

APPENDIXPreparation and Purification of n-Long Chain Alcohols and n-Alkoxy Ethanols.

Since the surface properties of the long chain surface active materials are highly sensitive to impurities, it is desirable to prepare these compounds in a very pure form for a study of their physical chemical study. The details of the method of preparation and of purification of the compounds used in the present investigation are described in the following.

Purification of n-long chain alcohols.

$C_{16}-H_{33}OH$, $C_{18}-H_{37}OH$ and $C_{20}-H_{41}OH$, commercially available good quality materials (Fluka make), have been rigorously purified by the cyclic method of crystallisation, acetylation, distillation and hydrolysis. The material, after repeated crystallisation from pure dry acetone, gave white crystalline product with a constant melting point. This alcohol was then subjected to acetylation, using 2 mols. of pure acetic anhydride and 1.5 mol. of anhydrous sodium acetate (B.D.H.). The reaction mixture is treated with hot water and acetate of the alcohol finally obtained, was purified by careful fractional distillation. Middle fraction distilling at a constant temperature was collected and it gave a single peak in the G.L.C. analysis. The above fraction was then deacetylated by refluxing with 2N alcoholic alkali and then the material was finally redistilled under vacuum. The purity of these compounds after crystallisation was checked by G.L.C. and was found to be better than 99.9%.

$C_{22}H_{45}OH$: Behenyl alcohol (Docosanol) which could not be obtained commercially was prepared by alcoholysis of refined mustard oil using ethyl alcohol containing sulphuric acid as catalyst to convert fatty acids to ethyl esters. These esters are fractionated by vacuum distillation and the last fraction comprised of ethyl behenate was hydrogenolysed at $250^{\circ}C$ in the presence of copper chromite catalyst under a hydrogen pressure greater than 200 kg/sq.cm. The alcohol thus obtained was filtered in hot condition and distilled. The product was found to be 95% pure. Further purification was effected by repeated crystallisation and fractionation of the acetate derivative as followed in case of other alcohols to obtain 99.9% pure material.

Preparing alkoxy ethanols: The pure alcohols were brominated by bubbling dry, pure HBr (obtained by adding liquid bromine to tetralin). The alcohol was heated to about $110^{\circ}C$ to remove most of the water formed. The bromide, extracted with petroleum-ether, was freed of the unreacted alcohol by sulfation, followed by washing of the alcohol sulphates by methanol and subsequently by distilled water after neutralising the reaction mixture with aqueous ammonia. The bromide was recovered by stripping with petroleum ether and purified by vacuum distillation. Pure bromides were condensed with 1 mole of monosodium glycolate by adding requisite amount of sodium to large excess of ethylene glycol. The reaction temperature was varied with the chain length of the alkyl bromide, viz. 140° - 180° from C_{16} to C_{22} . The reaction time was 70-100 hours. The reaction product was extracted with petroleum ether, when ethylene glycol

and sodium bromide separated. The portion of the reaction product soluble in petroleum ether contained ethylene glycol monoalkyl ether along with dialkyl ether and 1 alkenes as a result of side reactions. The alkenes distilled over as a first liquid fraction. The middle fraction (solid at room temperature) contains the major component, i.e. mono-ether, while di-ether remains as residue in the distillation flask. The mono-ethers are lastly crystallised several times from petroleum ether (60-80°C). The purity was checked by G.L.C. The C₁₆- and C₁₈-alkoxy ethanols prepared gave purity of 99.9% while C₂₀- and C₂₂- ethanols were 98% pure.

TABLE XI

Compound	Purity by GLC %	M.pt. by capi- llary °C	Mol. wt.	Compound	Purity by GLC %	M.pt. by capi- llary °C	Mol. wt.
C ₁₆ -OH	99.9	49.7	242.43	C ₁₆ -OC ₂ H ₄ OH	99.9	42.7	286.48
C ₁₈ -OH	99.9	58.5	270.48	C ₁₈ -OC ₂ H ₄ OH	99.9	51.2	314.53
C ₂₀ -OH	99.9	64.9	298.53	C ₂₀ -OC ₂ H ₄ OH	98.0	59.8	342.58
C ₂₂ -OH	99.9	70.3	326.58	C ₂₂ -OC ₂ H ₄ OH	98.0	64.4	370.64