have an identical nucleus. For such systems it was shown that log $1/\tau_2$ varies linearly with the log of *cmc* and the slope of such a plot can be used to determine the nucleus aggregation number[16]. As can be seen from Figure 7. this is also the case for decylammonium halides. From the slope, a value of $r = 9$ can be obtained. This value is very similar to the one obtained for nuclei of dodecyl- and tetradecylpyridinium surfactants. It seems therefore that the number of monomers that have to aggregate together to form a stable nucleus is very insensitive to the chain length of the alkyl group.

For dodecylammonium halides however, the slope is much larger as seen from Figure. 7. The slope also explains why the τ_2-values for the DNH_3I could not be measured. If the slope for DNH_3Cl and DNH_3Br is extrapolated to the *cmc*-values of DNH_3I, relaxation times of more than 10 s should be expected. The high value of the slope ($r = 19$) seems very much surprising and it is yet completely unclear at present why the distribution minimum is shifted so much

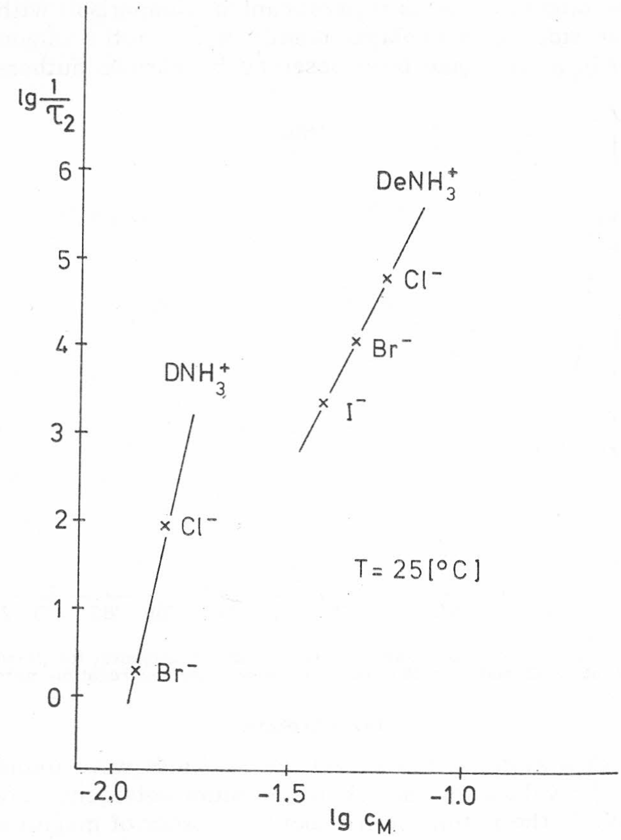

Figure 7. Plot of the log of the reciprocal slow relaxation time τ_2 near the cmc at 25 °C for decyl- and dodecylammonium halides against the log of the *cmc*.

to higher values in comparison to dodecylpyridinium halides. There is actually a chance that the micellar aggregation number for the nucleus of dodecylammonium micelles is really smaller and that these high values are a result of the way in which the data were evaluated. In the calculation of the r value it was assumed that all parameters but A_1 in the equation for τ_2 remain constant. Smaller values for instance would result if the micellar aggregation number decreases considerably from chloride to iodide. On the other hand the larger temperature dependence of DNH_3Cl in comparison to $DeNH_3Cl$ also indicates that the r values for DNH_3Cl might be larger than for $DeNH_3Cl$. The system DNH_3Cl has one of the largest temperature dependences that were ever observed for a relaxation process in a micellar solution.

All the available information from τ_1 and τ_2 can be used to draw a micellar distribution curve. This is done in Figure 8. for the TNH_3Cl at 35 °C. In order to see the large variation in the aggregation for the species as a function of the aggregation number, a log scale was used for these species. Due to the fast drop of oligomers with increasing aggregation number, the amount of material on the oligomer side is insignificant in comparison with the material on the micellar side. This explains readily why on the oligomer side only dimers were believed to have been observed by various authors.

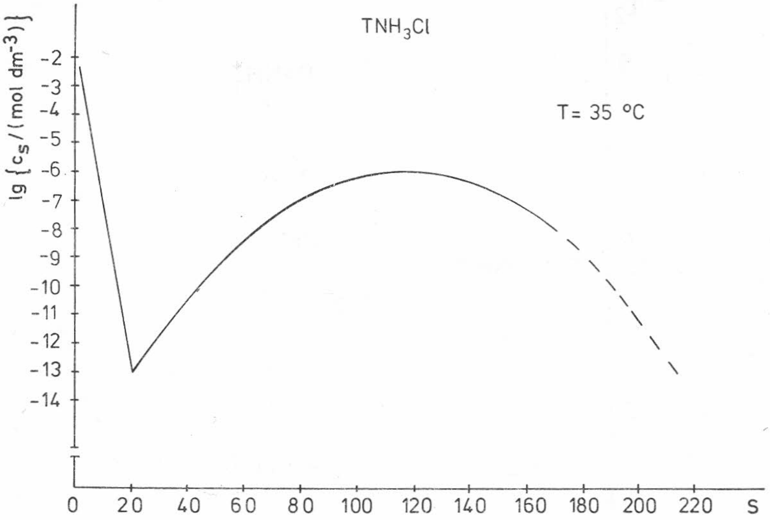

Figure 8. Plot of the log of the concentration of the aggregates for tetradecylammonium chloride at 35 °C and $c_0 = 10^{-2}$ mol/dm^3 against the aggregation number s.

CONCLUSION

For all studied systems, the τ_1 and the τ_2-values were found to be considerably above the values for the alkylpyridinium detergents having the same chain length. While the τ_1-times were about one order of magnitude longer, the increase for the τ_2-values was often of more than three orders of magnitude. Consequently, the ratio of τ_2 and τ_1 is much larger for alkylammonium halides than for the alkylpyridinium halides. These observations on the alkylammonium halides can be explained on the basis of micellar distribution curves having large mean aggregation numbers and a considerable width. As a result, the shift from one micellar equilibrium distribution to another involves more individual steps for the reequilibration process. In addition the residence times of alkylammonium ions in micelles are longer than for alkylpyridinium halides of similar *cmc*-values. Thus all observations that can be made from kinetic measurements are in agreement with conclusions derived from light scattering data.

REFERENCES

1. K. Shinoda, T. Nagakawa, B. Tamaushi, and T. Isemura, *Colloidal Surfactants,* Academic Press, London, 1963.
2a. G. C. Kresheck, E. Hamori, G. Davenport, and H. A. Sheraga, *J. Amer. Chem. Soc.* **88** (1966) 246.
b. G. Bennion, L. Tong, L. Holmes, and E. Eyring, *J. Phys. Chem.* **73** (1969) 3288.
c. T. Yasunaga and K. Takeda, *J. Colloid Interface Sci.* **40** (1972) 127.
3a. R. Folger, H. Hoffmann, and W. Ulbricht, *Ber. Bunsenges. Phys. Chemie* **78** (1974) 986.

b. J. Lang, C. Tondre, R. Zana, R. Bauer, H. Hoffmann, and W. Ulbricht, *J. Phys. Chem.* **79** (1975) 276.
4a. E. A. G. Aniansson and N. S. Wall, *J. Phys. Chem.* **78** (1974) 1024.
b. E. A. G. Aniansson and N. S. Wall, *J. Phys. Chem.* **79** (1975) 857.
5. P. Mukerjee, *Advances in Colloid and Interface Science,* Elsevier Publishing Company, Amsterdam 1 (1967) 241.
6. E. A. G. Aniansson, M. Almgreen, N. S. Wall, J. Lang, C. Tondre, R. Zana, H. Hoffmann, J. Kielmann, and W. Ulbricht, *J. Phys. Chem.* **80** (1976) 905.
7. H. Hoffmann, R. Nagel, G. Platz, and W. Ulbricht, *Colloid Polym. Sci.* **254** (1976) 812.
8. C. Tanford, *The Hydrophobic Effect,* Wiley-Interscience, New York 1973.
9a. R. D. Geer, E. H. Eylar, and E. W. Anacker, *J. Phys. Chem.* **75** (1971) 369.
b. M. T. Emerson and A. Holtzer, *J. Phys. Chem.* **71** (1967) 1898.
10. D. Stigter, *J. Phys. Chem.* **78** (1974) 2480.
11. H. Strehlow and M. Becker, *Z. Elektrochem.* **63** (1959) 457.
12. G. Platz and H. Hoffmann, *Ber. Bunsenges. Phys. Chemie* **76** (1972) 491.
13. C. Tondre, J. Lang, and R. Zana, *J. Colloid Interface Sci.* **52** (1975) 372.
14. P. Mukerjee and A. Ray, *J. Phys. Chem.* **70** (1966) 2144.
15. J. Rassing, P. J. Sams, and E. Wyn-Jones, *J. Chem. Soc. Faraday Trans* 2, **70** (1974) 1247.
16. H. Hoffmann, H. Nüßlein, and W. Ulbricht, *Proceedings of the Symposium on Micellisation, Solubilisation and Microemulsions,* Albany, N. Y. 1976, Plenum Press 1977.

SAŽETAK

Kinetička mjerenja alkilamonijevih halogenida

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Dan je prikaz kemijskih relaksacijskih mjerenja na alkilalmonijevim halogenidima s 10 do 16 C-atoma u lancu. Za većinu proučavanih sistema opažena su dva relaksacijska vremena. Rezultati su objašnjeni s pomoću teorije G. Anianssona i S. Walla. U skladu s tom teorijom brzi proces pripada promjeni micelarne raspodjele. Vrijeme ostajanja molekule detergenta u miceli i poluširina krivulje raspodjele micela izvedena je iz brzog procesa. Spori relaksacijski proces karakterističan je za promjenu koncentracije micela i omogućava procjenu koncentracije nukleusa micela i njihovih termodinamičkih svojstava. Dobiveni rezultati su uspoređeni s podacima dobivenim na alkilpiridinijevim halogenidima.

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