

ground state frequencies has been found with the Raman frequencies of the molecule.

A comparison of these spectra with those of phenol and of the corresponding chlorophenols has revealed many interesting features. These are under investigation with spectrographs of higher dispersion and resolution. A detailed investigation of these spectra and their analyses will be published shortly.

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Surface-active Characteristics of Sodium Salts of Anacardic Acids of Varying Unsaturation

CASHEW nut (*Anacardium occidentale* Linn.) shell liquid chiefly consists of anacardic acid, an *ortho*-carboxymeta-alkyl phenol. Earlier workers¹⁻³ have shown that the unsaturated alkyl side-chain in the acid consists of 15 carbon atoms and that the acid is a mixture of saturated and mono-, di-, and tri-olefinic compounds, in proportions that give, on average, about two double bonds per molecule. Properties of the sodium salt of the whole anacardic acid have been reported earlier⁴⁻⁶. However, considerable interest remains in the examination of surface-activity unsaturation relationship in the anacardic acid series. The work recorded here is an extension of previous work⁵ on whole anacardic acid.

In the present investigation, low-temperature fractionation and chromatographic resolution were used as tools for segregating anacardic acid into fractions. Anacardic acid with iodine value 124.7 (as determined by the method of Kale and Kamath⁷) and corresponding to 1.689 double bonds per molecule (on the basis of iodine value of mono-olefinic anacardic acid which is 73.82) was taken as the starting material and was separated into five different fractions *A*, *B*, *C*, *D* and *E* having their iodine values 50.66, 103.00, 125.80, 140.90 and 162.4, respectively.

For evaluating comparative surface-active properties, tetrahydro-anacardic acid (THA) with zero iodine value (obtained by hydrogenating anacardic acid in alcoholic medium in presence of platinum catalyst, followed by repeated crystallization from ligroin) and the fractions *B* (nearly mono-unsaturated acid), *D* (nearly di-unsaturated acid) and *E* were chosen.

The acids were separately converted into disodium salts⁵ and their various surface-active properties were examined:

(a) Surface tension at 30° C (determined by Du Nouy's tensiometer) of 0.01 per cent solutions of the disodium salts of THA and of the fractions *B*, *D* and *E* were 31.2, 41.0, 43.0 and 45.0 dynes/cm respectively.

(b) While the interfacial tension of water against *n*-heptane was 39.39 dynes/cm at 30° C (determined by the Stalagmometer method), 0.01, 0.02, 0.05 and 0.10 per cent sodium tetrahydroanacardate in aqueous solution lowered the values to 24.33, 14.33, 8.53 and 4.79 dynes/cm respectively. The values for fraction *B* were 28.38, 15.81, 5.18 and < 1.00 dynes/cm and those for fraction *E* were 37.38, 25.85, 12.38, 8.73 dynes/cm respectively.

(c) The critical micellar concentration of the fractions *B*, *D* and *E* as determined by the conductance-concentration curve method (for details, see previous communications⁵) were 0.032, 0.052 and 0.06 per cent solution.

(d) Emulsification test (with *n*-heptane) and foam-height experiments were conducted according to procedures already outlined⁶. The volumes of emulsified layers after shaking 15 ml. of 0.1 per cent solutions of sodium salts of

THA and of the different fractions with 5 ml. of *n*-heptane for 1 h were 5.4 ml., 5.6 ml., 5.5 ml., and 5.4 ml. respectively. Foam heights 1 min after the complete discharge of the foregoing solutions were 12.4, 14.8, 14.5 and 15.2 cm respectively.

The results presented here reveal that whereas at low concentration, namely, 0.01 per cent, saturated- or tetrahydroanacardic acid is most surface-active, surface activity of unsaturated products is more manifest at comparatively higher concentrations. The rule that critical micellar concentration increases with unsaturation in a homologous series⁸ is found valid in the sodium anacardate series.

As unsaturation increases, emulsifying and foaming characteristics undergo a slight increase and then a slight fall. Neither the saturated nor the most unsaturated anacardate gives the best surface-active and bulk properties; optimum hydrophilic-lipophilic balance lies near the mono- and di-unsaturated anacardate. The whole anacardic acid as such is a good surfactant as shown before^{5,6}; its unsaturation falls more or less in the optimum hydrophilic-lipophilic balance zone.

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Thermal Decomposition of Benzyl Borate

In recent years, the mechanism of the thermal decomposition of esters has been thoroughly investigated, and at the present time extensive evidence has been presented to support a *cis* elimination pathway¹. A similar mechanism was also suggested to explain the pyrolysis of borate esters²⁻⁴; however, the recent work of Chapman and Borden⁵ has disclosed the carbonium ion nature of this decomposition.

In an investigation of the secondary decomposition mechanisms in the pyrolysis of esters, the degradation of the borate of benzyl alcohol was attempted. This carbinol is of some interest, since it cannot undergo the normal elimination reaction. The experimental method developed by O'Connor and Nace³ was used in the decomposition. A mixture of benzyl alcohol (5.00 g, 0.046 mole) and boric acid (2.85 g, 0.046 mole) was slowly heated to 140°. The mixture was then kept at this temperature for 2 h. After this time, the temperature of the heating bath was slowly raised to 300°–310°. Decomposition was complete after 1 h. The crude products were then dissolved in benzene and chromatographed on alumina. Elution with benzene-hexane afforded anthracene (0.860 g, 21 per cent), and a yellow gum (2.73 g).

In contrast to the borate, the thermal decomposition of benzyl acetate⁶ and benzoate^{7,8} has been investigated, and the major products of these decompositions are benzaldehyde, toluene, and the corresponding anhydride. There is some evidence of a bimolecular decomposition in