In HLDH the apparent correlation time is so small that it cannot be determined accurately. And within the error of τ_{app} and the experimental error in the net relaxation rates, this internal correlation time is also consistent with the value of 1 ns.

Thus the only deviant internal correlation time is that for the HLDH-NADH complex. However, since the crystal structure studies on this complex[6,7] show that the probable binding site[15] (the guanidinium group of arginine-109) is severely restricted by the presence of NADH, then this may reflect an actual difference.

Although it is not profitable to try to interpret the individual results until the actual quadrupole coupling constants can be determined, these calculations do show that the chloride binding studies can be given a consistent explanation in terms of internal motion at the binding sites.

Conclusion

We have shown that the chlorine relaxation data for chloride binding to several proteins can be explained in a consistent way by taking into account the effects of internal motion at the binding sites. When the actual quadrupole coupling constant for the bound ion is known, the measured NMR relaxation times can be converted into two parameters that are a measure of the extent and speed of the internal motion. And with this conversion, NMR studies of ion binding to macromolecules should prove to be a powerful tool for investigating the internal motions of charged side groups in macromolecules.

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Alkali Ion Binding to Aggregates of Amphiphilic Compounds Studied by Nuclear Magnetic Resonance Chemical Shifts

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Abstract: The NMR chemical shifts of $^{23}Na^+$, $^{35}Cl^-$, and $^{133}Cs^+$ counterions were investigated for a range of amphiphilic systems. From variable concentration studies, the intrinsic shifts, δ_m, of counterions bound to the micelles were deduced. The δ_m values are informative as regards the interactions of the counterions. From the detailed studies of δ_m of $^{23}Na^+$ it is found that counterion binding does not change appreciably with the alkyl chain length but varies very sensitively with the polar head group. The shielding of Na^+ at the micellar surface follows the sequence $-OSO_3^- > aryl\text{-}SO_3^- > alkyl\text{-}SO_3^- > -CO_2^-$ and this is interpreted in terms of Na^+-hydration water overlap and head group induced polarization of the Na^+ ion's hydration sphere. Chemical shifts were also found to be valuable for studies of other phases, i.e., lyotropic liquid crystals and reversed micellar solutions. For the system sodium octanoate–octanoic acid–water, a specific complex formation is inferred for the water-poor solution phase. The difference in an ion's chemical shift between H_2O and D_2O solutions is found to be useful for probing into the hydration of counterions in amphiphilic systems. The $^{133}Cs^+$ counterion is found to retain its inner hydration sphere up to high concentrations of cesium octanoate, while in the reversed micellar solutions of cesium octanoate and water in octanoic acid, the dehydration can be followed in detail. The significance of counterion water contact down to rather low water contents is suggested by these results. The chemical shift studies were complemented with investigations of the $^{23}Na^+$ quadrupole relaxation rates.

Introduction

The interest in ionic interactions in systems of synthetic and biological amphiphiles, the latter serving as models of biological membranes, has grown markedly in recent years. To study alkali ion binding to micellar aggregates and liquid crystalline phases of different types, both the quadrupole relaxation[1,2] and the quadrupole splitting methods[3-5] were introduced and these techniques are currently used by several groups.[6-11] Some time ago we proposed the study[12] of NMR chemical shifts of ions as a complement to these methods and presented an initial study giving inter alia some insight into the specificity of ion binding to micellar aggregates.[13] In the present report, we propose to present a systematic study mainly of $^{23}Na^+$ chemical shifts in solutions of a large number of
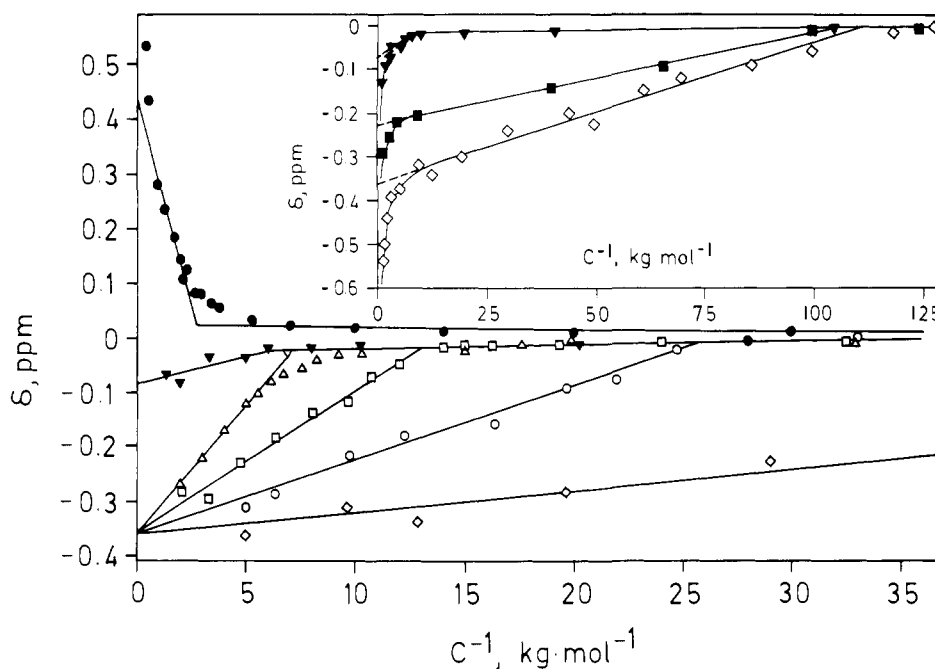
Figure 1. ^{23}Na NMR chemical shifts, δ (ppm), as a function of the inverse amphiphile concentration (molality), for aqueous solutions of sodium octanoate (●), octyl sulfonate (▼), octyl sulfate (△), nonyl sulfate (□), decyl sulfate (○) and dodecyl sulfate (◇), and (in the insert) *p*-octylbenzene sulfonate (■). The insert shows that deviations from the used model occur especially in the high concentration region.

different amphiphilic compounds, differing in alkyl chain length and head group. Several other aspects of alkali ion binding in amphiphilic systems will also be discussed and, furthermore, the chemical shift studies are complemented by investigations of the quadrupole relaxation rates. Preliminary reports of part of the present results have been given elsewhere.[14,15]

Experimental Section

Chemicals. The following commercial chemicals were used without further purification: sodium *n*-octyl and *n*-nonyl sulfate (Merck AG), sodium *n*-decyl sulfate and *n*-dodecyltrimethylammonium chloride (Eastman Kodak), and sodium *n*-dodecyl sulfate, 1-decanol, and *n*-octanoic acid (British Drug Houses). Specially purified sodium *n*-octanoate was kindly supplied by Docent Krister Fontell and sodium *n*-octylbenzene sulfonate was a kind gift from Dr. Jacques Rouvière. Cesium *n*-octanoate and *n*-dodecanoate were prepared as described previously.[13] Octyltrimethylammonium chloride was prepared by reacting trimethylamine with octyl chloride and octylammonium chloride was obtained as a precipitate by introducing HCl gas into an ether solution of octylamine. These substances were recrystallized prior to use. The *n*-octanoic acid used in combination with D_2O in the studies of the water isotope effect in shielding (see below) was prepared by shaking several times with D_2O. Other chemicals used (solubilizates, alkali chlorides D_2O) were of pro analysi quality.

NMR Measurements. For the NMR investigations three spectrometers were used: a modified Varian XL-100 NMR spectrometer operating in the Fourier transform mode, a Varian V-4200 wide-line spectrometer modified to improve resolution and stability, and a Bruker Bk-322 s pulse spectrometer. Determinations of T_1 and T_2 were performed using the Bruker spectrometer as described previously[13] and served in this work mainly to establish the validity of the extreme narrowing situation. With a considerable improvement of the chemical shift determinations compared to the previous study,[13] all ^{23}Na NMR chemical shift measurements were performed on the XL-100 spectrometer. Most of the ^{133}Cs measurements were also performed using the XL-100 spectrometer while the wide-line spectrometer was used for most of the studies of ^{35}Cl. All measurements were performed at probe temperature, which was 27–28 °C. Chemical shifts were measured relative to a concentrated cesium chloride solution for ^{35}Cl and ^{133}Cs and a solution of sodium tetraphenylboron in CD_3CN for ^{23}Na$^+$. The reference solutions were contained in a capillary which was inserted coaxially into the sample tube. For the

presentation of the results the chemical shifts have been converted to shifts relative to infinitely dilute aqueous solutions. The definition of the chemical shift is such that a positive shift is to higher frequency. As argued previously,[13] and as confirmed in a number of cases by determinations of the susceptibility of the solutions, the appropriate correction for differences in macroscopic susceptibility between sample and reference solutions is much smaller than the observed effects. For ^{35}Cl and ^{133}Cs the corrections are completely negligible. The accuracy of the measurements varies widely with concentration as well as with the relaxation broadening. For the micellar solutions in water the shift measurements are precise to ±0.1 ppm or better while the error in the transverse relaxation rates, obtained from the line widths, is generally less than 5%.

Results

^{23}Na$^+$, ^{133}Cs$^+$, and ^{35}Cl$^-$ Chemical Shifts. The concentration dependence of the ^{23}Na$^+$ chemical shifts was investigated for aqueous solutions of the sodium salts of octyl sulfonate, *p*-octylbenzene sulfonate, nonyl sulfate, decyl sulfate, and dodecyl sulfate. We have previously[13] reported results for sodium octyl sulfate and sodium octanoate and these have now been complemented and made more precise. As a basis for the discussion of the interactions of the counterions with the micellar aggregates, it is useful to obtain the intrinsic shifts of the bound counterions. With the phase separation model for micelle formation and assuming a two-site model for the counterion binding (with free and bound counterions only), one finds that a plot of the chemical shift, δ, vs. the inverse amphiphile concentration (c_t) should consist of two straight-line segments intersecting at the critical micelle concentration (cmc). Thus we have

$$c_t > \text{cmc} \quad \delta_{obsd} = \delta_f + \beta(\delta_m - \delta_f) - \frac{\beta \cdot \text{cmc}}{c_t}(\delta_m - \delta_f) \quad (1a)$$

$$c_t < \text{cmc} \quad \delta_{obsd} = \delta_f \quad (1b)$$

where δ_f and δ_m are the intrinsic shifts for the free and bound counterions, respectively, and β is the ratio of counterions to surfactant ions in the micelles. Plots of the observed ^{23}Na$^+$ chemical shifts vs. the inverse amphiphile concentration are shown in Figure 1. In Figure 2 the ^{133}Cs$^+$ and ^{35}Cl$^-$ chemical
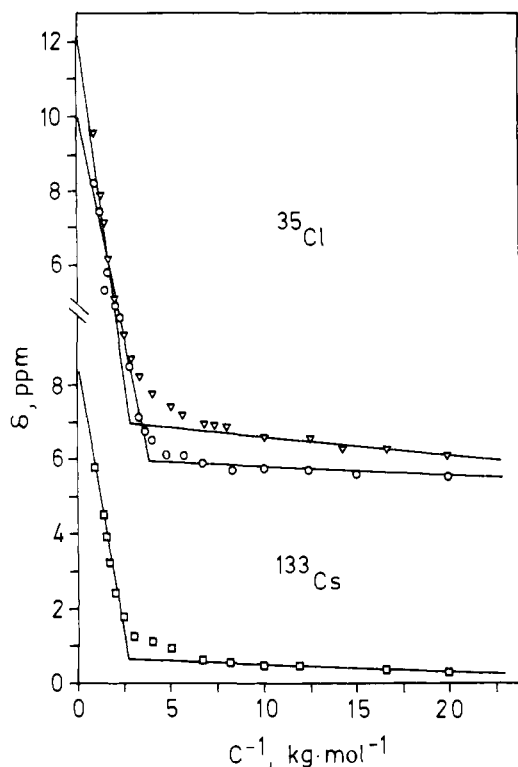
Figure 2. The variation in ^{133}Cs chemical shift (ppm) in aqueous cesium octanoate solutions (□) and ^{35}Cl shifts in octyltrimethylammonium (▽) and octylammonium chloride (○) solutions as a function of inverse amphiphile molality.

Figure 3. The effect of the water content on (a) the ^{23}Na chemical shift, (b) the ^{133}Cs chemical shift and (c) the ^{133}Cs water isotope effect on shielding ($\Delta\delta = \delta_{D_2O} - \delta_{H_2O}$) for the water-poor solution phase of the octanoic acid-octanoate-water system. The molar ratio acid to octanoate is 0.350 in (a) and 0.307 in (b) and (c).

Figure 4. ^{133}Cs chemical shifts (ppm) of H_2O (□) and D_2O (○) solutions of cesium octanoate as a function of amphiphile molality.

shifts are shown for aqueous solutions of cesium octanoate, octylammonium chloride, and octyltrimethylammonium chloride, respectively.

In addition to the studies of pure surfactant solutions we also investigated the effects of additives and Table I includes ^{23}Na$^+$ chemical shift data pertaining to the effect of addition of simple salt or of solubilizate.

The evolution of micellar aggregates in aqueous solutions into more complex structures at lower water contents and/or in the presence of a third component is a problem of great current interest. An insight into the accompanying changes in molecular interactions is helpful for estimation of the parameters entering the theoretical predictions of the energy of micelle formation. In Table I ^{23}Na$^+$ chemical shifts are given for some liquid crystalline phases and for water-poor isotropic solution phases. In Figure 3 the variation of the ^{23}Na$^+$ chemical shift with the water content is shown for the water-poor solution phase of the system sodium octanoate-octanoic acid-water. The considerable line broadening observed (cf. ref 2) reduces the accuracy of the chemical shifts at the lowest water contents. ^{133}Cs$^+$ chemical shifts for the corresponding cesium salt system are also included. In general the studies of the three-component systems were based on the phase equilibria studies of Ekwall and co-workers.[16] For the cesium octanoate-octanoic acid-water system, no phase diagram was available. It was found that at low water contents the solubility of cesium octanoate in octanoic acid is considerably lower than that of sodium octanoate.

Water Isotope Effect in the ^{133}Cs$^+$ Chemical Shifts. The chemical shifts of the halide ions and of the heavier alkali ions change appreciably if H_2O is replaced with D_2O as the solvent.[17-20] A detailed interpretation of this has not yet been established, but this should not prevent the effect from being useful in ion hydration studies. Thus the magnitude of the effect should be a measure of the extent of direct ion-water contact, and we have attempted to explore the hydration of
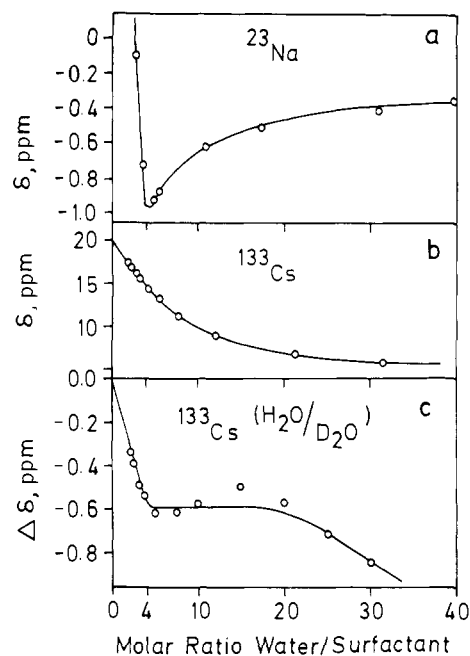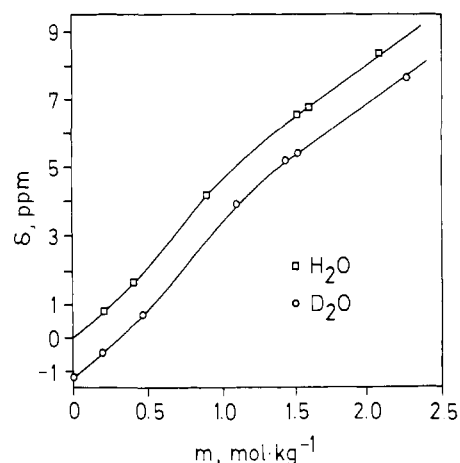
counterions bound to amphiphilic aggregates. The differences in ^{133}Cs$^+$ chemical shifts between D_2O and H_2O solutions, i.e., the isotope effect, are shown in Figure 4 for the case of cesium octanoate and in Figure 3 for the case of a system containing reversed micelles.

^{23}Na$^+$ Relaxation Studies. The strongly dominating magnetic relaxation mechanism of alkali and halide ions in diamagnetic solution is (except for Li$^+$ (^{6}Li, ^{7}Li) and F$^-$ (^{19}F)) the interaction of the nucleus' electric quadrupole moment with fluctuating electric field gradients. Quadrupole relaxation studies have been extensively used to examine counterion binding in amphiphilic systems.[1,2,6,13,21] Here the relaxation rates will be used for comparative purposes in combination with the shielding data. In some previous work,[13] rather extensive investigations mainly of the longitudinal ^{23}Na$^+$ relaxation time (T_1) have been reported as well as some Carr-Purcell-Meiboom-Gill determinations of T_2, the transverse relaxation time. Although the equality of T_1 and T_2 has been demonstrated previously[13] for several cases, the validity of the ex-

Table I. Chemical Shifts (δ) and Transverse Relaxation Rates (R_2) of ^{23}Na$^+$ Counterions in Amphiphilic Systems

solution composition[a,b]			phase[c]	δ, ppm	R_2, s^{-1}
0.08 m C$_8$PhSO$_3$Na			L$_1$	-0.14	44.0
0.08 m C$_8$PhSO$_3$Na + 0.016 m cyclohexane			L$_1$	-0.14	47.7
0.08 m C$_8$PhSO$_3$Na + 0.032 m cyclohexane			L$_1$	-0.17	53.3
0.08 m C$_8$PhSO$_3$Na + 0.016 m benzene			L$_1$	-0.11	43.6
0.08 m C$_8$PhSO$_3$Na + 0.040 m benzene			L$_1$	-0.13	43.4
0.08 m C$_8$PhSO$_3$Na + 0.020 m octanol			L$_1$	-0.12	41.1
0.08 m C$_8$PhSO$_3$Na + 0.032 m octanol			L$_1$	-0.12	39.5
1.08 m C$_8$OSO$_3$Na			L$_1$	-0.37	40.0
1.08 m C$_8$OSO$_3$Na + 0.24 m decanol			L$_1$	-0.35	41.2
1.08 m C$_8$OSO$_3$Na + 0.38 m decanol			L$_1$	-0.39	47.9
2.90 m C$_8$OSO$_3$Na			L$_1$	-0.60	48.1
2.90 m C$_8$OSO$_3$Na + 0.31 m decanol			L$_1$	-0.56	54.3
2.90 m C$_8$OSO$_3$Na + 0.53 m decanol			L$_1$	-0.60	56.9
2.90 m C$_8$OSO$_3$Na + 0.78 m decanol			L$_1$	-0.53	62.2
2.8 m C$_7$COONa			L$_1$	0.49	55.5
2.8 m C$_7$COONa + 0.10 m LiCl			L$_1$	0.53	56.9
2.8 m C$_7$COONa + 0.24 m LiCl			L$_1$	0.51	59.3
2.8 m C$_7$COONa + 0.64 m LiCl			L$_1$	0.51	60.3
2.8 m C$_7$COONa + 1.23 m NaCl			L$_1$	0.62	61.5
2.8 m C$_7$COONa + 0.34 m CsCl			L$_1$	0.58	55.3
2.8 m C$_7$COONa + 0.73 m CsCl			L$_1$	0.62	56.6
2.8 m C$_7$COONa + 1.76 m CsCl			L$_1$	0.74	57.3
2.8 m C$_7$COONa + 0.39 m RbCl			L$_1$	0.59	57.8
14.7% C$_7$COONa	37.8% C$_{10}$OD	47.5% D$_2$O	D	0.33	
19.3% C$_7$COONa	43.0% C$_{10}$OD	37.7% D$_2$O	D	0.73	
22.6% C$_7$COONa	39.7% C$_{10}$OD	37.7% D$_2$O	D	0.82	
27.0% C$_7$COONa	35.3% C$_{10}$OD	37.7% D$_2$O	D	0.92	
31.6% C$_7$COONa	38.6% C$_{10}$OD	29.8% D$_2$O	D	1.17	
22.8% C$_8$OSO$_3$Na	34.4% C$_{10}$OD	42.8% D$_2$O	D	-0.56	
25.0% C$_8$OSO$_3$Na	40.0% C$_{10}$OD	35.0% D$_2$O	D	-0.81	
38.3% C$_8$OSO$_3$Na	35.7% C$_{10}$OD	26.0% D$_2$O	D	-1.89	
14.5% C$_7$COONa	27.5% C$_7$COOH	58.0% H$_2$O	D	-0.22	
20.8% C$_7$COONa	30.9% C$_7$COOH	48.3% H$_2$O	D	-0.09	
26.7% C$_7$COONa	33.3% C$_7$COOH	40.0% H$_2$O	D	0.04	
34.4% C$_7$COONa	30.9% C$_7$COOH	34.7% H$_2$O	D	0.27	
42.6% C$_7$COONa	29.1% C$_7$COOH	28.3% H$_2$O	D	0.45	
28.8% C$_7$COONa	52.0% C$_7$COOH	19.2% H$_2$O	L$_2$	-0.59	
24.0% C$_7$COONa	60.0% C$_7$COOH	16.0% H$_2$O	L$_2$	-0.92	
14.3% C$_7$COONa	76.1% C$_7$COOH	9.6% H$_2$O	L$_2$	-1.71	
7.7% C$_7$COONa	87.2% C$_7$COOH	5.1% H$_2$O	L$_2$	-2.82	
40.0% C$_8$OSO$_3$Na		60.0% H$_2$O	L$_1$	-0.60	48.1
8.0% C$_8$OSO$_3$Na	80.0% C$_{10}$OH	12.0% H$_2$O	L$_2$	-0.67	82.9
6.05% C$_8$OSO$_3$Na	84.9% C$_{10}$OH	9.05% H$_2$O	L$_2$	-0.68	97.4
4.0% C$_8$OSO$_3$Na	89.9% C$_{10}$OH	6.1% H$_2$O	L$_2$	-0.83	123
2.1% C$_8$OSO$_3$Na	94.8% C$_{10}$OH	3.1% H$_2$O	L$_2$	-1.17	229

[a] Amphiphiles are abbreviated as follows: C$_8$PhSO$_3$Na = sodium *p*-octylbenzene sulfonate; C$_8$OSO$_3$Na = sodium octyl sulfate; C$_7$COONa = sodium octanoate; C$_7$COOH = octanoic acid; C$_{10}$OD = decanol-*O-d*. [b] Concentrations given in molalities (L$_1$ solutions) or weight percentages. [c] Phase notations: L$_1$ = water-rich isotropic solution phase; D = lamellar liquid crystal; L$_2$ = water-poor isotropic solution phase.

treme narrowing condition was verified in this work, for a number of cases. For the short correlation time case applicable here, the quadrupole relaxation rate may be written

$$R_2 = T_2^{-1} = \frac{2\pi^2}{5}\chi^2\tau_c \qquad (2)$$

for a nucleus with the spin quantum number $^3\!/_2$ like ^{23}Na$^+$, $\chi = e^2qQ/\hbar$ is the quadrupole coupling constant corresponding to the time-modulated field gradients, and τ_c the correlation time. It is often necessary to use more complex expressions;[22] for example, the decay of the field gradient may be considered to be due to one rapid and one slow motion over the dimensions of the micelles.

R_2 values of ^{23}Na$^+$ as a function of inverse amphiphile concentration for several surfactants are summarized in Figure 5. In Table I some data relating to the effect of solubilizate and electrolyte additions are included as well as results for solutions of reversed micelles.

Discussion

The general principles of the interpretation of counterion chemical shift and relaxation data have been discussed elsewhere.[13,19,20] The agreement of the new data presented here with the simple model (the pseudo-phase-separation approximation with two sites only for the counterions) can be judged from Figures 1, 2, and 5. The generally accepted equilibrium model gives results approaching those of the phase separation model, more and more, as aggregation becomes more pronounced. Of course, the cmc decreases and aggregation number increases with increasing alkyl chain length of the amphiphile, as is well known. This general expectation is fully consistent with the present findings. Thus the plots of chemical shifts or relaxation rate vs. c_t^{-1} are appreciably curved in the case of short-chain surfactants, while both experimental quantities follow our simple model to a very good approximation for the long-chain surfactants.

The intersection points of the straight-line segments of the plots of δ and R_2 vs. c_t^{-1} give the cmc values listed in Tables II and III. For comparison, cmc values from literature are given. A very good agreement with other experimental techniques justifies the validity of our approach.
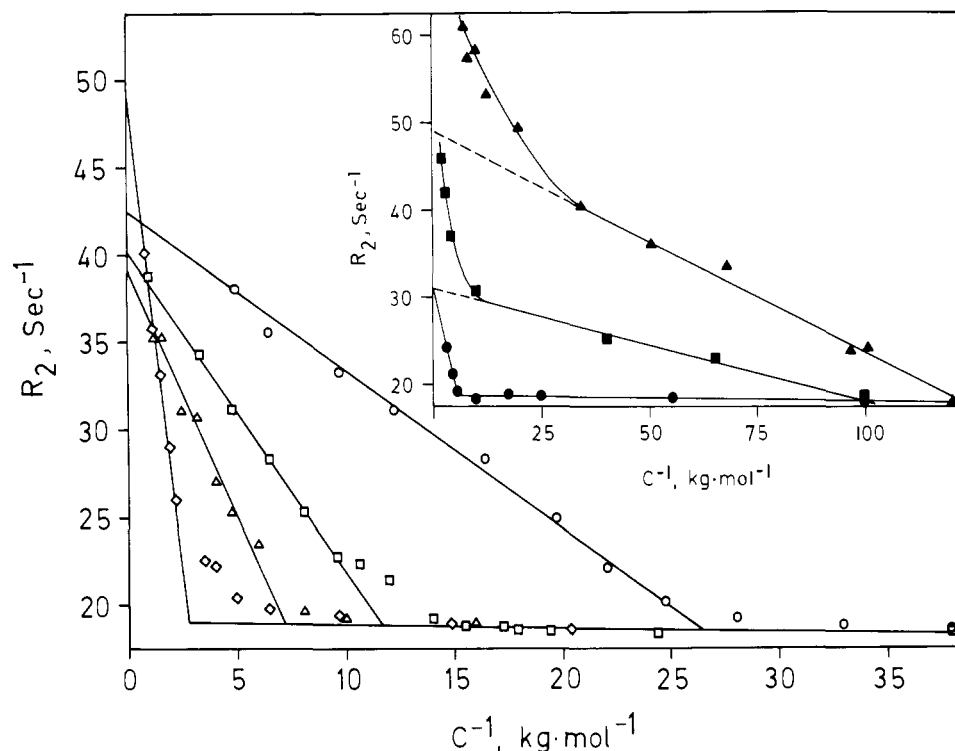
Figure 5. ^{23}Na relaxation rates, R_2, vs. the inverse amphiphile concentration for aqueous solutions of the sodium salts of octanoate ($\Diamond$), octyl sulfate ($\triangle$), nonyl sulfate ($\square$), decyl sulfate ($\bigcirc$), dodecyl sulfate ($\blacktriangle$), octylbenzene sulfonate ($\blacksquare$), and octyl sulfonate ($\bullet$). The data for the last three substances are shown in the insert where also some data for the high concentration region are included.

Table II. Quantities Deduced from Counterion Chemical Shifts in Micellar Solutions (cf. Text)[d]

amphiphile	cmc,[a] mol/kg	cmc,[b] mol/L	$\beta\delta_m$, ppm	δ_m, ppm	$100\delta_{red}$[c]
$CH_3(CH_2)_6COONa$ (32 °C)	0.37	0.36	0.41	0.68	1.12
$CH_3(CH_2)_6COONa$ (28 °C)	0.37		0.43	0.72	1.19
$CH_3(CH_2)_6COONa$ (18 °C)	0.37		0.46	0.77	1.27
$CH_3(CH_2)_7OSO_3Na$ (32 °C)	0.14	0.13	−0.36	−0.60	−0.99
$CH_3(CH_2)_7OSO_3Na$ (28 °C)	0.14		−0.37	−0.62	−1.02
$CH_3(CH_2)_7OSO_3Na$ (18 °C)	0.14		−0.41	−0.68	−1.12
$CH_3(CH_2)_8OSO_3Na$	0.077	0.065	−0.37	−0.62	−1.02
$CH_3(CH_2)_9OSO_3Na$	0.038	0.033	−0.37	−0.62	−1.02
$CH_3(CH_2)_{11}OSO_3Na$	0.0086	0.0084	−0.36	−0.60	−0.99
$CH_3(CH_2)_7SO_3Na$	(0.13)	0.16	(−0.08)	−0.13	−0.21
$CH_3(CH_2)_7C_6H_4SO_3Na$	0.013	0.015	−0.23	−0.38	−0.63
$CH_3(CH_2)_6COOCs$	0.39		8.1	13.5	3.9
$CH_3(CH_2)_7NH_3Cl$	0.27	0.17	10.0	14.3	4.6
$CH_3(CH_2)_7N(CH_3)_3Cl$	(0.37)		12.6	18.0	5.8

[a] From plots of chemical shift vs. inverse amphiphile concentration. [b] Mainly taken from ref 38. Temperature generally 25 °C. [c] δ_{red} is δ_m divided by the total chemical shift charge on transfer of the ion from the aqueous solution to the gas phase (cf. ref 19 and 20). [d] Temperature 28 °C if not indicated otherwise.

As can be inferred from eq 1 and the corresponding expression for R_2, the intercepts at the ordinate axis of our plots give $\delta_f + \beta(\delta_m - \delta_f)$ and $R_{2f} + \beta(R_{2m} - R_{2f})$, respectively. Since it is reasonable to assume that δ_f and R_{2f} are essentially independent of concentration we may deduce values of $\beta\delta_m$ and $\beta(R_{2m} - R_{2f})$. These are listed in Tables II and III, respectively, where we have also included values taken from studies reported in the literature.

If we first consider ^{23}Na$^+$ chemical shifts, which have been most systematically studied, we observe $\beta\delta_m$ to be very different for different end groups of the surfactant. On the other hand, it can be seen for the alkyl sulfates that to a very good approximation $\beta\delta_m$ is independent of the alkyl chain length, i.e., $\beta\delta_m = 0.37 \pm 0.01$ ppm. As canceling of opposite variations in the two quantities seems extremely unlikely, we can establish that both β and δ_m are constant in the series. The present type

of study does not permit the independent determination of either β or δ_m, but from tracer self-diffusion studies β has been found to be close to 0.6 for sodium ions in solutions of sodium octanoate,[23] sodium octylbenzene sulfonate,[24] and sodium dodecyl sulfate[25] over a wide concentration range. We have used this value throughout to deduce the δ_m values for the alkali ions given in Table II. Although there may certainly be some variation in β between the different amphiphiles, this is without doubt rather small. For a number of cationic amphiphiles it has been found that β is appreciably larger,[25,26] and here $\beta = 0.7$ was used.

It can be inferred from Table II that for a certain counterion, δ_m shows a strong variation with the polar head group while, as already stated, it is (at least for the alkyl sulfates) virtually independent of the alkyl chain length. One might expect a slight increase in the micellar surface charge density with in-

Table III. Quantities Deduced from Counterion Quadrupole Relaxation Rates in Micellar Solutions (cf. Text)[f]

amphiphile	cmc,[a] mol/kg	cmc[b] (lit. data), mol/L	$\beta(R_{2m} - R_{2f})$, s^{-1}	R_{2m}, s^{-1}	R_{2m}/R_{20}[c]	$R_{2m}[eQ(1 + \gamma_\infty)]^{-2}$ × 10^{-56}, s^{-1} m^{-4}
$CH_3(CH_2)_6COORb$[d]	0.32		582	1390	3.3	8.4
$CH_3(CH_2)_6COONa$	0.39	0.36	28	63	3.9	153
$CH_3(CH_2)_7OSO_3Na$	0.14	0.13	20	50	3.1	121
$CH_3(CH_2)_8OSO_3Na$	0.085	0.084	22	53	3.3	129
$CH_3(CH_2)_9OSO_3Na$	0.038	0.033	23	55	3.4	133
$CH_3(CH_2)_{11}OSO_3Na$	0.0087	0.0084	30	77	4.1	160
$CH_3(CH_2)_7SO_3Na$	0.17	0.16	14	40	2.5	97
$CH_3(CH_2)_7C_6H_4SO_3Na$	0.01	0.015	14	40	2.5	97
$CH_3(CH_2)_8N(CH_3)_3Br$[e]	0.18	0.14	17 500	26 100	24.8	33
$CH_3(CH_2)_9N(CH_3)_3Br$[e]	0.079	0.07	16 900	25 200	24.0	32
$CH_3(CH_2)_{13}N(CH_3)_3Br$[e]		0.0036	28 800	42 200	40.2	53
$CH_3(CH_2)_{15}N(CH_3)_3Br$[e]	0.000 99	0.000 95	36 900	53 800	51.2	68
$CH_3(CH_2)_8NH_3Br$[e]	0.13		55 100	79 800	76.0	100
$CH_3(CH_2)_9NH_3Br$[e]	0.047		55 100	79 800	76.0	100
$CH_3(CH_2)_9NC_5H_5Br$[e]	0.047		16 900	25 200	24.0	32
$CH_3(CH_2)_7N(CH_3)_3Cl$[e]	0.25	0.17	360	539	21.6	25
$CH_3(CH_2)_7NH_3Cl$[e]	0.27		1070	1554	62.1	73

[a] From plots of chemical shift vs. inverse amphiphile concentration. [b] Mainly taken from ref 38. Temperature generally 25 °C. [c] R_{20} is the relaxation rate at infinite dilution; cf. ref 19 and 20. [d] Data from ref 40. [e] Data from ref 36. [f] Temperature 28 ± 2 °C.

creasing hydrophobic character since stronger hydrophobic interactions are able to balance stronger electrostatic repulsions. Evidently this effect, if operating, is small enough not to affect either β or δ_m measurably.

From Table II we infer that the shielding of the micellarly bound Na$^+$ ions varies with the polar end group in the order OSO$_3^-$ > aryl-SO$_3^-$ > alkyl-SO$_3^-$ > H$_2$O (free hydrated Na$^+$ ion) > CO$_2^-$. Our understanding of the chemical shifts of monoatomic ions is still deficient, which makes a quantitative interpretation impossible. However, on the basis of the commonly used Kondo-Yamashita overlap approach,[27,19] a qualitative discussion may be given. For the chemical shifts of the counterions considered here the paramagnetic shift term dominates and we may write, using this model,

$$\delta_m = \sigma_p^0 - \sigma_p^m = \frac{4\mu_B^2\mu_0}{\pi\Delta E}\langle r^{-3}\rangle_p$$
$$\times (A^m_{M-W} + A^m_{M-X} - A^0_{M-W}) \quad (3)$$

Here σ_p^0 and σ_p^m are the paramagnetic shielding terms of the ion at infinite dilution in water and at the micellar surface, respectively. ΔE is an average excitation energy, $\langle r^{-3}\rangle_p$ the expectation value of r^{-3} for an outer p electron of the alkali ion, μ_B the Bohr magneton, and μ_0 the permeability constant. The A's denote sums of overlap integrals between the outer p orbitals of the ion studied (M) and the orbitals of other ions (X, in this case surfactant ions) or water molecules (W). It is generally believed that the univalent monoatomic ions retain their inner hydration spheres on binding to a micellar aggregate to a considerable extent, and NMR studies[1] have provided direct evidence for this. This point will be further discussed below on the basis of the water H/D isotope effect in the counterion chemical shifts. For a hydrated counterion it is only necessary to consider the ion–water overlap since *direct* ion–ion effects should be negligible. Thus, as reviewed in ref 20, only species in direct contact with the ion have any appreciable effect on the shielding. For the hydrated alkali ions, it is the overlap integrals between the ions' outer orbitals and orbitals on the oxygen of the hydrating water molecules which should mainly influence the shielding. According to our results, this overlap should increase in the sequence OSO$_3^-$ < aryl-SO$_3^-$ < alkyl-SO$_3^-$ < H$_2$O < CO$_2^-$ for micellarly bound Na$^+$. For the first three head groups there is a correlation between the expected negative charge density on the oxygens of the SO$_3^-$ grouping and the observed shifts. These results do not seem to

require the introduction of any other interaction attenuated by the interjacent hydration sheath. With CO$_2^-$ as end group, on the other hand, there is an appreciably larger paramagnetic shift term corresponding to a more pronounced Na$^+$–water oxygen overlap. In turn this suggests a considerable polarization of the water molecule. A very plausible explanation would be in terms of hydrogen bonding between a water molecule in the Na$^+$ hydration sphere and the CO$_2^-$ group.[13] Such a mechanism should contribute to the strength of counterion binding. Since the counterion polarization should increase with the micelle charge density, one would expect a contribution to counterion binding, decreasing along the alkali series from Li$^+$ to Cs$^+$. A simple electrostatic effect should follow the effective size of the hydrated ion, producing a binding increasing from Li$^+$ to Cs$^+$. The specificity of the alkali ion binding is already well established. Mukerjee et al.[28] demonstrated a variation of the cmc of alkali dodecyl sulfates with the alkali ion and also found a greater degree of dissociation for Li$^+$ than for Na$^+$. In the polyelectrolyte field, the opposite alkali ion affinity sequences of OSO$_3^-$ and CO$_2^-$ groups are well decumented in many cases.[29,30] Furthermore, the significance of hydrogen-bond interactions in the case of CO$_2^-$ end groups has been proposed previously.[29,31]

It would be of interest if the binding of different counterions could be compared directly. The use of the δ_m values for this purpose is made difficult since, as a result of the parameters characterizing the electronic structures (cf. eq 3), the chemical shift ranges are basically very different for different ions. It is not easy to find an unambiguous way around this problem but one possibility would be to introduce "reduced" chemical shifts defined as the ratio of δ_m to the chemical shift change on transfer of the ion from the gas state to infinite dilution in water. Through the work of Lutz and others (reviewed in ref 19 and 20), absolute shielding scales are becoming available for several ions. In Table II we have included reduced δ_m values thus defined. One observation which can be made is that the reduced δ_m value is small for Na$^+$, and considerably larger and of approximately equal magnitude for Cs$^+$ and Cl$^-$; these ions have approximately the same ionic radii. A straightforward interpretation of this finding seems to be that the solvation of Na$^+$ is much more difficult to perturb than that of the other ions.

Although our main concern in this work is the study of counterion binding to micelles in aqueous solution, it is evident

that the chemical shift method is very generally applicable in the field of amphiphile self-association. As regards counterion binding in concentrated surfactant systems, it may be observed from Figures 1 and 2 that the linear plots extend to quite high concentrations. This means that the product $\beta\delta_m$ (and, as argued above, probably both quantities individually) remains essentially constant. In a number of cases we observe that, at the highest concentrations, the chemical shift extends beyond the predictions of the simple model, suggesting an increase in $\beta\delta_m$. An increase in β is observed inter alia in diffusion studies,[23] but this cannot explain the observed effect by itself. From the rather scattered data on solubilization and electrolyte addition we note the marked downfield shift effect of decanol addition to concentrated sodium octyl sulfate solutions, suggesting a partial liberation of Na$^+$ ions from the micelles on solubilization, as well as the marked variation of the electrolyte effect with the alkali ion present. The larger downfield Na$^+$ shift on addition of CsCl to sodium octanoate solution compared to NaCl, or even more so LiCl, is in line with the alkali ion affinity sequence mentioned above.

A qualitative interpretation of the data for the other phases proceeds along similar lines. As regards the water-poor solution phases, it can be noted that, for the system sodium octyl sulfate–decanol–water, δ is not very different from that of concentrated normal micellar solutions as long as the decanol content is not too high. The approach to the decanol corner in the phase diagram is accompanied by a marked upfield shift which suggests an enforced interaction between Na$^+$ and $-$OSO$_3^-$ polar groups. It seems reasonable to attribute this to ion-pair formation as the reversed micelles cease to exist.

In view of the results of previous spectroscopic investigations[2,32] it was of particular interest to examine the water-poor solution phase of the system sodium octanoate–octanoic acid–water (Figure 3). The marked upfield ^{23}Na$^+$ chemical shift at intermediate water contents is especially striking in view of the finding that the interaction of Na$^+$ with carboxylate gives a downfield shift. On the other hand, it may be inferred from the work of Bloor and Kidd[33] that the interaction of Na$^+$ with carboxylic acid should give a positive shift. A reasonable interpretation of these results is therefore that an Na$^+$ ion interacts not only with $-$COO$^-$, but also with $-$COOH, and a specific complex between hydrated Na$^+$, $-$COO$^-$, and $-$COOH of the type suggested by Friberg et al.[32] seems to be of importance. When the water content is reduced below about 4 mol per mol of octanoate the decrease in sodium hydration probably results in the formation of direct contact ion pairs, $-$COO$^-$–Na$^+$, which are expected to give a downfield shift. From the results at higher water concentrations it can be deduced that the proposed change from normal to reversed micelles[34] is not accompanied by any appreciable change in δ of Na$^+$. The counterion binding to the two types of structures seems thus to be about the same as was previously reported for the sodium cholate–decanol–water system.[13] For the lamellar (D) phase of the system sodium octanoate–octanoic acid–water, the ^{23}Na$^+$ chemical shift varies systematically (although less strongly than in the L$_2$ phase) with the ratio of acid to soap. This points to an interaction of sodium ions with carboxylic acid groups when associated with the amphiphile lamellae.

It is important to note that the ^{133}Cs$^+$ chemical shifts of the system cesium octanoate–octanoic acid–water (Figure 3b) are fundamentally different from the corresponding ones of ^{23}Na$^+$. The shifts are downfield over the entire concentration range studied, and there is no rapid change at low water contents. It is therefore not necessary to invoke any specific complex formation involving octanoic acid to explain these results. Such a difference in the tendency to complex formation between Na$^+$ and Cs$^+$ is not unreasonable in view of the different ionic radii and polarizabilities.

The important role of water in the ionic interactions in surfactant systems can be studied in a rather direct way using the H/D water isotope effect in shielding. This technique has been successfully used to study preferential solvation phenomena in mixed solvent systems.[35] We have studied the solvation of the ^{35}Cl$^-$ and ^{133}Cs$^+$ ions by this method. For Cl$^-$ at infinite dilution, the shielding is larger in D$_2$O than in H$_2$O by 4.4 ppm, while for Cs$^+$ this water isotope effect is 1.5 ppm.[19,20] For aqueous solutions of NaCl, the ^{35}Cl$^-$ water isotope effect was studied as a function of temperature over a wide temperature range. No significant effect of temperature was found, and this is consistent with the hypothesis that the magnitude of the water isotope effect ($\Delta\delta$) is mainly determined by the degree of ion–water contact for a given ion while other factors are less important. For Cl$^-$ in solutions of dodecyltrimethylammonium chloride a slight reduction of $|\Delta\delta|$ with increasing concentration was observed: for example, for a 1.0 m solution $|\Delta\delta|$ = 3.9 while it is 3.8 ppm for a 2.0 m solution. However, the extensive line broadening reduces the precision of $\Delta\delta$ markedly in the case of Cl$^-$ and therefore most of our studies concerned Cs$^+$. (For Na$^+$, $\Delta\delta$ is too small to be useful.) $\Delta\delta$ of Cs$^+$ for solutions of cesium octanoate is given in Figure 4 and, as can be inferred, it is essentially independent of concentration over the entire range. Consequently, there seems to be no detectable elimination of the counterion hydration on binding of the ion to the micelles in this system. For cesium dodecanoate some reduction in the isotope effect was observed: $|\Delta\delta|$ is 0.96 for 1.0 m and 0.85 for 2.0 m. These values, though, are significantly larger than for the corresponding CsCl solutions.[18]

Figure 3 includes studies of the water isotope effect in shielding for the water-poor solution phase of the system cesium octanoate–octanoic acid–water. $\Delta\delta$ can be seen to vary considerably with the water concentration. In the concentration range studied there is first a decrease of $|\Delta\delta|$ from about 0.8 ppm at higher water concentrations down to about 0.6 ppm at around four molecules of water per Cs$^+$ ion. This slow decrease in cesium ion hydration over a wide concentration range is followed by a faster final dehydration at water concentrations below four water per Cs$^+$ ion.

The hydration properties of Cs$^+$ and Na$^+$ ions are certainly rather different because of their different sizes. It is, however, quite safe to assume that if the cesium ion is extensively hydrated down to low water concentrations in a system, then the sodium ion is hydrated to at least the same extent. We can therefore deduce that the sodium ion is extensively hydrated in micellar solutions of sodium octanoate as well as down to quite low water content in the water-poor solution phase of the system sodium octanoate–octanoic acid–water. This is in line with the results of the analysis of the ^{23}Na$^+$ chemical shifts above.

While studies of the counterion chemical shift and its water isotope effect are novel approaches, the counterion quadrupole relaxation method has been rather extensively used for studies of surfactant systems. In view of several reports on similar systems a very brief discussion of the ^{23}Na$^+$ quadrupole relaxation rates presented in Figure 5 and Table I will suffice. A good conformity of the results to the simple two-site model is evident from Figure 5 and, as regards the concentration dependence of R_2, the same remarks apply as those given above for δ. The cmc values obtained from these plots and given in Table III are again in good agreement with literature values. In Table III values of $\beta(R_{2m} - R_{2f})$ are also given, the evaluation of which follows from the discussion above. R_{2m} was deduced using the same values of β as used above. Two important points concerning the R_{2m} values are as follows. (1) For a given polar head group ($-$OSO$_3^-$), R_{2m} increases with increasing alkyl chain length. (2) For a given alkyl chain length, R_{2m} is quite different for different polar groups. The latter observation again points to a considerable specificity in

the counterion binding. The chemical shift studies suggest that the Na^+ interaction is essentially independent of alkyl chain length and therefore the variation of R_{2m} with alkyl chain length should be mainly a correlation time effect (cf. eq 2). A consideration of the variation of τ_c with alkyl chain length for motions over the dimensions of the micelles, such as micellar rotation and counterion lateral diffusion, shows that it is much stronger than the variation of the R_{2m} values. That a local motion is indeed governing the quadrupole relaxation can also be seen from the small changes in R_2 at phase transitions[37] or at micellar shape changes.[36] This local motion can be rotation or translation of hydrating water molecules or an exchange of the counterion between being bound at the micelle and free in the intermicellar solution.[22] Since the H/D water isotope effect on quadrupole relaxation is similar to that for infinite dilution, the motion causing relaxation must somehow be connected with the motion of water molecules. In view of the chemical shift results, we propose that the observed relaxation rate increase (Table I) on decanol solubilization in octyl sulfate micelles is mainly a correlation time effect. On the other hand, the considerable relaxation rate increase at the highest decanol contents in the water-poor solution phase is probably mainly a field gradient effect arising from the formation of ion pairs as the reversed micelles cease to exist. The observed increase in sodium ion diffusion rates[41] would also suggest formation of ion pairs rather than of reversed micelles at the highest decanol contents.

Again, a comparison between different counterions is of interest, and to allow this we have included two quantities in Table III: first, R_{2m} divided by R_{20}, the infinite dilution relaxation rate, and, secondly, R_{2m} divided by the square of the product of the quadrupole moment (eQ) and the Sternheimer antishielding factor $(1 + \gamma_\infty)$. (The latter takes into account the increased field gradient at the nucleus caused by distortions of the electron cloud which are due to an external field gradient.) The close similarity in the two quantities for Cl^- and Br^- is noteworthy and suggests that the binding of these counterions is the same to a good approximation. The high value of $R_{2m}/[eQ(1 + \gamma_\infty)]^2$ obtained for Na^+ is almost certainly due to a strong quenching of the field gradients in the reference state. This is due to hydration symmetry for the ion at infinite dilution (cf. ref 39 and 20).

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