323. *Alkyl Sulphates. Part II.** *Spectra of the* cyclo*Hexylammonium Salts in the* 800 *cm.*$^{-1}$ *Region.*

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For some 30 alkyl *cyclo*hexylammonium sulphates an absorption band of medium strength has a frequency of 790 cm.$^{-1}$ for all compounds having the substituent group attached at an even-numbered position on the hydrocarbon chain, whereas for odd-numbered substitution the frequency varies between 837 and 810 cm.$^{-1}$. Its position does not depend upon the number of carbon atoms in the hydrocarbon chain. Evidence is presented which suggests that the band arises from the skeletal stretching C–C modes in the hydrocarbon chain, but the possibility of the band's being assigned to another mode cannot be excluded.

IN Part I * we described the measurement of critical micelle concentrations as a means of identifying sodium alkyl sulphates $CHR^1R^2{\cdot}O{\cdot}SO_2{\cdot}ONa$, where R^1 and R^2 are unbranched. This property, together with molecular weight, affords satisfactory identification for pure compounds, but for mixtures the critical micelle concentration is of but limited value. Accordingly, the infrared spectra of the alkyl sulphates were examined to locate bands characteristic of the position of the substitutent group on the chain CHR^1R^2. An absorption band in the 800 cm.$^{-1}$ region was found to vary in a way which appears to be of theoretical interest.

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* Part I, *J.*, 1956, 579.

La Lau and Dahmen [1] found that, whereas the sodium alkyl sulphates are insoluble in the organic solvents spectroscopically most suitable, the alkyl *cyclo*hexylammonium sulphates are soluble in carbon disulphide. *cyclo*Hexylammonium chloride, from which these salts are prepared, is readily available pure; as a paste with white oil its spectrum showed that under the conditions used there would be 90—95% transmission over the 1250—800 cm.$^{-1}$ range for the *cyclo*hexylammonium ion.

As in Part I, L denotes the number of carbon atoms in the hydrocarbon chain CHR^1R^2, and P the position of the sulphate group along that chain.

RESULTS AND DISCUSSION

Spectra of Alkyl cyclo*Hexylammonium Sulphates.*—In preliminary work the infrared spectra of the *cyclo*hexylammonium tetradecyl sulphates ($L = 14$; $P = 1, 2, 3, 4, 5, 7$) in carbon disulphide and in the solid state were examined from 1450 to 650 cm.$^{-1}$. These spectra showed systematic differences in the 800 cm.$^{-1}$ region, and accordingly the remainder of the alkyl sulphates were examined particularly in this region. Fig. 1 shows the relevant portions of the spectra, except that of *cyclo*hexylammonium 1-tetradecylpentadecyl sulphate which has no specific absorption in this region.

FIG. 1. *Spectra near 800 cm.$^{-1}$ of alkyl* cyclo*hexylammonium sulphates.*

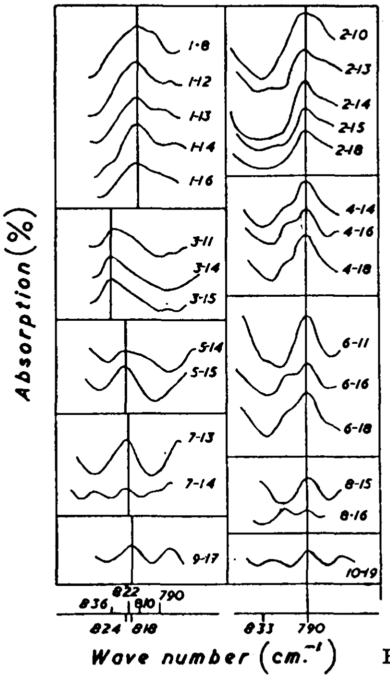
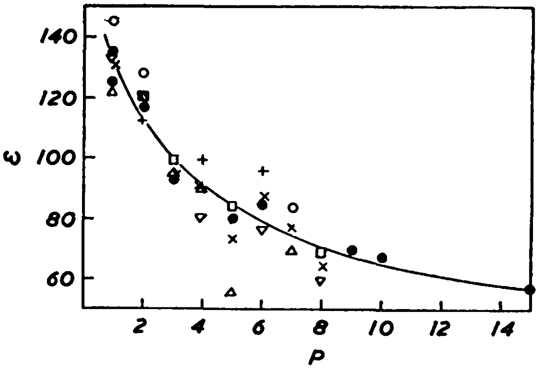


FIG. 2. *Decrease in ε with movement of substituent towards medial position in alkyl* cyclo*hexylammonium sulphates.*



L = ○ 13, △ 14, □ 15, ▽ 16, + 18, ● others, × average.

For identification of compounds, (P followed by L) see Table 3.

In the 800 cm.$^{-1}$ region each compound gives rise to an absorption band which has three salient features. First, its frequency depends on the position of the SO_4 group on the hydrocarbon chain; when P is even, the band occurs at 790 cm.$^{-1}$; when P is odd (1, 3, 5, 7, 9) it occupies the frequencies 810, 836, 824, 822, 818 respectively. Secondly, its position is independent of L, at any rate over the range $8 \leqslant L \leqslant 19$. Thirdly, when the molar extinction coefficient ε at the peak is plotted against P a smooth curve can be drawn (Fig. 2).

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[1] La Lau and Dahmen, Paper presented at International Colloquium on Applied Spectroscopy, Amsterdam, May 1956.

Interpretation.—That the values of ε lie about a smooth curve appears to indicate that the band in all compounds is associated with a single mode of vibration. It is not attributable to S–O stretching,[2] although La Lau and Dahmen [1] discuss the possibility that a band near 810 cm.$^{-1}$ for the dodecyl and tetradecyl sulphates is due to a covalent S–O stretching. That ε becomes less as the SO_4 group is removed from the vicinity of a terminal carbon atom and is not markedly or systematically affected by changes in L indicate that the mode of vibration is influenced mostly by groupings in the shorter branch of the carbon chain. When the substituent group is sufficiently far removed from a terminal carbon atom, as in *cyclo*hexylammonium 1-tetradecylpentadecyl sulphate, no specific absorption is evident.

Spectra in the Solid State of Other Salts of $CHR^1R^2{\cdot}O{\cdot}SO_2{\cdot}OH$.—To investigate the spectra further the following compounds were examined: Tri-(2-hydroxyethyl)ammonium tetradecyl sulphate ($L = 14$, $P = 1$) and 1-propylundecyl sulphate ($L = 14$, $P = 4$); sodium, potassium, ammonium, and tri-(2-hydroxyethyl)ammonium salts of 1-methyltridecyl sulphate ($L = 14$, $P = 2$). The sodium, potassium, and ammonium salts showed in the 800 cm.$^{-1}$ region the major bands found in the spectrum of solid *cyclo*hexylammonium 1-methyltridecyl sulphate but not the band at 790 cm.$^{-1}$, which is also absent from the spectrum of *cyclo*hexylammonium chloride. Hence the band arises from interactions of vibrations of more than one part of the molecule. For each of the three isomers the spectrum of the tri-(2-hydroxyethyl)ammonium salt was essentially the same as that of the *cyclo*hexylammonium salt. One may therefore deduce that the band of medium strength near 800 cm.$^{-1}$ has arisen from the addition of a heavy substituent group to the paraffinic part of the molecule, and is associated with vibrations in the hydrocarbon chain. Brown, Sheppard, and Simpson [3] detected a band at 795 cm.$^{-1}$ in the spectrum of *n*-tetradecane and *n*-decane (but not in *n*-dodecane), strong in the crystalline and weaker in the liquid state.

Spectra of Similar Molecules in the Liquid State.—Sheppard and Simpson found a weak band at 840—810 cm.$^{-1}$ in the spectra of the *n*-paraffins; its frequency in paraffins of even carbon number is less than in those containing an odd number.[4] Kohlrausch [5] examined the Raman spectra of the *n*-paraffins from $L = 5$ to $L = 12$, and found prominent bands varying in the same way in the same frequency range. Sheppard and Simpson assign this band to the lower limiting skeletal stretching modes of non-planar isomers.[4] Williams and Moscher [6] found in the spectra of alkyl hydroperoxides (C_3—C_{10}) a band of alternating frequency in the 830 cm.$^{-1}$ region for α-substitution. A band in the 770 cm.$^{-1}$ region appears to alternate in frequency as the substituent is moved along the chain, but this effect could not be confirmed from the scanty data given. Kohlrausch [7] found the same alternating frequency near 800 cm.$^{-1}$ in the Raman spectra of *n*-paraffinic alcohols.

We have examined the infrared spectra of the isomeric tetradecanols with the hydroxyl group attached in the 1, 2, 3, 4, 5, and 7 positions. Near 800 cm.$^{-1}$ the only band is at 785 cm.$^{-1}$, weak in tetradecan-3-ol and of medium strength in tetradecan-5-ol. In general, information on the changes in frequency caused by movement of the substituent group along a hydrocarbon chain of fixed length or on the effect of substituents other than hydroxyl is small.

Assignment of Band in 800 cm.$^{-1}$ Region.—It is probable that this band can be assigned either to the CH_2 rocking modes or to the skeletal stretching C–C modes of non-planar isomers. In the absence of nearby bands of comparable intensity, we assume that the relevant band of each spectrum originates from the same single rocking or stretching mode. In an attempt to decide which mode of vibration is involved, the following evidence was

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[2] Kohlrausch, " Raman Spectra," Leipzig, 1943, pp. 411—417.
[3] Brown, Sheppard, and Simpson, *Discuss. Faraday Soc.*, 1950, **9**, 261.
[4] Sheppard and Simpson, *Quart. Rev.*, 1953, **7**, 19.
[5] Kohlrausch and Köppl, *Z. phys. Chem.*, 1934, *B*, **26**, 209.
[6] Williams and Moscher, *Analyt. Chem.*, 1955, **27**, 517.
[7] Kohlrausch, ref. 2, p. 237.

collected: (1) Tschamler [8] has observed that in hydrocarbons the CH_2 rocking frequencies move regularly to a limiting value as the chain length increases; in our spectra there is no progressive shift in frequency as the length of a hydrocarbon branch R^1 or R^2 is increased. (2) The band is not split in the spectra of the solid *cyclo*hexylammonium tetradecyl sulphates; this suggests that it does not arise from the CH_2 rocking mode. (3) The band intensity decreases as the molecule approaches symmetry (*i.e.*, as the sulphate group moves towards a medial position on the hydrocarbon chain). A CH_2 rocking mode can hardly be responsible for such a change. (4) In the spectra of unbranched-chain alcohols the skeletal modes are usually enhanced by the presence of the polar C–O bond [9] (although we have not been able to detect this effect in the 800 cm.$^{-1}$ region in the tetradecanols examined); since the C–O bond in alkyl sulphates is undoubtedly polar, it should have a similar effect. (5) If the $C_6H_{11}\cdot\overset{+}{N}H_3\cdot O\cdot SO_2\cdot O$-group is regarded as being responsible for differences between the spectra of the alkyl *cyclo*hexylammonium sulphates and those of the corresponding paraffins because of its inertia in altering the vibrations of the paraffinic part of the molecule, then its mass will affect the stretching modes of the hydrocarbon chain rather than the CH_2 rocking modes of the individual carbon atoms.

The balance of evidence favours a C–C skeletal vibration. Assuming that the band arises from vibrations in the shorter portion (R^1) of the hydrocarbon chain, we can attempt a more detailed analysis of the individual spectra. The alkyl sulphates can be divided into four groups according as the number of C–C bonds in the two branches of the hydrocarbon chain is odd or even and according as *P* is odd or even. In the following Table, frequencies in col. 7 are observed values of the major band. Those in col. 8 are obtained by induction, and the plausibility of the assumptions made above rests on whether these bands can be detected in the spectra; the frequencies given will of course be those of minor bands, or, more probably, shoulders. In fact, the majority of Group *a* and *c* compounds conform to the predictions given in col. 8, whilst in Groups *b* and *d* only a small number of compounds have minor bands in the positions predicted. Also, the molar extinction coefficients at 790 cm.$^{-1}$ for Group *c* compounds should be greater than values for corresponding Group *a* compounds. Indeed, the molar extinction coefficients of compounds in which $P = 2$ are slightly greater for odd than for even values of *L* ("slightly" because the long-chain R^2 exerts only a very minor effect when $P = 2$); ε for *cyclo*hexylammonium 1-heptyloctyl sulphate ($L = 15$, $P = 8$) is considerably greater than the value for the 1-heptylnonyl sulphate ($L = 16$, $P = 8$), and ε for *cyclo*hexylammonium 1-pentylhexyl sulphate ($L = 11$, $P = 6$) is greater than the value for the 1-pentylundecyl sulphate ($L = 16$, $P = 6$) but less than for the 1-pentyltridecyl compound ($L = 18$, $P = 6$). Again, for symmetrical Group *d* compounds the molar extinction coefficients of the major band should be enhanced; thus *cyclo*hexylammonium 1-hexylheptyl sulphate ($L = 13$, $P = 7$) has $\varepsilon = 83{\cdot}8$ compared with $\varepsilon = 69{\cdot}7$ for *cyclo*hexylammonium 1-hexyloctyl sulphate ($L = 14$, $P = 7$). Overall, it appears that, although the balance of evidence is somewhat in favour of the assumptions made, some factor has been overlooked.

Group	*P*	*L*	Total no. of C–C bonds ($L - 1$)	No. of C–C bonds in R^1 branch	R^2 branch	Frequency (cm.$^{-1}$) for R^1 branch	R^2 branch
a	even	even	odd	odd	even	790	*ca.* 810
b	odd	,,	,,	even	odd	>790	790
c	even	odd	even	odd	,,	790	790
d	odd	,,	,,	even	even	>790	*ca.* 810

This hypothesis does not explain the position of the 810 cm.$^{-1}$ band in the spectra of the primary alkyl sulphates. If the major band in the 800 cm.$^{-1}$ region is assigned to C–C skeletal stretching vibrations in the shorter part of the hydrocarbon chain, it should

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[8] Tschamler, *J. Chem. Phys.*, 1954, **20**, 1845.

[9] Brown, Sheppard, and Simpson, *Phil. Trans.*, 1954, **247**, 35.

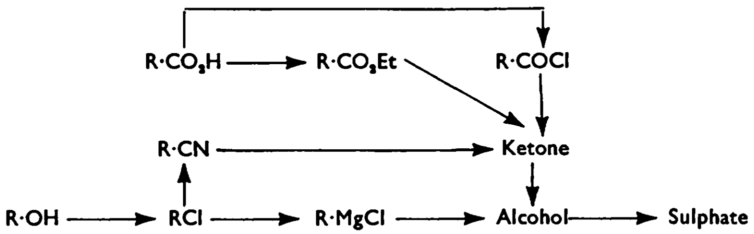
be absent from the spectra of the primary alkyl sulphates; and in fact there is no band at *ca.* 855 cm.$^{-1}$, the frequency at which one might be expected if the frequencies for the other odd values of P are extrapolated to $P = 1$ (Fig. 1). It is therefore possible that the 810 cm.$^{-1}$ band is not part of the P (odd) series as regards its position, although as regards its intensity the band is not anomalous because ε for the primary alkyl sulphates conforms with the other data (Fig. 2).

Calculations showed that the frequency could not be localised in either of the chains R^1 and R^2 and would appear to depend on the existence of a C–O bond. A model consisting of a normal carbon chain with a heavy substituent linked to it through an oxygen atom might well account for the effect, provided that the C–O vibration were only loosely coupled to the chain vibrations.

EXPERIMENTAL

Synthesis of Sodium Alkyl Sulphates.—For all except two compounds each of the steps is common to several preparations. The seven different steps are briefly described and are followed by Tables giving the nature and analytical details of the intermediate products. In the Tables each entry begins with the key number of the alkyl sulphate being made (see Table 3). In several instances one of the intermediate compounds was made by more than one route, and the entry appears twice in the Tables.

The starting point for each synthesis is the alkanol R·OH or the acid R·CO$_2$H; from these the chloride or the acid chloride was made by reaction with thionyl chloride. The various routes are summarised by the following scheme:



It was necessary to make, by standard methods, decanol (n_D^{20} 1·4372; b. p. 120°/12 mm.) from octanol, undecanol (n_D 1·400; b. p. 127°/14 mm.) from pelargonic acid, and pentadecanoic acid (m. p. 52·3°) from myristic acid.

1. *Preparation of Ketones.*—(a) *Claisen autocondensation.*[10] Standard methods were used except that sodium ethoxide was replaced by a suspension of sodium in toluene (see Table 1*a*).

(b) *Reaction between acid chloride and metal alkyl.* The acid chloride was added to the metal alkyl (*via* the Grignard reaction) in dry ether at such a rate that gentle refluxing was maintained, 4N-acid was added until the two phases were clear, and the aqueous layer was then separated and washed with ether. The combined ether layers were washed successively with N-acid, 10% sodium hydroxide solution, and water. The liquid was dried (MgSO$_4$) and distilled under reduced pressure, and the product was further purified by crystallisation from methanol (see Table 1*b*).

(c) *Reactions between alkyl cyanide and Grignard compound.* These are summarised in Table 1*c*.

(d) *Undecan-6-one and nonacosan-15-one.* Undecan-6-one was prepared from hexanoic acid by Herbst and Manske's method.[11] To prepare nonacosan-15-one, tetradecyl chloride was gradually added to lithium in dry ether in a nitrogen atmosphere and refluxed for 1 hr. The cooled, filtered product was poured on a large excess of solid carbon dioxide, dilute hydrochloric acid added, and the ether layer separated. After removal of the ether the *ketone* was crystallised from benzene–ethanol (yield 53%) (Found: C, 82·4; H, 13·9; CO, 6·6. $C_{29}H_{58}O$ requires C, 82·5; H, 13·7; CO, 6·6%).

2. *Preparation of Alcohols.*—(a) *Reduction of the ketone.* Reductions were effected chiefly

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[10] Briese and McElvain, *J. Amer. Chem. Soc.*, 1933, **55**, 1699.

[11] Herbst and Manske, *Org. Synth.*, Coll. Vol. II, 1944, 389.

by the Meerwein–Pondorff–Verley method (aluminium *iso*propoxide) and by hydrogen over Raney nickel. In the latter, a solution in alcohol was reduced with hydrogen at 135° and 70 atm. over Raney nickel for 17 hr. After separation of the catalyst the alcohol was distilled under reduced pressure and crystallised from light petroleum (see Table 2*a*).

(b) *Grignard compound + aldehyde.* See Table 2*b*.

(c) *Grignard compound + ethyl formate.* See Table 2*c*.

(d) *n*-Tetradecanol was made from dodecyl chloride *via* reaction with the sodium derivative of diethyl malonate; the resulting ester was hydrolysed to the free dibasic acid, which was decarboxylated by heating. The tetradecanoic acid thus obtained was reduced to tetradecanol by the Bouveault–Blanc reaction.

TABLE 1*a*.

Key no. of alkyl sulphate		Starting material		
P	*L*		B. p.	n_D^{20}
8	15	$C_7H_{15}\cdot CO_2C_2H_5$	94—98°/16 mm.	1·4180
9	17	$C_8H_{17}\cdot CO_2C_2H_5$	110—112°/20 mm.	—
10	19	$C_9H_{19}\cdot CO_2C_2H_5$	147—149°/44 mm.	1·4260

TABLE 1*b*.

Key no. of alkyl sulphate		Acid chloride		Grignard precursor	Metal alkyl
P	*L*		B. p.		
4	16	$C_3H_7\cdot COCl$	102—103°/765 mm.	$C_{12}H_{25}Cl$ *	$Cd(C_{12}H_{25})_2$
4	18	$C_{14}H_{29}\cdot COCl$	148—153°/3 mm.	C_3H_7Br †	$Cd(C_3H_7)_2$
5	14	$C_9H_{19}\cdot COCl$ ‡	104°/18 mm.	C_4H_9Br †	$Zn(C_4H_9)_2$
5	15	$C_{10}H_{21}\cdot COCl$	129—131°/17 mm.	C_4H_9Br †	$Cd(C_4H_9)_2$
5	19	$C_{14}H_{29}\cdot COCl$	—	,,	,,
6	16	$C_{10}H_{21}\cdot COCl$	—	$C_5H_{11}Br$ †	$Cd(C_5H_{11})_2$

* For physical properties see Table 2*b*. ‡ n_D^{20} 1·4399.
† Not prepared in this laboratory.

TABLE 1*c*.

Key no. of alkyl sulphate		Alkyl cyanide		Grignard precursor
P	*L*		B. p.	
5	15	$C_{10}H_{21}\cdot CN$	134—137°/20—22 mm.	C_4H_9Br
6	16	,,	,,	$C_5H_{11}Br$
8	16	$C_8H_{17}\cdot CN$	64/0·8 mm.	$C_7H_{15}Cl$ *

* For physical properties see Table 2*b*.

3. *Preparation of Alkyl Sulphates.*—The method, essentially that described by Dreger *et al.*,[12] employs reaction of the alcohol with a solution of chlorosulphonic acid in ether at −50°. Because of the extreme readiness of the products, especially those in which the sulphate group is near the medial position on the chain, to undergo hydrolysis, the solutions must be kept alkaline to phenolphthalein at all stages. Only the sulphates for which $P = 1$ and 2, and sodium 1-tetradecylpentadecyl sulphate ($L = 29$, $P = 15$) could be obtained in the crystalline state; the remainder were non-crystalline solids and were used as aqueous solutions. The sulphates ($P = 1$ and 2) were crystallised from water and recrystallised from aqueous butan-2-one. The tetradecylpentadecyl sulphate, obtained as a 5% emulsion in water, was dissolved in four vols. of alcohol, cooled to 25—30°, and the precipitate filtered off. The compound precipitated overnight from the filtrate was recrystallised from alcohol. The purity of the materials was assessed by Epton's method,[13] and the amount of inorganic salt was found by ashing a sample and correcting for the amount of sodium sulphate obtained from the alkyl sulphate (see Table 3).

Sodium 1-ethylnonyl sulphate was prepared as a 24% aqueous solution;[14] the remaining compounds were supplied in crystalline form containing <0·5% of inorganic salt by associates in Holland.

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[12] Dreger, Keim, Miles, Shedlovsky, and Ross, *Ind. Eng. Chem.*, 1944, **36**, 610.
[13] Epton, *Trans. Faraday Soc.*, 1948, **44**, 226.
[14] Winsor, *ibid.*, 1950, **46**, 766.

Alkyl cyclo*Hexylammonium Sulphates.*—Solutions of these sulphates were prepared by shaking a 2·5% (w/w) aqueous solution of sodium alkyl sulphate and excess of 20% aqueous *cyclo*hexylammonium chloride with five successive portions of carbon disulphide (pure, for spectroscopy). The combined extracts were dried (Na_2SO_4) and filtered; the residual sodium sulphate was washed with carbon disulphide and the washings were combined with the extract to make a total of 50 ml. of solution. With some compounds, particularly those of high molecular weight in which $P = 1$ or 2, very stable emulsions were formed. Experiments showed that (*a*) very little (<1%) of the alkyl *cyclo*hexylammonium sulphate was adsorbed on the sodium sulphate, (*b*) stable emulsions prevented the estimation of alkyl sulphates remaining in the aqueous phase. The concentration of salt in the organic phase was, therefore, determined by a modification of the methylene-blue titration method [13] by diluting an aliquot part with chloroform and titrating it against standardised cetylpyridinium bromide.

TABLE 2*a*.

Key no. of alkyl sulphate		Ketone			Method of reduction
P	*L*		M. p.	B. p.	
4	16	$C_{12}H_{25}\cdot CO\cdot C_3H_7$	36—37°	173—178°/24 mm.	Al *iso*propoxide
4	18	$C_{14}H_{29}\cdot CO\cdot C_3H_7$	42—45	—	,,
5	14	$C_9H_{19}\cdot CO\cdot C_4H_9$	22·6	145—146°/16 mm.	Na + C_2H_5OH
5	15	$C_{10}H_{21}\cdot CO\cdot C_4H_9$	31	120—122°/1 mm.	Al *iso*propoxide
5	19	$C_{14}H_{29}\cdot CO\cdot C_4H_9$	48—49	—	,,
6	11	$C_5H_{11}\cdot CO\cdot C_5H_{11}$ *	—	108—112°/12 mm.	H_2 (Raney nickel)
6	16	$C_{10}H_{21}\cdot CO\cdot C_5H_{11}$	35—36	127—128°/0·6 mm.	Al *iso*propoxide
6	18	$C_{12}H_{25}\cdot CO\cdot C_5H_{11}$	45	—	,,
8	15	$C_7H_{15}\cdot CO\cdot C_7H_{15}$	42·5	—	H_2 (Raney nickel)
8	16	$C_8H_{17}\cdot CO\cdot C_7H_{15}$	37·5—38	—	Al *iso*propoxide
9	17	$C_8H_{17}\cdot CO\cdot C_8H_{17}$	52—53	—	,,
10	19	$C_9H_{19}\cdot CO\cdot C_9H_{19}$	58	—	H_2 (Raney nickel)
15	29	$C_{14}H_{29}\cdot CO\cdot C_{14}H_{29}$ †	80—81	—	Al *iso*propoxide

* n_D^{20} 1·4285.

† Found: C, 82·4; H, 13·9; CO, 6·6. $C_{29}H_{58}O$ requires C, 82·5; H, 13·7; CO, 6·6%.

TABLE 2*b*.

Key no. of alkyl sulphate		Grignard precursor					Aldehyde
P	*L*		n_D^{20}	B. p.	Cl (found)	Cl (theory)	
2	10 *	$C_8H_{17}Cl$	1·4302	71°/15 mm.	23·9	23·9	$CH_3\cdot CHO$ †
2	14 *	$C_{12}H_{25}Cl$	1·4425	139°/23 mm.	17·2	17·3	,,
2	18 *	$C_{16}H_{33}Cl$	1·4513	149°/1 mm.	13·6	13·7	,,
3	14	$C_{11}H_{23}Cl$	1·4401	118°/18 mm.	18·3	18·6	$C_2H_5\cdot CHO$ †
3	15	$C_{12}H_{25}Cl$	—	—	—	—	,,
4	14	$C_{10}H_{21}Cl$	1·4377	102°/14 mm.	19·9	20·1	$C_3H_7\cdot CHO$ †
7	14	$C_7H_{15}Cl$	1·4254	49·5°/10 mm.	26·1	26·3	$C_6H_{13}\cdot CHO$

* Large-scale preparation: yield of alcohol 3—4 kg. † Not prepared in this laboratory.

TABLE 2*c*.

Key no. of alkyl suphate		Grignard precursor		
P	*L*		n_D^{20}	B. p.
7	13	$C_6H_{13}Br$	1·4478	49—55°/16 mm.
8	15	$C_7H_{15}Cl$		
9	17	$C_8H_{17}Cl$		

Alkyl Tri-(*2-hydroxyethyl*)*ammonium Sulphates.*—To a solution of sodium alkyl sulphate in 65% *n*-butanol a large excess (*ca.* 4-fold) of tri-(2-hydroxyethyl)ammonium sulphate was added. After being shaken, the aqueous layer was removed and the alcohol layer was washed 3 times with a little tri-(2-hydroxyethyl)ammonium sulphate. The free base was added to neutrality, and the solution was evaporated to dryness. Since molar extinction coefficients were not to be measured no precautions were taken to ensure that complete recovery of the alkyl sulphate was obtained.

In the solid state *n*-tetradecyl tri-(2-hydroxyethyl)ammonium sulphate was crystalline and the 1-propylundecyl sulphate a gum. The 1-methyltridecyl sulphate was obtained originally as a gum which became crystalline after a few days.

Infrared Measurements.—The spectra of about three-quarters of the samples were recorded from about 860 cm.$^{-1}$ to 775 cm.$^{-1}$ by means of the Grubb-Parsons S.4. double-beam spectrometer and the remainder were recorded over the same range with the Grubb-Parsons S.3. single-beam spectrometer. Spectral slit widths of 7·9 and 6·6 cm.$^{-1}$ at 831 and 790 cm.$^{-1}$ were employed, together with cell lengths of 0·021 cm. and 0·095 cm. Calculation of extinction coefficients is subject to several errors, including the titration error affecting the concentration. Values for six different solutions of *cyclo*hexylammonium 1-methyltridecyl sulphate at concentrations between 30 and 140 mmoles/l. indicate that the standard deviation of a single observation is $\pm 5·9$ for an average ε of 114·2. For compounds of lower ε the standard deviation is proportionately reduced.

TABLE 3. *Analysis of alkanols, and of alkyl sulphate products made therefrom.*

Key no. of alkyl sulphate		Alcohol and properties						Alkyl sulphate		
					Active H		Yield from pre-cursor (mol. %)	Concn. of aq. solu-tion (% w/w)	In-organic salt (% of alkyl sulphate)	Yield from alcohol (mol. %)
P	*L*		n_D^{20} or m. p.	B. p.	found	theory				
1	8	C_8H_{17}·OH †	1·42999	195—196°	—	—	—	‡	<0·1	~100
1	12	$C_{12}H_{25}$·OH †	—	141—142°/ 12 mm.	0·54	0·54	—	‡	0·2	—
1	14	$C_{14}H_{29}$·OH	37·4—37·7°	170°/18 mm.	—	—	76	‡	0·1	64
2	10 *	C_8H_{17}·CH(OH)·CH_3	1·4343	106°/14 mm.	0·64	0·64	79	‡	<0·1	53
2	14 *	$C_{12}H_{25}$·CH(OH)·CH_3	29—31°	159°/17 mm.	0·47	0·47	54	‡	0·2	54
2	18 *	$C_{16}H_{33}$·CH(OH)·CH_3	48—51°	156—160°/ 0·4 mm.	—	—	66	‡	1·0	43
3	14	$C_{11}H_{23}$·CH(OH)·C_2H_5	29·5°	150°/15 mm.	0·475	0·47	33	17·3	1·1	—
3	15	$C_{12}H_{25}$·CH(OH)·C_2H_5	37·5°	167—168°/ 16 mm.	0·44	0·44	48	24·0	—	—
4	14	$C_{10}H_{21}$·CH(OH)·C_3H_7	26·4°	160—161°/ 18·5 mm.	0·475	0·47	59	30·2	0·3	—
4	16	$C_{12}H_{25}$·CH(OH)·C_3H_7	39—40°	—	—	—	92	2·83	<0·1	55
4	18	$C_{14}H_{29}$·CH(OH)·C_3H_7	48—49°	—	0·375	0·37	85	5·1	<0·5	54
5	14	C_9H_{19}·CH(OH)·C_4H_9	27·5°	157°/17 mm.	0·475	0·47	66	19·5	1·5	—
5	15	$C_{10}H_{21}$·CH(OH)·C_4H_9	35·5—36·5°	—	0·44	0·44	83	4·75	<0·1	81
5	19	$C_{14}H_{29}$·CH(OH)·C_4H_9	54—55°	—	0·35	0·355	76	3·7	<0·5	65
6	11	C_5H_{11}·CH(OH)·C_5H_{11}	1·4355 18°	145°/53 mm.	—	—	84	5·8	3·0	34
6	16	$C_{10}H_{21}$·CH(OH)·C_5H_{11}	41°	—	—	—	82	5·2	1·1	83
6	18	$C_{12}H_{25}$·CH(OH)·C_5H_{11}	45°	192—195°/ 16 mm.	0·345	0·37	89	3·8	5·8	—
7	13	C_6H_{13}·CH(OH)·C_6H_{13}	38·5°	—	—	—	67	6·2	4·5	36
7	14	C_7H_{15}·CH(OH)·C_6H_{13}	42·8°	154—155°/ 15 mm.	0·47	0·47	—	20·4	2·0	—
8	15	C_7H_{15}·CH(OH)·C_7H_{15}	49·5°	120—124°/ 0·4 mm.	—	—	77	5·3	0·4	84
8	16	C_8H_{17}·CH(OH)·C_7H_{15}	49·5°	—	0·41	0·415	95	1·26	2·6	16
9	17	C_8H_{17}·CH(OH)·C_8H_{17}	59°	—	—	—	71	3·3	2·7	74
10	19	C_9H_{19}·CH(OH)·C_9H_{19}	63°	—	—	—	36	3·1	5·5	75
15	29	$C_{14}H_{29}$·CH(OH)·$C_{14}H_{29}$ §	86°	—	0·24	0·24	88	‡	0·7	47

* Large-scale preparation : yield of alcohol 3—4 kg., of alkyl sulphate 1·5—2 kg.

† Not made in this laboratory. ‡ Obtained in crystalline state.

§ Found : C, 82·1; H, 14·2. $C_{29}H_{60}O$ requires C, 82·1; H, 14·2%.

Effect of water. Water gives a broad diffuse band in the 800 cm.$^{-1}$ region, and if the drying procedure failed to remove all the moisture from the carbon disulphide solution the measured values of ε might be in error. In fact, a few spectra showed a weak band at 3400 cm.$^{-1}$ indicative of water, but solutions contained only about 0·2% of water (Karl Fischer method). Nevertheless, the extent of possible interference by water in the 800 cm.$^{-1}$ region was determined.

Solutions of isomeric tetradecyl sulphates ($P = 2$ and 7) were made in carbon disulphide solution as described; half of each solution was evaporated to dryness under vacuum at room temperature and replaced by an equal volume of dry distilled carbon disulphide. It was found that the absorption band at 3400 cm.$^{-1}$ in the untreated solution was absent from the treated solution, proving that water may indeed be present in solutions prepared by the normal procedure, and ε at the peak was decreased by $<5\%$ for both compounds. This difference is within the reproducibility of replicate determinations of ε. It may be concluded that, even if traces of water are present in the solutions examined, ε is affected only to an extent within the expected error of the observations.

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