

Vibrational Spectra of Metal Salts of Bis(2-ethylhexyl)sulfosuccinate (AOT)

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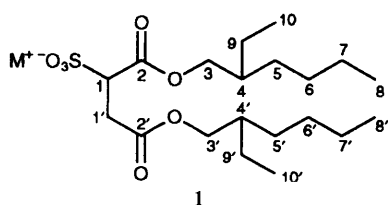
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The vibrational spectra of sodium bis(2-ethylhexyl)sulfosuccinate (NaAOT), and NaAOT exchanged with alkali-metal (Li^+ , K^+ , Rb^+ , Cs^+), Ba^{2+} and Ce^{3+} and tetraphenylarsonium (TPA^+) cations have been investigated. The effect of the charge-to-radius ratio of the counterion on the symmetric and antisymmetric sulfonate stretching modes has been studied to obtain a more comprehensive assignment of these modes for NaAOT. The symmetric sulfonate stretching mode shifted to lower wavenumber with increasing counterion radius, due to a decrease in the interaction between the cation and the SO_3^- group. A difference was observed between the IR and Raman spectra for the wavenumber of the symmetric sulfonate stretching mode, which was attributed to correlation coupling. This difference also decreased with increasing counterion radius. In the limiting case involving the large (TPA^+) counterion, the symmetric sulfonate stretching mode appeared at the same wavenumber in the Raman and IR spectra. The spectrum of a model compound, bis(2-ethylhexyl)succinate (i.e. NaAOT without the sulfonate moiety), was used to assign bands in the $1300\text{--}1100\text{ cm}^{-1}$ region of the IR spectrum of NaAOT. This region consists of C—C and C—O stretching modes associated with the succinate backbone, and non-degenerate, antisymmetric stretching modes of the SO_3^- group. The correlation splitting yields four antisymmetric sulfonate stretching modes. The splitting decreases with increasing counterion radius, due to a reduction in the interaction between the cation and the SO_3^- group. The doubly degenerate, antisymmetric sulfonate stretching mode appeared as a single, broad band in the spectrum of (TPA^+)AOT. The carbonyl stretching mode of NaAOT appears as an asymmetric band between 1720 and 1740 cm^{-1} . This asymmetry was attributed to different conformations about the acyl C—C bond. Weak interactions between the Na^+ counterion and the carbonyl group may also contribute to the intensity of the lower-wavenumber band.

A large number of studies of reverse micelles and micro-emulsions have employed sodium bis(2-ethylhexyl)sulfosuccinate (NaAOT) as the surfactant. Vibrational studies^{1–17} have largely involved interpretation of the IR and Raman spectra of water in reverse micelles,^{2–10} or the skeletal hydrocarbon modes.^{11–14}

The vibrational spectra of AOT salts (**1**) are dominated by



vibrations associated with the hydrophobic 2-ethylhexyl chains.^{11–14} Vibrational modes of the hydrophilic head-group (i.e. the sulfonate and ester moieties) also give rise to well defined bands in the $500\text{--}700$, $1000\text{--}1300$ and $1710\text{--}1750\text{ cm}^{-1}$ regions of the spectra.^{9,12} However, the vibrational spectrum of NaAOT is complex, and the assignments reported have not been comprehensive.¹⁴ The wavenumber assigned to the symmetric sulfonate stretching mode of the head-group differs in the Raman and IR spectra. The antisymmetric sulfonate stretch is very weak in the Raman spectrum, but has a complex band profile in the IR. There is also a lack of clear understanding of the doublet structure of the carbonyl stretching mode, and the low-wavenumber SO_3 bending, O—C(O) bending and C—S stretching modes have not been studied.

In order to assign the vibrational spectrum of NaAOT, we have investigated the FTIR and FT-Raman spectra of alkali-metal and tetraphenylarsonium salts of bis(2-ethylhexyl)sulfosuccinate (AOT). The vibrational spectrum of bis(2-ethylhexyl)succinate (BEHS), a molecular analogue of NaAOT in

which the SO_3^- group is absent, has also been analysed to help in the assignment of the modes associated with the head-group of the molecule.

Experimental

Materials

Sodium bis(2-ethylhexyl)sulfosuccinate (NaAOT, 99%) was obtained from Sigma (D-0885, lot 32H0565) and was used without further purification. The Na^+ counterion was ion-exchanged with either Li^+ , K^+ , Rb^+ , Cs^+ , Ba^{2+} , Ce^{3+} or tetraphenylarsonium (TPA^+) cations, using the method of Eastoe *et al.*¹⁸ The exchanged AOT salts were vacuum desiccated for 48 h at 60°C to help remove water. The amount of residual water in NaAOT was found to be 0.1 moles per mole of surfactant, as measured by Karl-Fischer titration. Inspection of the IR spectra of the salts revealed that the amount of residual water increased very slightly as the charge-to-radius ratio of the cation increased. It is important to remove as much of the water as possible, as the wavenumber of the symmetric SO_3 mode is perturbed by bound water.¹

Bis(2-ethylhexyl)succinate (BEHS) was synthesized by the esterification of succinic acid (BDH LR grade) with two mole equivalents of 2-ethylhexanol (Unilab LR grade) at 100°C . The yellow oil was purified by column chromatography, using a silica-alumina support and eluting with 20 vol % ethylacetate in cyclohexane, to yield a colourless oil. The purity of the resulting sample was confirmed by refractive index and boiling point determination, by comparison with published results.¹⁹

Spectroscopy

The FTIR spectra of the exchanged AOT salts and BEHS were obtained using a Digilab FTS-60 spectrometer, equipped with a Globar infrared source, a KBr beamsplitter and a

liquid-nitrogen-cooled MCT detector. Spectra were scanned in the range 4000–500 cm^{-1} , with an effective resolution of 2 cm^{-1} . The samples were pressed into thin films between two KBr windows, and the sample compartment was continuously purged with dry nitrogen during data acquisition. Typically, 16 scans were co-added to achieve an acceptable signal-to-noise ratio.

FT-NIR Raman spectra were acquired using a Digilab FT-Raman II spectrometer, equipped with a liquid-nitrogen-cooled Ge detector. The 1064 nm exciting line of a Lee Nd-YAG laser was used in all cases, with 200 mW of power at the sample. Spectra were obtained by co-adding 1024 scans, at a resolution of 2 cm^{-1} .

Unless stated otherwise, the intensities of all spectra were normalised by using the intensities of the C–H stretching modes. Spectra were processed by using the Spectralcalc software package (Galactic Industries).

Results and Discussion

The FTIR and FT-Raman spectra of NaAOT are illustrated in Fig. 1, while the corresponding band assignments are given in Tables 1 and 2.

Symmetric Stretching Mode of the SO_3^- Group

The effect of alkali-metal ion-exchange on the symmetric sulfonate stretching mode in the Raman and IR spectra are illustrated in Fig. 2 and 3; the corresponding band wavenumbers and their difference [$\Delta\nu_s(\text{SO}_3^-)$] are plotted as a function of counterion radius in Fig. 4. Inspection of Fig. 4 and Table 2 reveals that the wavenumber of the mode decreases with increasing counterion radius. Similar behaviour was observed by Zundel²⁰ for salts of polystyrenesulfonic acid, and by Lowry and Mauritz²¹ for exchange of alkali-metal cations on perfluorosulfonate resins. In those studies, the shift to lower wavenumber was attributed to a weakening of the cation–anion interaction. The strength of the interaction between the cation and the SO_3^- group would be expected to be a function of the charge-to-radius ratio (polarising power) of the cation. Thus, the extent of ionic interaction (and hence the wavenumber of the symmetric sulfonate stretching

mode) should be inversely proportional to the ionic radius for the alkali cation series (as evident in Fig. 4). A shift to lower wavenumber has also been observed following hydration of NaAOT in reverse micelles,^{1,9,22} where hydration leads to a reduction in the strength of the sulfonate–counterion interaction.²²

Inspection of Fig. 2 and 3 shows that the full-width-at-half-maximum (FWHM) of the symmetric sulfonate stretching mode also decreases with increasing counterion radius, in both the IR and Raman spectra. This trend can be similarly attributed to a reduction in the strength of the interaction between the cation and the SO_3^- group. An increase in the FWHM as the counterion radius decreases indicates a stronger interaction, leading to a faster vibrational relaxation rate and band-broadening, or a broader distribution of locally different environment-oscillator perturbations, or both.¹ In addition, the integrated peak areas and the peak intensities of the Raman band due to the symmetric sulfonate stretching mode increase with increasing cation radius, Fig. 2. This may reflect an increase in the change in polarisability associated with this mode due to an increase in the electron density on the SO_3^- group, as the interaction between the SO_3^- group and the counterion is reduced.

The wavenumber of the symmetric stretching mode of the SO_3^- group is higher in the Raman than in the IR spectrum (Fig. 2 and 3). The difference $\Delta\nu_s(\text{SO}_3^-)$ decreases with increasing counterion radius (Fig. 4). This effect is attributed to a correlation splitting, resulting from in-phase and out-of-phase coupling of the symmetric sulfonate stretching mode of adjacent SO_3^- groups in the solids, as shown in the scheme.

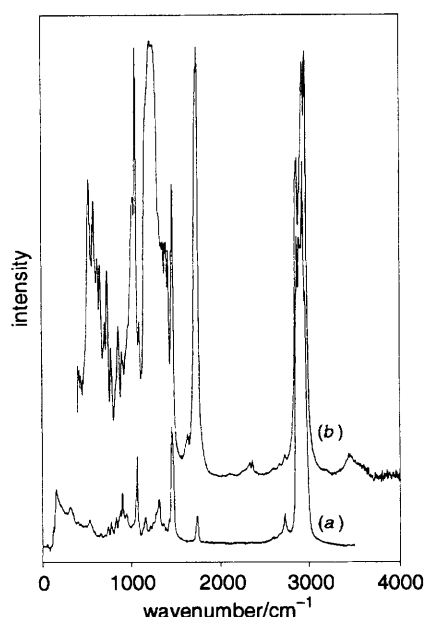
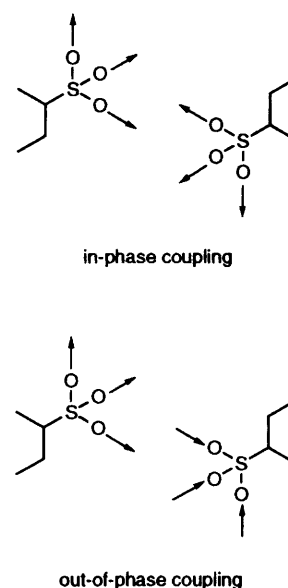


Fig. 1 (a) FT-Raman and (b) FTIR spectra of NaAOT

An analogous coupling has been observed for the symmetric carbonate stretching mode of calcite.²³ X-Ray diffraction studies by Ekwall *et al.*²⁴ have shown that solid NaAOT has a reversed, two-dimensional hexagonal structure, consisting of rods of six radially arranged AOT anions. These appear to be arranged into two subgroups, each containing three SO_3^- groups, located one above the other. Molecular modelling studies²⁴ suggest that there is insufficient space for six head-groups within the same plane in the centre of the rod. However, such an arrangement could be readily achieved if the molecules were oriented with the succinate groups parallel to the axes of the rod, and the carbon atom attached to each SO_3^- group alternating upwards and downwards. The neighbouring sulfonate head-groups would then interact, yielding

Table 1 Assignment of bands in the Raman and IR-spectra of AOT salts and BEHS

wavenumber/cm ⁻¹ and relative band intensities						
NaAOT		(TPA)AOT		BEHS		assignment
Raman	IR	Raman	IR	Raman	IR	
314 w						δCOR
346 vw sh						
402 vw						
430 vw						
530 m	530 m	520 m	523 m	483 m	—	$\delta_d(\text{SO}_3)^a$
575 vw sh	584 w		580 w	556 m sh	563 w	$\delta_d(\text{SO}_3), \delta(\text{CCO})^{a,b}$
	626 w					$\delta(\text{C}=\text{O}/\text{OC}=\text{O})$
650 w	653 w				653 w	$\delta(\text{C}=\text{O}/\text{OC}=\text{O})^{b,c}$
				—	—	$\nu(\text{C}-\text{S})$
701 vw	705 vw				704	$\delta(\text{C}=\text{O}/\text{OC}=\text{O})^{b,c}$
738 w	733 w	729 w			734 vw	CH_2 rock (aliphatic) ^d
770 w	773 w	769 w		765 w	773 vw	CH_2 rock (isolated)
					802 w	
826 m		822 w		827 m		$\nu(\text{C}-\text{C})$
	857 w		852 w			$\nu(\text{C}-\text{C})$
874 w		874 w			881 w	$\nu(\text{C}-\text{C})$
893 m	894 vw	893 w		894 vw		$\nu(\text{C}-\text{C})^b$
943 w				958 m	921 vw	$\nu(\text{C}-\text{C})$
	983 w			993 vw	984 m	$\nu[(\text{RH}_2)\text{C}-\text{O}]$
	1020 m-w			1040–1065 m b		$\nu[(\text{RH}_2)\text{C}-\text{O}]$
1063 s	1050 vs	1036 s	1036 s	—	—	$\nu_s(\text{SO}_3)^e$
	1092 w					
1155 m	1150–1170 s	1164 m	1160 s	1149 m	1161 s	$\nu[\text{C}-\text{C}(\text{O})-\text{O}]$
1210–1265 vw	1180–1280 vs b		1235 vs	—	—	$\nu_{as}(\text{SO}_3)$
	1280 w	1280 w			1270 m	CH_2 twist ^e
1310 m	1310 w	1306 w		1304 m	—	
			1323 m	—		comb. $\nu(\text{C}-\text{S}) +$
	1340–1395 w			1338 w sh.	1315–1385	$\delta_d(\text{SO}_3)^a$
	1416 w				1416 w	$\delta(\text{CH}_2)$
1450 s	1465 s	1448 s	1466 m	1450,1460 s	1467 m	$\delta(\text{CH}_2)$
1723,1735 w	1723,1735 vs	1732 m	1733 s	1742 m	1739 vs	$\nu(\text{C}=\text{O})^e$
2734 w				2721 w	2732 vw	$2 \times \delta(\text{CH}_2)$
2875,2897	2861,2874	2873,2898	2860,2873	2874 vs	2873 m	$\nu_s(\text{CH}_2, \text{CH}_3)^e$
2937,2959 vs	2934,2962 s	2937,2960 vs	2933,2962 s	2932,2958 vs	2931,2959 s	$\nu_{as}(\text{CH}_2, \text{CH}_3)$
	3446 vw				3459 vw	$2 \times \nu(\text{C}=\text{O})$

s = strong, m = medium, w = weak, b = broad, sh = shoulder. ^a Ref. 29. ^b Ref. 30. ^c Ref. 31. ^d Ref. 32. ^e Ref. 6. ^f Ref. 26.

Table 2 Band wavenumbers of the functional groups within the head-group of the AOT salts

wavenumber/cm ⁻¹						
AOT Salts	$\delta_d(\text{SO}_3)$	$\nu(\text{C}-\text{S})$	$\nu_s(\text{SO}_3)$	$\nu_{as}(\text{SO}_3)$	$\delta_d(\text{SO}_3) + \nu(\text{C}-\text{S})$	$\nu(\text{C}=\text{O})$
$\text{Li}^+ \begin{cases} \text{R} \\ \text{IR} \end{cases}$	—	—	1052,1072	—	—	1712,1736
	—	—	1058	1180–1280	—	1715,1736
$\text{Na}^+ \begin{cases} \text{R} \\ \text{IR} \end{cases}$	530	—	1048,1063	—	—	1718,1735
	530	—	1050	1180–1280	—	1718,1735
$\text{K}^+ \begin{cases} \text{R} \\ \text{IR} \end{cases}$	528	689	1052	—	—	1722,1730
	528	689	1047	1198,1220 1235,1255	1335	1722,1730
$\text{Rb}^+ \begin{cases} \text{R} \\ \text{IR} \end{cases}$	528	685	1049	—	—	1722,1730
	528	684	1045	1198,1220 1231,1251	1333	1722,1730
$\text{Cs}^+ \begin{cases} \text{R} \\ \text{IR} \end{cases}$	528	678	1046	—	—	1721,1730
	528	679	1043	1198,1220 1229,1246	1331	1721,1730

two distinct bands corresponding to in-phase or out-of-phase coupling of the symmetric stretching modes.

Assuming a similar orientation for the SO_3^- groups in the other alkali-metal AOT salts, the magnitude of the vibrational coupling of the SO_3^- groups should decrease with increasing separation. This is reflected in the observed decrease in $\Delta\nu_s$

(SO_3^-) with increasing ionic radius (Fig. 4). In contrast, the wavenumbers of the symmetric sulfonate stretching mode are coincident in the Raman and IR spectra of (TPA)AOT (1036 cm^{-1}). This effect is due to the large TPA cation significantly increasing the distance between adjacent SO_3^- groups, preventing correlation coupling. Based on the band

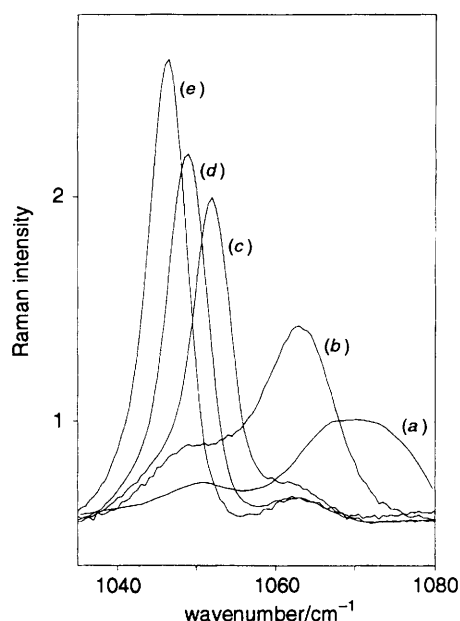


Fig. 2 FT-Raman spectra of the symmetric sulfonate stretching mode of the alkali-metal-exchanged salts of AOT. (a) LiAOT, (b) NaAOT, (c) KAOT, (d) RbAOT and (e) CsAOT.

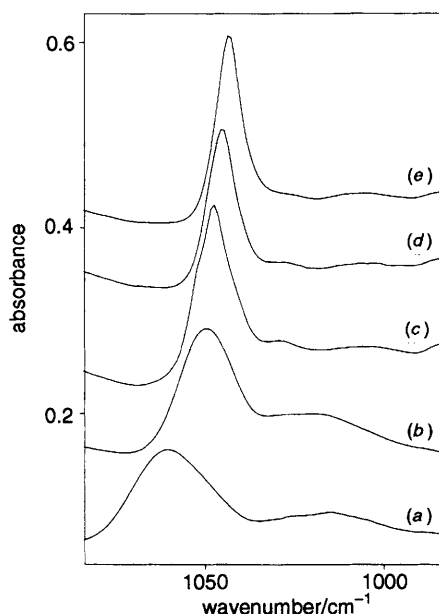


Fig. 3 FTIR spectra of alkali-metal-exchanged salts of AOT. (a) LiAOT, (b) NaAOT, (c) KAOT, (d) RbAOT and (e) CsAOT.

assignment for the calcite system,²³ we have assigned the in-phase vibration to be predominantly Raman-active and occurring at a higher wavenumber, while the out-of-phase vibration is predominantly IR-active and at a lower wavenumber. On the basis of the structural models discussed above, it is evident that the adjacent SO_3^- groups would exist in a non-centrosymmetric environment. Therefore, both the in-phase and out-of-phase modes should be IR- and Raman-active. For the LiAOT and NaAOT salts, the correlation splitting is large enough to yield two distinct bands in the Raman spectra. The more intense band in the Raman spectrum corresponds to the weaker band in the IR spectrum and *vice versa* (Fig. 2 and 3). However, for the KAOT, RbAOT and CsAOT salts, the two bands are not evident, as they both appear within the bandwidth observed in the spectra.

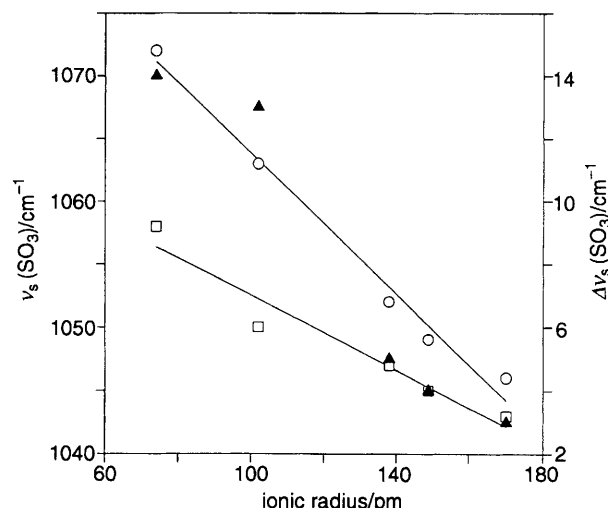


Fig. 4 Wavenumber of the band-maximum in the infrared (□) and Raman (○) spectra, and their difference [▲; $\Delta\nu_s(\text{SO}_3)$], vs. ionic radius for the alkali-metal salts of AOT

1100–1300 cm^{-1} Region

Vibrations in this region give rise to weak bands in the Raman spectrum, which showed only minor variation on exchange with alkali-metal counterions, Table 1. However, the corresponding region of the infrared spectrum, Fig. 5 and 6, consists of a complex mixture of symmetric C—O and C—C stretching, antisymmetric SO_3 stretching and CH_2 twisting modes, which have not been unambiguously assigned.^{6,9,15,17} To assist in the assignment, the spectrum of BEHS (*i.e.* NaAOT without the sulfonate moiety) was investigated, Fig. 6(c). In contrast to the salts of AOT, the ester groups of the succinate backbone in BEHS are chemically equivalent. Therefore, the vibrational modes of C—O, C—C and CH_2 linkages in BEHS (Table 1) can serve only as a guide in the interpretation of the AOT spectrum.

From the IR spectrum of BEHS [Fig. 6(c)], only the strong mode at 1161 cm^{-1} , assigned to a combination of C—O and

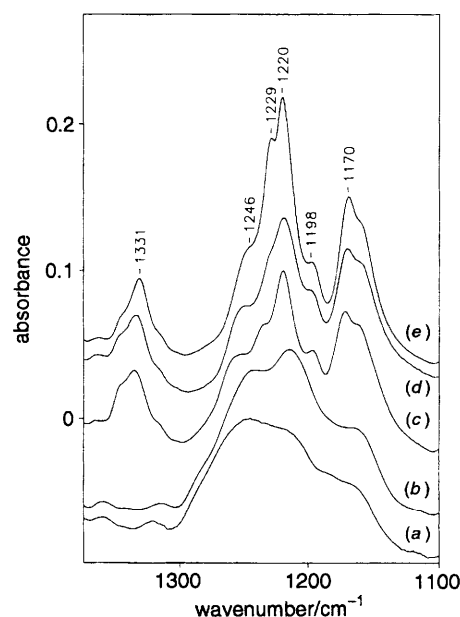


Fig. 5 FTIR spectra of the antisymmetric sulfonate stretching mode of the alkali-metal-exchanged salts of AOT in the $1100\text{--}1350\text{ cm}^{-1}$ region. (a) LiAOT, (b) NaAOT, (c) KAOT, (d) RbAOT and (e) CsAOT.

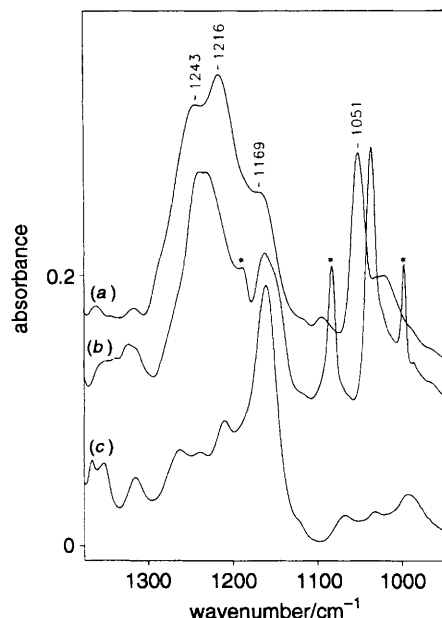


Fig. 6 FTIR spectra of the symmetric and antisymmetric sulfonate stretching mode region of (a) NaAOT, (b) (TPA)AOT and (c) BEHS. *Denotes bands due to the TPA⁺ cation. Spectra not shown to scale.

C—C stretching modes of the ester linkage [C—C(O)—O], would be expected to contribute significantly to the intensity in this region of the spectra for AOT salts. The infrared spectrum of BEHS in this region is very similar to dimethylsuccinate and diethylsuccinate, indicating that contributions to the intensity of the 1161 cm⁻¹ band by the 'iso' linkages of the 2-ethylhexyl chains are not significant.²⁵ This band appears as a doublet in the spectra of the salts (Fig. 5), where the higher-wavenumber component shifts to lower wavenumber with increasing counterion radius. The splitting of this band is due to the asymmetric attachment of the sulfonate moiety to the succinate backbone, where the component at higher wavenumber is assigned to the ester linkage closest to the SO₃⁻ group. This splitting is not evident in the IR spectra of LiAOT or NaAOT, since this region is obscured by broad bands associated with the antisymmetric sulfonate stretching mode (Fig. 5).

Since the local symmetry of the free, delocalised SO₃⁻ group is C_{3v}, one symmetric sulfonate stretching and a doubly degenerate, antisymmetric stretching mode would be expected.²⁰ In the solid state, the antisymmetric stretch often appears as a resolved doublet, indicating that the local symmetry has been reduced from C_{3v} to C_s and the degeneracy of the mode removed (E → A' + A''), by interaction with the counterion. The extent of splitting depends on the degree of interaction between the metal ion and the sulfonate head-group, and is, therefore, a function of the charge-to-radius ratio of the cation (Fig. 7). However, the additional effect of correlation coupling (see previous section) would be expected to yield four bands associated with the antisymmetric sulfonate stretching mode. This is evident in Fig. 5, where four bands are observed in the 1200–1260 cm⁻¹ range for the KAOT, RbAOT and CsAOT salts, and the coupled C—C and C—O modes of the ester linkages become resolved from the antisymmetric sulfonate stretching modes. The splitting of the two central bands (1200–1300 cm⁻¹) decreases with increasing cation radius (NaAOT: 27 cm⁻¹; CsAOT: 9 cm⁻¹). Indeed, the splitting is so large for NaAOT that only two bands are clearly evident. In contrast, the interaction between the large TPA cation and the SO₃⁻ group is reduced such that the

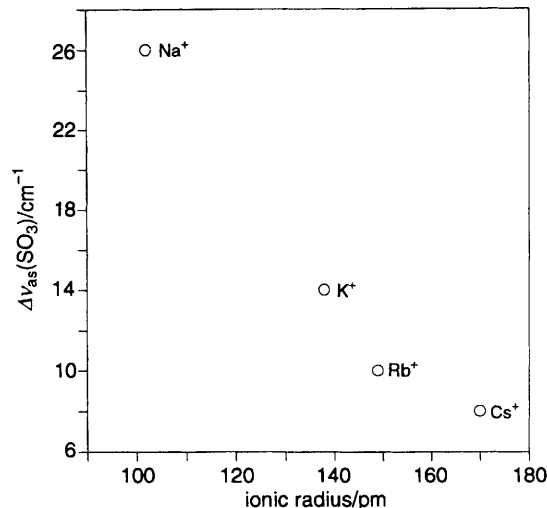


Fig. 7 Splitting of the infrared band due to the antisymmetric sulfonate stretching mode of the alkali-metal-exchanged salts of AOT vs. ionic radius

antisymmetric stretching mode almost appears as a single band at ca. 1235 cm⁻¹ [Fig. 6(b)].

C=O Stretching Vibration

For NaAOT, two bands are observed in the carbonyl stretching region of the Raman, Fig. 8 and IR spectra, Fig. 9.^{1,6,9,12,15,16} Such a spectral profile would be expected, since the two carbonyl groups are chemically inequivalent due to the asymmetric attachment of the SO₃⁻ group to the succinate backbone. Three explanations have been proposed to account for the magnitude of the splitting.

(1) The lower-wavenumber band at ca. 1720 cm⁻¹ may result from an inductive effect due to the sulfur atom being attached to the neighbouring carbon atom.²⁶ However, this explanation can be discounted, since only a single carbonyl band was observed at 1732 cm⁻¹ in the Raman [Fig. 10(e)]

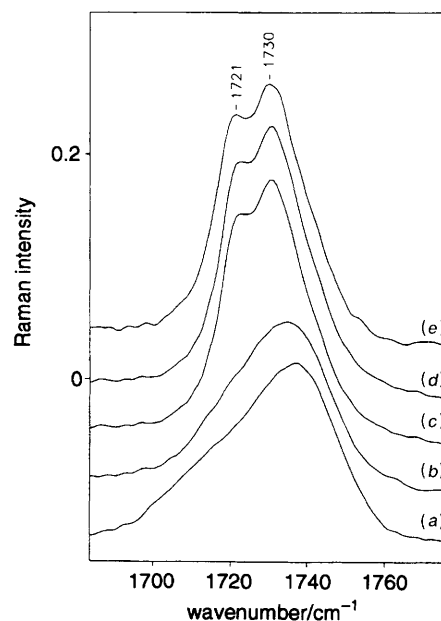


Fig. 8 FT-Raman spectra of the carbonyl stretching mode of the alkali-metal-exchanged salts of AOT in the 1650–1800 cm⁻¹ region. (a) LiAOT, (b) NaAOT, (c) KAOT, (d) RbAOT and (e) CsAOT.

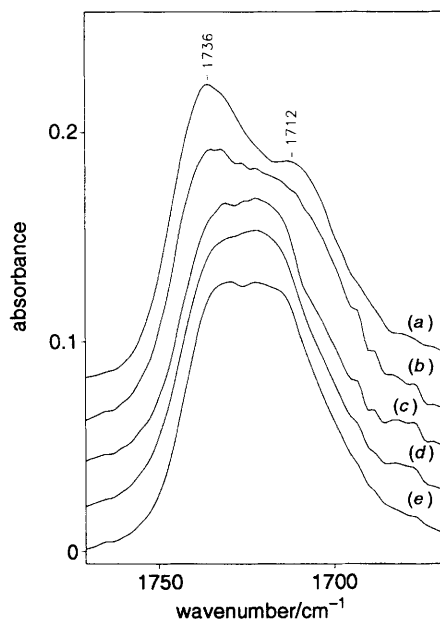


Fig. 9 FTIR spectra of the carbonyl stretching mode of the alkali-metal-exchanged salts of AOT in the 1650–1800 cm^{-1} region. (a) LiAOT, (b) NaAOT, (c) KAOT, (d) RbAOT and (e) CsAOT.

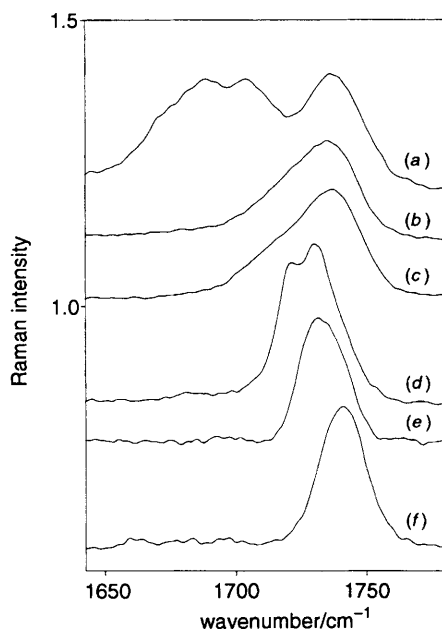


Fig. 10 FT-Raman spectra of the carbonyl stretching mode region of (a) $\text{Ce}(\text{AOT})_3$, (b) $\text{Ba}(\text{AOT})_2$, (c) LiAOT, (d) CsAOT, (e) (TPA)AOT and (f) BEHS

and 1733 cm^{-1} in the IR spectrum [Fig. 11(e)] of (TPA)AOT, even though the carbonyl groups are chemically inequivalent.

(2) Coupling of the carbonyl groups across the succinate backbone. This can also be rejected, as this effect is expected to be weak for 1,4-diester compounds,²⁶ and is not observed in the spectra of BEHS [Fig. 10(f) and 11(f)].

(3) Different conformations about the C1–C2 or C1'–C2' bond (acyl C–C) of the succinate backbone, as suggested by Bicknell-Brown *et al.*²⁷

In the Raman spectra of anhydrous, crystalline dilauryl-phosphatidylethanolamine (DLPE), the band at *ca.* 1734 cm^{-1} was assigned to an approximately *gauche* conformation, and the band at *ca.* 1720 cm^{-1} to an approximately *trans* conformation.²⁷ We do not agree with previous assignments^{1,6}

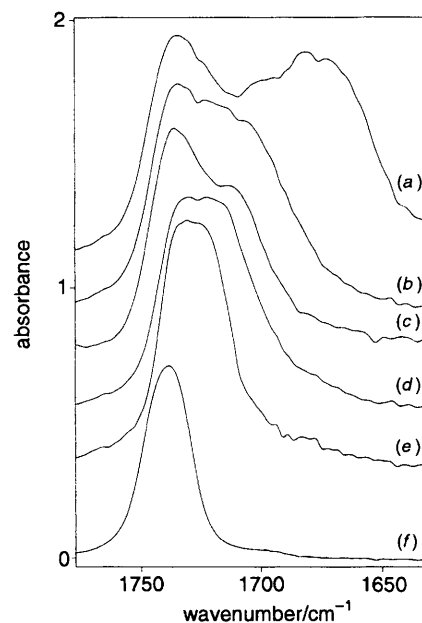


Fig. 11 FTIR spectra of the carbonyl stretching mode region of (a) $\text{Ce}(\text{AOT})_3$, (b) $\text{Ba}(\text{AOT})_2$, (c) LiAOT, (d) CsAOT, (e) (TPA)AOT and (f) BEHS. Spectra not shown to scale.

of the observed splitting in the IR spectrum to rotational isomerism about the C1–C1' bond, with the higher-wavenumber band corresponding to the *trans* conformation.

In the Raman and IR spectra of NaAOT, there is a broad, asymmetric band at 1735 cm^{-1} [Fig. 8(b) and 9(b)]. The FWHM of the carbonyl stretching mode decreases with increasing cation radius (Fig. 8), yielding two bands at 1721 and 1730 cm^{-1} for CsAOT, with the higher-wavenumber mode exhibiting greater intensity. The increase in the FWHM can be attributed to an increase in the strength of interaction between the counterion and the carbonyl group (analogous to the earlier discussion for the SO_3^- group). However, this effect is not as evident in the IR spectra of these salts, where the band splitting is not as well defined (Fig. 9).

In the Raman and IR spectra of LiAOT, the band maximum at 1712 cm^{-1} is *ca.* 10 cm^{-1} lower than that assigned in the Raman spectrum to a *trans* conformation of DLPE.²⁷ The relatively low wavenumber observed for this vibration may result from the formation of a chelation complex between the carbonyl and sulfonate oxygens and the cation. Such complexes have been proposed for a range of ion-exchanged AOT salts (Ba^{2+} , Li^+ *etc.*)²⁸ Inspection of Fig. 10 and 11 reveals that the spectra of LiAOT and $\text{Ba}(\text{AOT})_2$ are very similar in this region. An additional band is evident at *ca.* 1690 cm^{-1} for $\text{Ce}(\text{AOT})_3$, Fig. 10 and 11, which is attributed to a stronger interaction between the cation and one of the carbonyl groups. The band at *ca.* 1735 cm^{-1} in the spectra of these AOT salts, Fig. 10 and 11, is assigned to the non-chelating carbonyl group (*i.e.* the carbonyl group furthest away from the sulfonate site), based on a comparison with the spectra of BEHS [Fig. 11(f)].

500–800 cm^{-1} Region

The bands in this region of the IR spectrum are shown in Fig. 12. We have assigned the band at *ca.* 530 cm^{-1} to the doubly degenerate deformation mode of the SO_3^- group (Table 1). A corresponding band has been assigned for the Raman and IR spectra of sodium methanesulfonate.²⁹ This mode appears as a broad band in the IR spectrum of NaAOT, Fig. 12(c). The FWHM decreases with increasing ionic radius

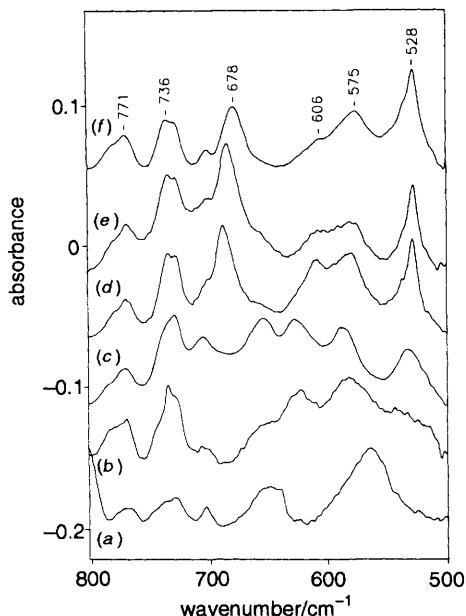


Fig. 12 FTIR spectra of the 500–900 cm^{-1} region of (a) BEHS, (b) LiAOT, (c) NaAOT, (d) KAOT, (e) RbAOT and (f) CsAOT

of the counterion. This can be attributed to a reduction in the interaction between the counterion and the SO_3^- group (as discussed previously).

The band at $\text{ca. } 580 \text{ cm}^{-1}$ is assigned to a mixture of the symmetric bending mode of the SO_3^- group and the bending mode of the C–C–O linkage of the succinate backbone. A corresponding band was assigned in the IR and Raman spectra of sodium methanesulfonate,²⁹ the IR spectrum of succinic acid³⁰ and for the broad band in the IR spectrum of BEHS. The bands at $\text{ca. } 650$ and 701 cm^{-1} in the IR spectra of BEHS and alkali-metal AOT salts are assigned to bending modes of either the C=O group or the O–C=O linkage. These modes appear in the 550–700 cm^{-1} region for related compounds, such as succinic acid³⁰ and alkyl fumarates.³¹ However, they are difficult to assign, since they may be inherently coupled (see band assignments in Table 1).

The band at 630 cm^{-1} in the IR spectrum of LiAOT and NaAOT, Fig. 12, is attributed to the bending mode of the carbonyl group associated with the cation. It was stronger in the IR spectra of $\text{Ba}(\text{AOT})_2$ and $\text{Ce}(\text{AOT})_3$. Its intensity decreased with decreasing charge-to-radius ratio of the metal counterion, reflecting a weakening of the interaction between the cation and the carbonyl group, as discussed above.

The band at $680\text{--}690 \text{ cm}^{-1}$ in the spectra of CsAOT, RbAOT and KAOT is assigned to the C–S stretching mode. This mode is extremely sensitive to the alkali-metal cation, and shifts to higher wavenumbers with decreasing counterion radius. The observed shift of 11 cm^{-1} is relatively large compared to the shifts observed in the Raman and IR spectra for the symmetric sulfonate stretching modes of these salts (6 and 4 cm^{-1} , respectively). It is significant that the mode is not observed in the Raman and IR spectra of LiAOT and NaAOT, since the factors that broaden the symmetric sulfonate stretching mode for these salts may similarly broaden and reduce the relative intensity of the C–S stretching mode. One might be tempted to assign the band at $\text{ca. } 700 \text{ cm}^{-1}$ in the spectra of NaAOT to this mode. However, since it is also observed in the spectra of BEHS (*i.e.* NaAOT without the SO_3^- group), it is assigned to a bending mode of the ester linkage.

The band observed at $1331\text{--}1335 \text{ cm}^{-1}$ in the IR spectra

of the KAOT, RbAOT and CsAOT salts (Fig. 5) is assigned to a combination mode resulting from the C–S stretching mode and the deformation mode of the SO_3^- group. This mode has also been assigned in the IR spectrum of sodium methanesulfonate.²⁹ The combined effects of a weak C–S stretching mode and a broad sulfonate deformation mode is responsible for the absence of this band in the IR spectra of LiAOT and NaAOT.

Conclusions

The vibrational modes of the hydrophilic head-group of NaAOT have been assigned by investigating the IR and Raman spectra of the alkali-metal salts of AOT, in conjunction with those of (TPA)AOT and BEHS.

(1) The symmetric sulfonate stretching mode shifted to lower wavenumber with increasing counterion radius, due to a decrease in the interaction between the cation and the SO_3^- group.

(2) The difference observed between the IR and Raman spectra for the wavenumber of the symmetric sulfonate stretching mode was attributed to correlation coupling. This difference also decreased with increasing counterion radius.

(3) A correlation splitting in the solid state of NaAOT produces two symmetric sulfonate stretching modes, and four antisymmetric sulfonate stretching modes.

(4) The intensity of the bands in the carbonyl stretching region was sensitive to isomerisation about the acyl C–C linkage and to interactions with the counterion.

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