

NONIONIC SURFACTANTS

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CHAPTER 22

CONFIGURATION OF THE POLYOXYETHYLENE CHAIN IN BULK

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22.1. INTRODUCTION

Studies of polyoxyethylene compounds in their bulk form have been the subject of several recent investigations for the elucidation of the configuration and fine-structure of the polyoxyethylene chain. Although it is not yet possible to present a definite picture of the structure of the polyoxyethylene chain based on these results, important conclusions and speculations can be made. The phenomenological part is covered first in Sections 22.2 to 22.4, followed by a speculative part in Section 22.5. Finally, in Section 22.7 an attempt is made to summarize in the light of our present knowledge the concepts of the configuration of the

polyoxyethylene chain in polyoxyethylene or its derivatives, such as nonionic surfactants, making allowance for some inherent uncertainties.

Our experimental knowledge of the "configuration of the polyoxyethylene chain in bulk" is mainly based on X-ray investigations. Therefore, in this chapter, results from X-ray investigations which have contributed so significantly to the general understanding of the configuration and fine-structure of organic chain-molecules are covered extensively in Sections 22.2 to 22.4. Besides the so-called short-distance- or wide angle-diffraction techniques, principally the low-angle-diffraction patterns have contributed to the characterization of the structure and dimensions of organic chain molecules. It is well-known that the crystal or crystallite structure as well as the unit cell dimensions in high-molecular-weight substances can be determined from both wide- and low-angle-diffraction patterns of the same object. Since the X-ray method has only recently been applied more extensively to investigations of nonionic surfactants, it appears desirable to review briefly in Section 22.3 our extensive knowledge from the preceding X-ray investigations of ionic surfactants.

The investigation of the fine structure of the polyoxyethylene chain by alternate experimental methods is covered in Section 22.6. Another object of this chapter, besides the specific discussion of nonionic surfactants, is also to review general concepts applicable to the fine-structure of paraffin chain compounds.

22.2. X-RAY INVESTIGATIONS OF ORGANIC CHAIN-MOLECULES

Early work has led to the generally accepted zigzag structure of paraffin-chain compounds, in which the centers of the C atoms lie in one plane and the distance between alternate CH_2 groups in the backbone chain amounts to 2.5 Å (1-3). This was followed by a complete structural analysis of the unit cell of paraffins (4-7). The paraffin chains are parallel to the c axis of the orthorhombic (odd number of C atoms) unit cell or of the monoclinic (even number of C atoms) unit cell with a cross-sectional area of 18.5 Å², lateral distances d_1 of 3.7 and 4.1 Å, and a distance of 3.5 Å between the CH_3 groups in the terminal positions of paraffin-chain layers.

Figure 22.1 presents the fine-structure of the paraffin chain. It is worth noting in connection with the subsequent considerations of polyoxyethylene derivatives that Mueller and Shearer in 1923 discussed various configurations of the paraffin chain, namely the zigzag, the screw, and a kind of meander structure (8). The schematic configuration of paraffin chain layers is illustrated in Figure 22.2, together with the reflections of the long period of paraffin chains.

Similarly, a lamellar crystal structure comparable to that of paraffins has been found for fatty acid esters and high-molecular-weight ketones (9). Although some analogy with paraffin chains exists, a difference in chain orientation was observed with the high-molecular-weight ketones, and especially with the fatty acids, and is illustrated in Figure 22.3. Dimers of carboxyl groups (linked by hydrogen bridges) connect the layers of paraffin chains, and the distance between the layer planes corresponds to two rather than one molecular length as determined from

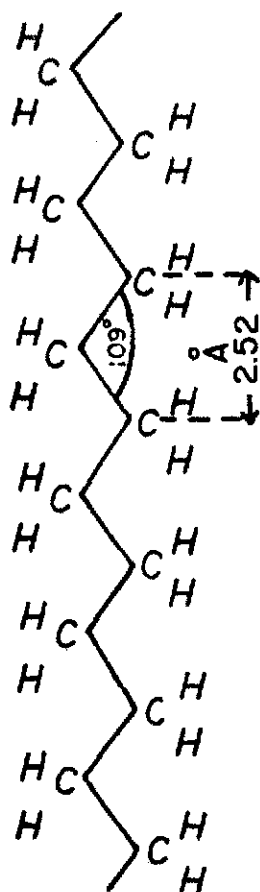


Fig. 22.1. Fine structure of paraffin chain.

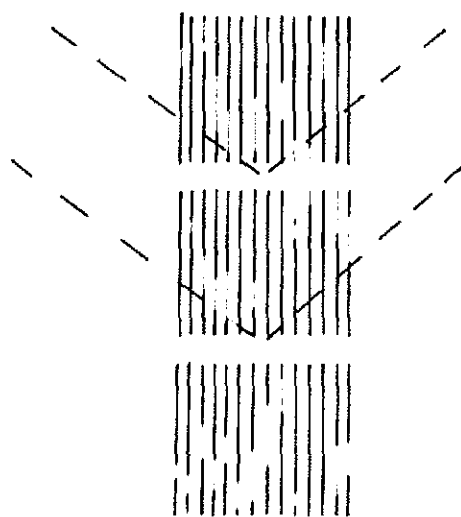


Fig. 22.2. Schematic arrangement of paraffin chains.

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