

NOTES

Infrared Characterisation of Zirconium(IV) Soaps

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Zirconium(IV) soaps (C_6 to C_{16}) were prepared by metathesis and their characteristics in the solid state were studied by the infrared technique to obtain the structural information.

The surfactants have been characterised and identified in the solid state and information on their structures has been obtained using infrared spectroscopy which has been found to be the most successful tool to analyse the molecular structure¹⁻³. Although Zr(IV) soaps have been prepared⁴⁻⁶ by treating an aqueous Zr(IV) salt solution with aqueous alkali soap of fatty acid, their IR studies have not been reported. In this communication Zr(IV) soaps (C_6 to C_{16}) have been prepared and their purity tested by IR techniques.

AnalaR (BDH) $Zr(NO_3)_4$, *n*-caproic, caprylic, capric, lauric, myristic and palmitic acids were used. The fatty acids were purified by distillation under reduced pressure and their purity was confirmed by determination of melting and boiling points. Double distilled water was used throughout this work.

Soaps were prepared by the interaction of the metal salt solution in a small quantity of distilled water with a hot solution of sodium soap, the latter being added dropwise while stirring at 50-55°C. The precipitate was filtered off and washed with hot water. It was recrystallised with benzene. After initial drying in an air oven ($100 \pm 5^\circ C$) final drying was carried out under reduced pressure.

Zirconium soaps are found to decompose on heating rather than melting and the decomposition temperatures ($^\circ C$) are recorded as 160.6, 150, 155, 200, 212.2 and 166.66 for caproate, caprylate, caprate, laurate, myristate and palmitate respectively.

The infrared spectral data of Zr(IV) soaps are shown in Table 1. In general the fatty acids forming these soaps exist as dimer⁷ in liquid as well as in solid state. The absorption due to —OH group occurs in the region of 3050-3000 cm^{-1} . The COO^- stretching vibrations of monomer saturated fatty acid occur in the region of 1720-1706 cm^{-1} . One of the characteristic bands of dimeric carboxylic acid results from the out-of-plane bending of OH^- group appearing near 920 cm^{-1} . The complete disappearance of the absorption bands near 1700 cm^{-1} in spectra of Zr(IV) soaps indicates that there is a complete resonance in the two carboxylate bands of carboxylic groups of soap molecules and the group has an ionic structure.

TABLE 1
 INFRARED ABSORPTION SPECTRAL FREQUENCIES (cm^{-1}) of Zr(IV) SOAPS WITH THEIR ASSIGNMENTS

Assignments	Caproate	Caprylate	Caprate	Laurate	Myristate	Palmitate
CH_2 , C—H, antisymmetrical stretching	2900 (vw)	2900 (vw)	2900 (vw)	2875–2850 (w)	2875 (m)	2850 (w)
CH_2 , C—H, symmetrical stretching	2800 (vs)	2800 (w)	2800 (s)	2800 (s)	2775 (w)	2775 (s)
COO^- , C—O, antisymmetrical stretching	1560–1525 (s)	1550–1510 (w)	1530–1510 (s)	1540–1510 (m)	1540–1505 (m)	1530–1510 (m)
COO^- , C—O, symmetrical stretching	1420 (s)	1410 (w)	1420 (s)	1430 (s)	1420 (m)	1410 (vs)
CH_2 (Adjacent to COOH group deformation)	1410 (s)	1410 (w)	1420 (s)	1420 (s)	1420 (m)	1420 (s)
CH_3 symmetrical	1350 (w)	1360 (vw)	1330 (w)	1345 (w)	1340 (w)	1330 (s)
Deformation progressive bands (CH_2 -twisting and wagging)	1310 (w)	—	1310 (w)	1305 (vw)	1300 (vw)	1300 (w)
CH_3 rocking	1080 (s)	1080 (w)	1075 (w)	1080 (vw)	1070 (vw)	1070 (w)
$\nu(\text{Zr—O})$	610 (s)	600 (w)	630 (w)	630 (vw)	610 (vw)	610 (vw)

m = medium; s = strong; w = weak; vs = very strong; vw = very weak.

The appearance of two absorption bands of the carboxylic group corresponding to the symmetric and asymmetric vibrations of the carboxylate ion at 1430–1410 cm^{-1} and 1560–1505 cm^{-1} in the spectra of soaps instead of one band of the carboxyl group at 1700 cm^{-1} in the fatty acid confirm the formation of soaps. These soaps show no peak between 3650–3590 cm^{-1} due to the absence of water of crystallization. The mode of coordination and eventually the molecular structure on the basis of $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ and $\Delta\nu(\nu_{\text{as}}\text{COO}^- - \nu_{\text{s}}\text{COO}^-)$ measurements can be proposed. If the COO^- frequencies of the Zr(IV) soaps are compared it is evident that these frequencies are not shifted much by the increase in chain length. Therefore Zr—O (carboxylate) bond strength can be presumed to be approximately the same and thus could not cause any difference on $\nu_{\text{s}}(\text{COO}^-)$ and $\nu_{\text{as}}(\text{COO}^-)$.

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REFERENCES

1. D. Humme, Identification and Analysis of Surface Active Agents by Infrared and Chemical Methods, Interscience, New York (1962).
2. K.M. Mehrotra, Tenside Detergents, **17**, 304 (1980); **19**, 92 (1982); **19**, 290 (1982); *J. Macromol. Sci. Chem.*, **19A**, 181 (1983).
3. V.P. Mehta, M. Hasan and L.C. Heda, *J. Macromol. Sci. Chem.*, **17A**, 513 (1982).
4. Nippon Mining Co. Ltd., Nippon Oils and Fats Co. Ltd., Japan Kokai Tokkyo Koho JP, 76,70,205 (Dec. 14, 1974).
5. Nippon Mining Co. Ltd., Japan, Kokai Tokkyo Koho JP, 57–116,020 (Jan. 10, 1981).
6. W.B. Blumethal, U.S. 2,802,847 (Aug. 13, 1957).
7. R.J. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, Prentice-Hall of India Pvt. Ltd., New Delhi, p. 46 (1969).

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