CHAPTER 2

Properties of Water in Capillaries and Thin Films

J. Clifford

Unilever Research Port Sunlight Laboratory
Wirral, Cheshire, England

1. INTRODUCTION

One of the most controversial aspects of the study of water is research into its properties when present in capillaries and thin films, and the interpretation of these properties in terms of the effect of surfaces on water structure. The surface of a liquid can be considered to be a "fault" in its structure and, in principle, there can be no doubt that the presence of a boundary must influence to some extent the properties of the liquid near it. It has often been supposed that for a highly structured liquid like water the effect may be larger and more dependent on the nature of the surface than for a less structured liquid.

In addition, it has been suggested that the properties of water in the presence of surfaces depend not only directly on the interaction of the surface with water but also on the distance between adjacent surfaces, i.e., on the extent of the water domain. This concept is based on the idea that the structure which determines the properties of bulk water can only exist if a certain minimum number of water molecules can take part in it. The magnitude, range, and permanence of these effects on properties have been much debated, and water in thin films, pores, or capillaries has been investigated to determine their nature and importance.

Among the first systematic experimental investigations were those by Hardy in 1912. In the 1920's and 1930's the investigations of Bangham, Griffiths, Bastow and Bowden, and Frumkin contributed...
much to this field but it has been Derjaguin and his co-workers who have
been most active in investigating the modification of water properties by
interfaces. Over the last forty years they have carried out very many
quantitative studies of the physical properties of liquids near surfaces.

In recent years the availability of spectroscopic and similar techniques
has resulted in studies of the molecular properties of liquids at interfaces
and in thin films, though these methods have often been hampered by the
need to develop special devices to make possible the investigation of the
small quantities involved. They have the advantage of providing informa­
tion directly about molecular rotations, vibrations, etc., and are free from
some of the assumptions involved in deriving molecular properties from
thermodynamic or bulk rheological measurements. It seems likely that the
main advances in the study of water in thin films in the next few years will
come through the use of such methods.

To an increasing extent, the practical importance of investigating the
effect of surfaces on water has been realized. The solution of many industrial
problems, connected, for example, with lubrication, corrosion, flotation,
foaming, emulsification, colloid stability, wetting, precipitation of obnoxious
materials from effluents, etc., depends in part at least on the understanding
of the properties of thin liquid layers. Postulated changes in the properties
of liquid near a surface have frequently been used as a convenient but
unverifiable explanation of differences between experimental results and
theoretical treatments, particularly in aqueous disperse systems, and the
need for a more productive approach is obvious.

Biological systems in particular involve chemical and physical inter­
actions in water in or near interfaces and if the structure and properties of
water are much influenced by the presence of surfaces, this must greatly
affect life processes. It has been postulated, for example, that all the
water in living cells is in a state profoundly different from normal water
and the ion selectivity of cells has been explained on this basis.

Another system in which thin water films may be of great practical
importance is ice. The existence of a thin liquid film on ice was first sug­
gested by Faraday and the concept has recently been used to explain
meteorological phenomena.

Another recent development has been the controversy about anomalous
water. It has been suggested that water condensed on to silica or glass
surfaces takes up a form which has a different structure and very different
properties from ordinary water and that it retains this form when removed
from the surface. Although its unusual properties are now generally attrib­
uted to the presence of impurities, the study of anomalous water has