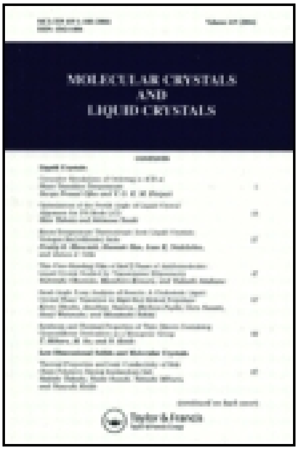

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Cholesteric Behaviour in Lyotropic Liquid Crystals

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Cholesteric Behaviour in Lyotropic Liquid Crystals

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Cholesteric lyotropic liquid crystals prepared from the potassium salts of *N*-hexadecanoyl-*l*-proline and *N*-dodecanoyl-*l*-alanine have been studied as mixed systems with tetradecyltrimethylammonium bromide. The twist, induced by the chiral centre, was studied as a function of the mole fraction, X, of chiral amphiphile in total amphiphile. It was found that the twist showed a maximum for the neutrally charged mesophases ($X = 0.5$) and that for the pure chiral systems ($X = 1.0$) the alaninate system showed a much larger twist than the corresponding prolinate material. The results were discussed in terms of a micelle distortion model for the generation of cholesteric behaviour. Alkali metal ion binding to the carboxylate groups of these amphiphiles was investigated and the results compared to those for the dodecanoate amphiphile. A three site model of binding was used in order to determine the number of liganding amphiphiles in the pure anionic mesophase ($X = 1.0$). It was found that the number decreased through the series dodecanoate, alaninate and prolinate with the maximum number of liganding amphiphiles being 2 for prolinate, 3 for alaninate and 4 for the dodecanoate system.

INTRODUCTION

Cholesteric lyotropic liquid crystalline materials prepared from aqueous solutions of chiral amphiphiles have not been intensively studied materials. Unlike the thermotropic analogues where a pitch axis is generated by the interactions between chiral centres on adjacent molecules, the lyotropic materials generate a helical axis via interactions between micelles. The micelles are separated from each other by the interstitial water which promotes mesophase formation. Two mechanisms have been proposed for the transfer of information between micelles, the first involves pairwise interactions between the chiral molecules of adjacent micelles.[1] The second model, a distortion model, suggests that when chiral molecules are incorporated into a micelle they cause distortion of the micelle, twisting it into a chiral shape. The subsequent interactions between the chiral micelles generate the macroscopic twist.[1-5]

Arguments for the pairwise interaction model of cholesteric behaviour have been advanced[1] but there is at present little support for that model. Some evidence for the distortion model of cholesteric behavior model has accumulated;[3-5] however, it is clear that many aspects of cholesteric behavior in the amphiphile systems are not well understood and perhaps not yet recognized.

In this study, properties of the mixed liquid crystalline systems, potassium *N*-dodecanoyl-*l*-alaninate/tetradecyltrimethylammonium bromide and potassium *N*-hexadecanoyl-*l*-prolinate/tetradecyltrimethylammonium bromide were investigated. This system provides a means of studying the development of cholesteric behaviour as an achiral amphiphile is replaced in a stepwise fashion by a chiral amphiphile; furthermore since the two amphiphiles carry opposite charges, information concerning the relationship between micellar charge and cholesteric behaviour is provided.

The pitch induced in the nematic mesophase by the optical centre is readily measured by laser diffraction where the twist, the inverse pitch ($1/P$), is given simply by Bragg's Law for diffraction. Microscopy also can provide the pitch length and furthermore, can provide information concerning the structure of the micelle which produces the nematic material,[6] notably whether they derive from the lamellar or cylindrical mesophases.

Independent of the problems concerning cholesteric behaviour, chiral amphiphiles provide a means of investigating aspects of ion binding which are not readily investigated otherwise. This has been clearly demonstrated for the potassium *N*-dodecanoylalaninate mesophase system where a direct linearity between headgroup alignment and quadrupole splitting from the alkali metal ions was observed.[5] In the present system variation of surface charge on the micelles allows ion binding to be studied as binding sites are successively eliminated by changing surfactant proportions. This approach has proven to be successful for the study of alkali metal and halide ion binding[7,8] and has been applied in the investigation of the binding of various tetrahedral ions.[9]

The model of ion binding is a three site model where the sites are taken to be: Site I, ions held in the bilayers surface between amphiphile headgroups where the number of liganding headgroup is provided by the experimental results and generally varies between 2 and 4; Site II, a site corresponding to binding to 1 amphiphile, this binding may include diffuse binding; Site III, this site corresponds to free ions in the interstitial water between micelles. Each binding site generates a characteristic quadrupole splitting, $\Delta\nu_i$, so that the observed quadrupole splitting is a weighted average from the various sites as given in Eq. 1 where the

$$\Delta\nu = \Delta\nu_{\mathrm{I}}X_{\mathrm{I}} + \Delta\nu_{\mathrm{II}}X_{\mathrm{II}} + \Delta\nu_{\mathrm{III}}X_{\mathrm{III}} \tag{1}$$

various X_i give the mole fraction of ions in that site. With some assumptions, Eq. 1 can readily be rewritten in terms of the mole fraction of binding amphiphile in total amphiphile, the number of liganding amphiphiles in Site I and the total amphiphile and electrolyte concentration. The calculated curve can then be fit to the observed curve to provide the desired information.[7,8]

EXPERIMENTAL

Preparation of potassium *N*-hexadecanoyl-*l*-prolinate (*l*-KHDP)

The preparation of the free amide followed closely the literature procedures for the formation of amides from amino acids.[10] 30 gm of *l*-proline was dissolved in 200 mL of water containing 7 g NaOH. The solution was cooled to less than 10°C and 50 g of hexadecanoyl chloride was added dropwise to the continuously stirred solution. Throughout the addition of the acid chloride, the temperature was maintained at less than 20°C and the pH controlled to greater than pH 10 by addition of 40% NaOH solution. After standing for 2 days 500 mL of diethyl ether was added and the mixture acidified with 30% H_2SO_4. The organic layer was separated then washed with water and dried over $MgSO_4$. The ether solution was evaporated to provide a residue which was dissolved in ethanol then made basic with a small excess of KOH. The solution was evaporated to give a crystalline residue which was recrystallized twice from ethyl acetate then dried in a vacuum desicator. Purity was checked by ^{13}C magnetic resonance to ensure in particular the absence of potassium hexadecanoate, a contaminent which is extremely difficult to remove. Yield 38 g mpt 44° $[\alpha]_D^{20} = -46.0$ ($C = 0.1$ H_2O). Analysis: Calc. for $C_{21}H_{38}NO_3K$; C 64.5, H 9.7, N 3.6; found C 58.7, H 10.2, N 3.8. Analysis indicates presence of two moles of H_2O per mole salt.

Potassium *N*-dodecanoyl-*l*-alaninate (*l*-KDDA) was prepared as previously described (4).

Samples

Sample compositions are provided in Tables I and II. The components were weighed into test tubes and homogeneously mixed as has been described.[4] Samples were placed in 5 mm nuclear magnetic resonance (nmr) sample tubes and the tubes sealed.

Measurements

Nmr spectra from the prolinate mesophases were obtained at 298°C while those for the alaninate liquid crystals were obtained at 303°C. Spectra from the alkali metals were obtained using the broadbanded probes of a 400 MHz nmr spectrometer.

Laser diffraction measurements were made on the nmr samples after the samples had been homogeneously aligned by the magnetic field of the nmr spectrometer. Sample alignment provided sharp diffraction bands. Temperature measurements were made by placing the sample tubes in a brass holder suitably constructed for flow of thermostated water and having an unobstructed path for laser light.

Various samples were investigated by microscopy using polarized light and a temperature of 22°C. The samples were contained in

TABLE I

Mesophase compositions and measured parameters for the mixed detergent system of potassium *N*-hexadecanoyl-*l*-prolinate/tetradecyltrimethylammonium bromide

Composition (mg)[a]				Quadrupole Splittings (KHz)					
X[b]	*l*-KHDP[b]	TDMABr[b]	Decanol	$\Delta\nu_{Li}$	$\Delta\nu_{Na}$	$\Delta\nu_{K}$	$\Delta\nu_{Rb}$	$\Delta\nu_{Cs}$	$\Delta\nu_{D_2O}$
0.0	—	336	40	0.021	0.51	0.54	2.64	0.015	0.002
0.1	38	303	35	0.009	0.26	0.29	1.32	0.007	0.020
0.2	77	270	30	0.002	0.03	0.02	0.21	0.002	0.044
0.3	115	236	22.5	−0.008	−0.28	−0.30	−1.58	−0.010	0.062
0.4	154	202	17.5	−0.007	−0.45	−0.51	−2.55	−0.014	0.081
0.5	192	168	15	−0.004	−0.57	−0.69	−3.32	−0.018	0.109
0.6	231	134	15	0.028	−0.56	−0.75	−3.50	−0.017	0.151
0.7	269	101	17.5	0.059	−0.27	−0.54	−2.44	−0.007	0.157
0.8	308	67	27.5	0.122	0.29	0.10	0.0	0.017	0.215
0.9	346	34	37.5	0.172	1.04	0.66	3.81	0.050	0.243
1.0	384	—	50	0.176	1.55	1.34	7.00	0.076	0.218

[a] Each sample was prepared with 850 mg of D_2O containing: LiBr, 0.5%; NaCl, 0.5%; $KClO_4$, 1.0%; RbCl, 0.5%; CsCl, 2.0%; NH_4Cl, 3.75%; $(CH_3)_4HCl$, 2.5% by weight.

[b] Potassium *N*-hexadecanoyl-*l*-prolinate, *l*-KHDP; tetradecyltrimethylammonium bromide, TDTMABr; mole fraction *l*-KHDP in total detergent, X.

TABLE 2

Mesophase compositions and measured parameters for the mixed detergent system of potassium *N*-dodecanoyl-*l*-alaninate/tetradecyltrimethylammonium bromide

Composition (mg)[a]				Quadrupole Splittings (KHz)					
X[b]	*d*-*l*-KDDA[b]	TDTMABr[b]	Decanol	$\Delta\nu_{Li}$	$\Delta\nu_{Na}$	$\Delta\nu_{K}$	$\Delta\nu_{Rb}$	$\Delta\nu_{Cs}$	$\Delta\nu_{D_2O}$
0.0	—	336	55	0.021	0.62	0.73	3.58	0.21	0.001
0.1	31	303	40	0.014	0.31	0.36	1.78	0.010	0.007
0.2	62	270	35	0.004	0.14	0.14	0.82	0.004	0.013
0.3	93	236	25	−0.003	−0.10	−0.12	−0.57	−0.004	0.023
0.4	125	202	15	−0.010	−0.34	−0.42	−2.03	−0.12	0.035
0.5	155	168	10	−0.003	−0.35	−0.45	−2.25	−0.013	0.039
0.6	185	134	10	0.024	−0.32	−0.48	−2.34	−0.012	0.054
0.7	216	101	20	0.081	< 0.01	−0.28	−1.23	< 0.001	0.089
0.8	247	67	40	0.197	1.18	0.87	4.81	0.051	0.138
0.9	278	34	65	0.385	3.22	3.14	16.90	0.145	0.189
1.0	309	—	80	0.223	2.65	4.00	15.30	0.127	0.125

[a] Each sample was prepared with 900 mg of D_2O which contained: LiCl, 0.25%; NaCl, 0.5%; RbCl, 0.5%; CsCl, 2%; KBr, 0.5% by weight.

[b] Potassium *N*-dodecanoyl-*d*, *l*-alaninate, *d*, *l*-KDDA; tetradecyltrimethylammonium bromide; TDTMABr; mole fraction *d*, *l*-KDDA in total detergent, X.

unsealed CAM LAB microslides or between microscope slides and a cover slip. Concentration gradients were obtained by allowing the evaporation of water from the sample edges. Dimensionally ordered mesophases adjacent in the phase diagram were identified. From this the structure of the micelles of the nematic/cholesteric mesophase could be inferred.[6]

RESULTS AND DISCUSSION

The structure of the micelles which form the mesophases utilized in this study were determined from studies with a polarizing microscope. Samples contained in microslides or between glass plates were allowed to dry from the edges, thus setting up concentration gradients. Regions of low water concentration next to the cholesteric/nematic regions showed the oily streaks and pseudo isotropic texture characteristic of the lamellar structure. The cholesteric/nematic phases are therefore formed from disk-like micelles.[6]

It has been found experimentally that there is a linear relationship between the twist of a cholesteric mesophase and the mole fraction of chiral amphiphile when the composition is varied from racemate to resolved amphiphile, provided other parameters are maintained constant.[3,4] A suggestion that partioning of *d* and *l* amphiphiles into regions or possibly even micelles consisting predominantly of *d* or *l* substituents occurs has been made,[5] a process reminiscent of the spontaneous separation of a racemic mixture on crystallization to provide the two crystalline forms. The above linearity would be a natural consequence of such behaviour. Such a linearity would not be expected if the chiral amphiphile replaced an achiral material in a stepwise manner.

Fig. 1 shows the results of replacing tetradecyltrimethylammonium bromide by potassium *N*-hexadecanoyl-*l*-prolinate. The vertical bars represent the range of twist measured for the mesophase as the temperature is varied between 25° and 30°. The compositions employed in the study and other parameters measured are given in Table I.

The striking characteristic of the induced twist is that it maximizes when approximately one-half of the achiral detergent is replaced by the chiral material. Furthermore, complete replacement of the trimethylammonium amphiphile gives a twist similar to magnitude to that observed with only 10% replacement. This result indicates that surface change on the micelles is an important factor in determining

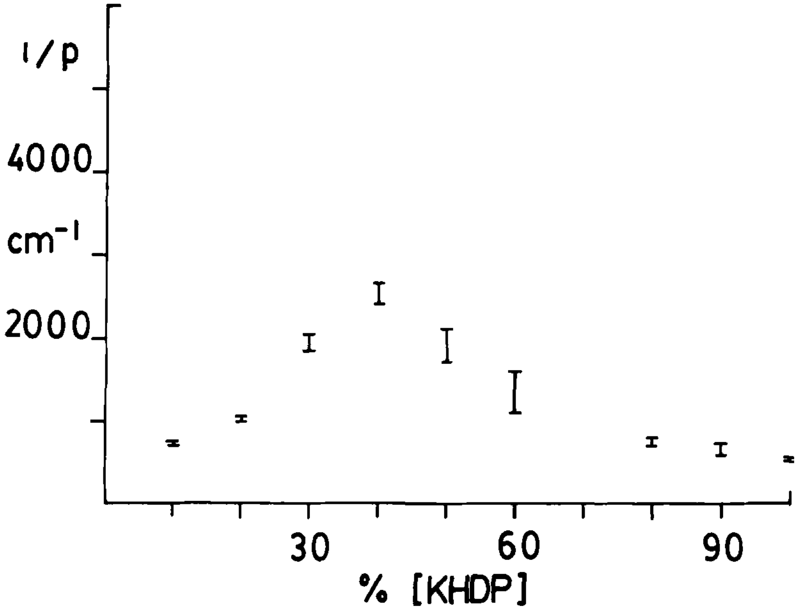


FIGURE 1 The inverse pitch ($1/P$) measured for the mixed mesophase system potassium *N*-hexadecanoyl-*l*-prolinate (*l*-KHDP)/tetradecyltrimethylammonium bromide (TDTMABr) as a function of the portion of *l*-KHDP in total detergent is shown. The variation of the inverse pitch as the temperature is raised from 25° to 30°C is represented by the vertical bars. The inverse pitch decreases with increase in temperature.

the twist. Since the two amphiphiles are oppositely charged, the micelle is neutral when the mole fraction, X, of chiral amphiphile in total detergent is 0.5. Neutral micelles can be expected to approach each other more freely than those carrying a surface charge. This factor seems to be more important than that of increased overall chirality as X approaches 1, a result not necessarily applicable to other amphiphiles since this presumably is a reflection of the ability of the chiral detergent to induce distortion into the micelles.

Fig. 2 shows the behaviour of the twist as potassium *N*-dodecanoyl-*l*-alaninate replaces the trimethylammonium amphiphile. The vertical bars again represent the variation in temperature between 25° and 30C. This curve clearly shows two maxima. The maximum at $X = 0.5$ again is taken to correspond to interactions between neutrally charged molecules leading to an enhanced twist. The maximum twist, unlike for the prolinate system, is obtained for the pure chiral amphiphile ($X = 1.0$) and reflects the efficiency of this amphiphile in twisting the micelle into a chiral shape.

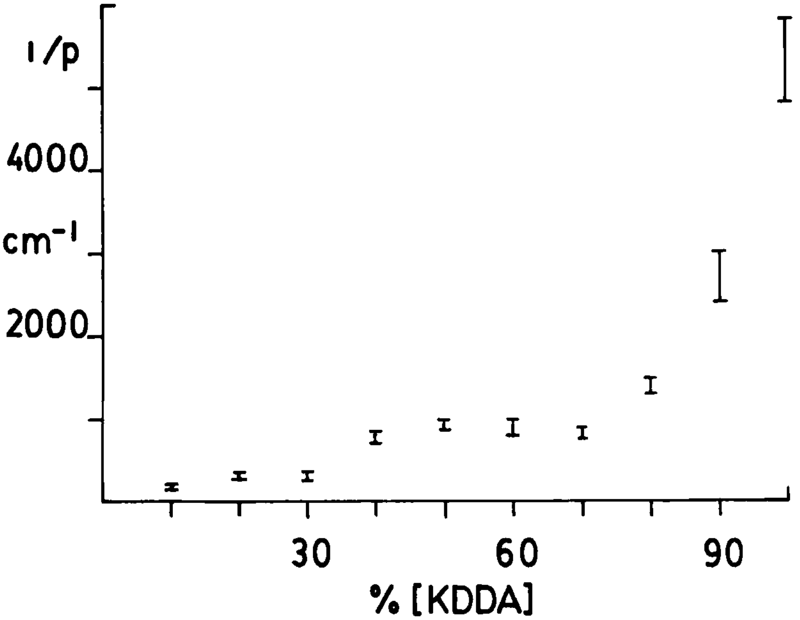


FIGURE 2 The inverse pitch $(1/P)$ is displayed for the mixed mesomorphic system of potassium *N*-dodecanoyl-*l*-alaninate (*l*-KDDA) as a function of the mole fraction of *l*-KDDA in total detergent. The vertical bars represent the variation of $1/P$ as the temperature is varied from 25° to 30°C. The inverse pitch decreases with increase in temperature.

When these results are discussed in terms of the distortion model of cholesteric behavior, it is necessary to consider the interplay between the two major mechanisms for producing a macroscopically observed twist. The first involves the amount of twist induced into the individual micelles by the chiral centre, the second is the efficiency of transfer of information between micelles. The latter has the major effect when micelles are close together since then the twist of one micelle will exert the strongest influence on the alignment of its neighbour. Close approach of micelles will be favored when the micelles do not carry a charge. Other things being equal, maximum distortion of a micelle will occur when the density of the chiral amphiphile is also maximum. Chemically distinct amphiphiles having different interactions, will confer different twists to the micelles and through them to the medium.

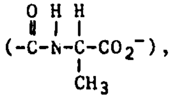
Studies of ion binding in cholesteric carboxylate systems presents some problems which do not appear in the achiral systems. Investigation of the alaninate system has shown that the headgroup orientation is directly related to the twist and is very sensitive to composition and that quadrupole splittings of the alkali metal ions follow the headgroup splittings linearly.[5] Replacement of the chiral carboxylate by the achiral alkyltrimethylammonium undoubtedly has effects on the ion quadrupole splittings which are not accounted for in the three site model of ion binding utilized here. The general behavior of the quadrupole splittings from the alkali ions does, however, parallel that observed for the achiral system. The results clearly indicate the presence of at least three binding sites for all ions and, provided the points corresponding to $X = 1.0$ for the chiral systems are ignored in the calculations, the three site analysis of the results proceeds readily. It is not yet clear whether such an approach is too simplistic for these chiral systems. Table III gives the results of the calculations; the number of liganding amphiphiles in Site I and the characteristic quadrupole splitting for each site. Results of the calculations for the binding of ions to three carboxylic acid derivatives, dodecanoate, *l*-alaninate and *l*-prolinate, are given. Clearly binding of ions by the amphiphile is dependent on the nature of the headgroup. More work

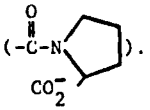
TABLE 3

The number of liganding amphiphiles (n) and characteristic quadrupole splittings (KHz) for the various alkali metal ions binding to the dodecanoate, alaninate and prolinate amphiphiles respectively

Ion	n	$\Delta\nu_{I}$	$\Delta\nu_{II}$	$\Delta\nu_{III}$	k_{I}
Li^+	2	1.98	−0.267	0.033	0.36
	2	0.64	−0.391	0.004	1.31
	2	0.84	−0.391	0.018	0.58
Na^+	3	9.00	6.43	0.69	0.41
	3	5.83	−2.37	0.58	0.85
	2	5.20	−16.1	0.46	0.79
K^+	4	8.23	−5.62	0.96	0.18
	3	5.46	−2.34	0.65	0.82
	2	3.60	−17.6	0.50	0.76
Rb^+	4	36.6	−26.5	3.80	0.39
	3	29.7	−12.0	3.13	0.86
	2	24.9	−94.7	1.41	1.02
Cs^+	4	0.38	−0.193	0.021	0.69
	3	0.27	−0.096	0.019	0.98
	2	0.27	−0.603	0.012	0.93

is required in order to determine whether the major factor is one of steric requirements or is stereochemical in nature. The number of liganding amphiphiles decreases through the series

dodecanoate $(-CO_2^-)$, alaninate  $(-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-CO_2^-)$,

and prolinate .

The demands imposed by the packing of the headgroups with respect to each other could well be the predominant factor in determining the maximum number of amphiphiles liganding to specific alkali ion. Results similar to those found here have also been observed for the binding of tetrahedral ions.[9] One further consideration is the question of electrolyte concentration on ion binding. This may be important here where the concentration of electrolyte in the prolinate system is about a factor of ten greater than in the other two systems.

Of some interest in Table III are the values of k_1. This number provides a crude measure of the effect of micellar charge on the binding of ions.[7] Values near zero indicate that the alkali metal binding is insensitive to the development of positive charge on the micellar surface, those near one indicate a reasonably high sensitivity to charge development. To the extent that this can be related to the strength of ion binding, Table III indicates that binding to the carboxyl group of dodecanoate is stronger than to that of the alaninate or prolinate.

For the studies of binding in the alaninate system (Table II) the racemic amphiphile was used. The result obtained for the sodium and cesium ions in this racemic system were compared to those obtained by using the corresponding optically pure amphiphile. No significant differences in ion quadrupole splittings from the two systems was observed. Fig. 3 demonstrates this for the sodium ion. The cesium ion splittings similarly show a close agreement. This result is analogous to the observation from the alaninate system that replacement of *d*, *l* by *l*-alaninate has no effect on ion quadrupole splittings or headgroup alignment (4). This result is in keeping with the suggestion that a spontaneous separation of racemic amphiphile into regions of *d* or *l* detergent occurs (5).

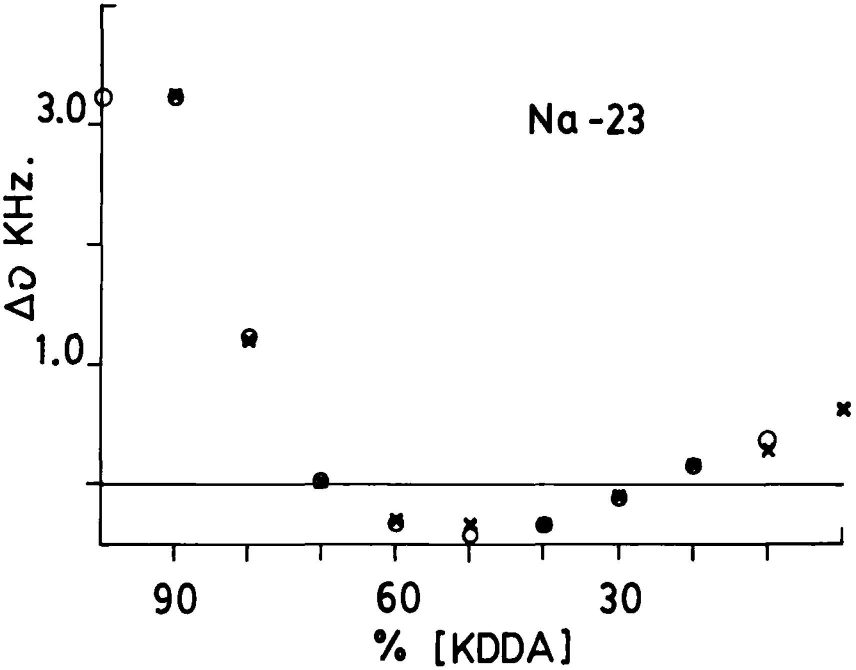


FIGURE 3 Sodium quadrupole splittings are shown as a function of the fraction of potassium *N*-dodecanoylalaninate (KDDA) in total amphiphile. Open circles (○) correspond to *l*-KDDA, the closed circles (●) to *d*, *l*-KDDA.

Acknowledgements

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