Waterborne Coatings

Surface Coatings—3

Edited by

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CONTENTS OF VOLUME 1

CONTENTS OF VOLUME 2

Preface

Following the favourable reception of *Surface Coatings—1* and *—2*, the present volume has been prepared as the third in the series. The subject of surface coatings continues to undergo development, thanks to the ingenuity of researchers and technologists alike, and we offer this volume as an anthology of timely reviews of the subject.

In preparing this volume we have made a change in editorial policy. Instead of following the pattern of Volumes 1 and 2, and providing a wide coverage of a range of new technologies within the field, we have chosen to spread our net less widely. Accordingly, *Surface Coatings—3* is concerned exclusively with waterborne coatings. These materials are of growing importance in a world that is becoming ever more concerned about pollution. The adverse effects that arise from the indiscriminate use of technology are a subject of great importance in the technologically advanced nations of the world, and waterborne coatings have a role to play in reducing one important source of atmospheric pollution.

The present volume begins with a comprehensive outline of the chemical nature of water in a chapter by M. J. Blandamer; next, other fundamental physico-chemical aspects of the use of waterborne coatings are covered in the chapter by J. W. Nicholson and E. A. Wasson. These opening two chapters set the scene for a series of reviews of individual waterborne coatings technologies. Thus, Bunte salt polymers are covered by S. F. Thames, urethane dispersions by R. Arnoldus, loop emulsion polymerisation by K. R. Geddes, silicone emulsion paints by W. Sittenthaler, acrylic ionomers by J. W.

Nicholson and A. D. Wilson, and novel dispersing/curing agents for waterborne epoxies by F. B. Richardson. Lastly, striking a contrasting note, G. R. Hayward has prepared a chapter which outlines some of the problems associated with the use of waterborne coatings. This last chapter reminds us that there is still much to do and that scope remains for innovation in the field of environmentally friendly surface coatings. If this book stimulates effort in that direction, as we believe it will, then we have achieved our aim.

Finally, we wish to place on record our thanks to all our contributors for their co-operation and support in the preparation of this volume.

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ix

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Contents

Aqueous Solutions; Small Molecules

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1. INTRODUCTION

Water and aqueous solutions continue to fascinate chemists.[1] The major impetus for studying the properties of these systems comes from their environmental, economic and biological importance. The environmental importance is highlighted by the fact that most of the surface of this planet is covered by moderately concentrated aqueous salt solutions. The biological interest is linked with the observation that an adult human comprises over 40% by weight water. From an economic standpoint, industrial development and associated improvement in standards of living are accompanied by increased demand for potable water. This chapter sets the stage for subsequent chapters which consider the properties of aqueous solutions containing macromolecules. We start with a discussion of the properties of water, commenting on a model for the pure liquid. We use this model as a basis for a review of the properties of aqueous solutions containing neutral solutes[2] and salts.[3]

Chemists are not normally interested in the properties of water as such. Their interests centre on water as a medium in which to disperse other substances, solutes. A key requirement of a solvent is that it keeps solute molecules apart and trapped in local potential energy wells.[4] In so doing a solvent inhibits precipitation of solids, phase separation of liquid systems and escape to the gas phase of volatile solutes. At the same time, the potential energy wells must not be too deep, but should allow a measure of control with respect to the

tendency of solute molecules to come together and hence with respect to rates of chemical reactions in aqueous systems.[5–9]

The importance of aqueous solutions means that the amount of information concerning these systems is enormous and so is impossible to cover completely in a chapter of manageable size. Therefore we identify a number of important themes. For two reasons the discussion is biased towards thermodynamic properties of aqueous systems. First, thermodynamics provides the basis for analysing experimental results. Second, most theories of aqueous solutions are aimed at explaining trends in thermodynamic properties; e.g. solubilities and related hydration parameters. We concentrate attention on the properties of aqueous solutions at close to ambient temperatures and pressures. Of course, the properties of these systems remain equally fascinating at, for example, high pressures.[10] We also note the interest in the properties of water[11,12] and aqueous solutions at near-critical conditions,[13–15] where, for example, partial molar heat capacities of salts are extremely large.[15–21] Several interesting phenomena have been reported in conjunction with chemical equilibria and extent of reactions under close to critical conditions[22–24] where a crucial factor is the geometry of the thermodynamic surface near the critical point of the solvent.[25]

In a review of this length it is not possible to delve too deeply into the history of the subject. However, there are several landmarks. The foundation of many models of aqueous solutions is the seminal paper written by Bernal and Fowler[26] in 1933, followed more than a decade later by an important paper by Frank and Evans.[27] One of the most fascinating books on water was written around this time by Dorsey.[28] The paper by Frank and Wen[29] attracts considerable attention. Némethey and Scheraga[30] showed how qualitative ideas about the structure of aqueous solutions can be placed on a quantitative footing. The review by Franks and Ives,[31] with a recent update by Franks and Desnoyers,[32] brought developments in this subject to a wider audience. At about the same time, Robertson showed how activation parameters for chemical reactions involving solutes in aqueous solutions can be understood only in terms of the role of water ↔ water and water ↔ solute interactions.[33,34]

2. WATER MOLECULES AND HYDROGEN BONDING

The dimensions,[35,36] energies and spectroscopic properties[35] of an isolated water molecule are well established. The OH bond is strong,
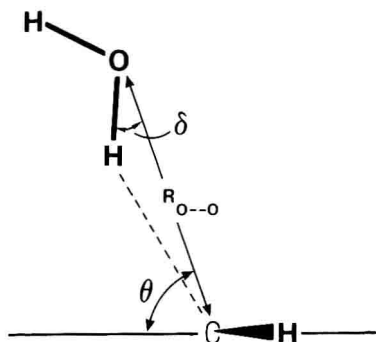
FIG. 1. *Trans* near-linear dimer for two hydrogen-bonded water molecules; distance $R(O—O) = 298$ pm with $\theta = 60 \pm 10$ and $\delta = 0 \pm 10°$; redrawn from Ref. 40.

the average bond energy (at 0 K) being 460 kJ mol^{-1}. The HOH angle is $104\cdot523°$ and the OH bond length is $95\cdot72$ pm. Both bond angle and length differ in the isotopic derivatives.[36] This simple non-linear molecule associates to form dimers via hydrogen bonding.[37–40] One stable structure for dimers is the *trans* near-linear dimer[40] (Fig. 1). The energy of this hydrogen bond is approximately 22 kJ mol^{-1}; indicating a strong cohesive interaction.[41,42] However, when a hydrogen bond forms between two nearest-neighbour water molecules, their centres of mass move apart. In these terms, hydrogen bonding has an important repulsive component. Within the context of aqueous solutions, this feature of hydrogen bonding is extremely important. It means that a water molecule which is strongly hydrogen bonded to a neighbouring water molecule is in a region which has low local density.[43] Further, if, as a consequence of adding a solute to water, water–water interactions are enhanced then a change occurs from high to low local density. The possibility that strong cohesion produces low local density, high volume is almost unique to water. An equally important feature is the co-operative aspect of hydrogen bonding; i.e. energies of this interaction are not additive.[44,45] In terms of spectroscopic properties, formation of hydrogen bonds between water molecules produces large changes in frequencies of O—H stretching modes and associated extinction coefficients in the IR region.[46,47]

3. ICE

The space-filling potential of hydrogen-bonded water molecules is illustrated by Fig. 2, which shows a pentameric unit, four water molecules being hydrogen-bonded to a central water molecule.[36,48]

FIG. 2. Pentameric unit; shaded circles represent hydrogen atoms and open circles represent oxygen atoms; $d(O \cdots O) = 274$ pm and $d(O \cdots H) = 101$ pm; redrawn from Ref. 36.
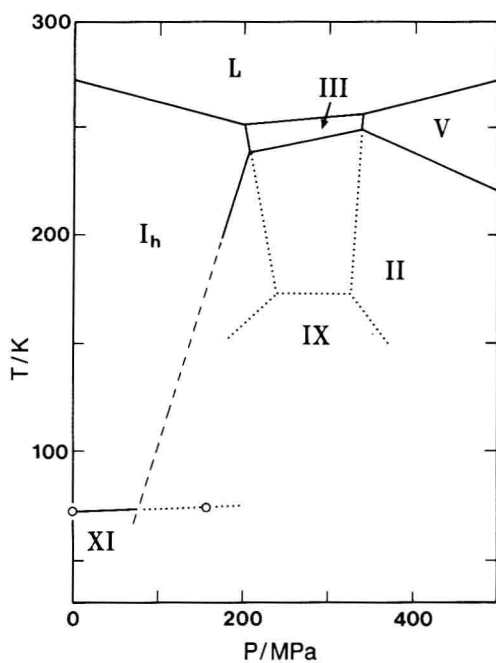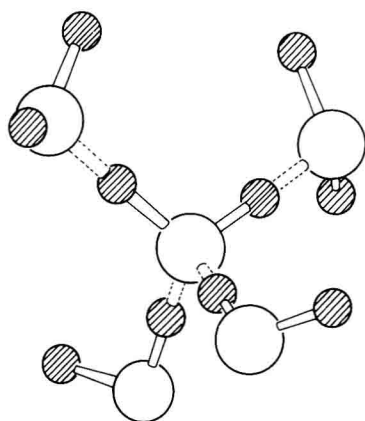

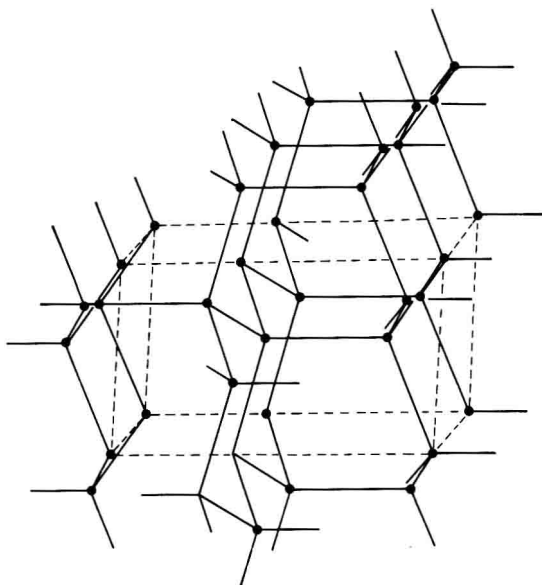FIG. 3. Phase diagram; redrawn from Ref. 52.

FIG. 4. Ice-Ih; oxygen positions are located at the vertices; redrawn from Ref. 2.

These elementary units assemble in various ways to form many different structures. Common ice, ice-Ih, has an hexagonal unit cell.[48,49] Eleven polymorphs are described in the phase diagram for ice, ice-XI being a recently discovered phase.[50–53]

Part of the phase diagram is shown in Fig. 3. There are also several metastable forms; e.g. ice-Ic and ice-IV. Some of the high-pressure polymorphs comprise interlocked (i.e. interpenetrating) but not inter-connected networks; e.g. ice-VI, -VII and -VIII. The oxygen positions in ice-Ih are shown in the structure given in Fig. 4. Many of the interesting properties of this polymorph stem from the disordered proton configuration. On a time-averaged basis, there are two half-hydrogen atoms on each O—O link. This half-hydrogen model accounts for the zero-point entropy, the high electric permittivity and complicated vibrational spectra of ice-Ih.[54]

Although ice-Ih is the stable phase, below 273·15 K and at ambient pressure, liquid water can be supercooled to around 243 K.[55] With fall in temperature below 273 K, the molar volume (continuing the trend

from the temperature of maximum density), the isothermal compressibility and the relative electric permittivity increase. In addition, the isobaric heat capacity increases with decrease in temperature.[56] Compressibility and heat capacity data point to a singularity near 228 K. This singularity reflects the intrinsic thermodynamic instability of supercooled water, any local fluctuation, linked with turbulence,[57] leading to nucleation[55,58] and hence solidification.

4. CLATHRATE HYDRATES

There is no critical point associated with solid–liquid phase boundaries comparable to those observed for the liquid–vapour phase boundaries. In other words, transitions from solid to liquid always require that a phase boundary is crossed. Nevertheless, considerable speculation is generated by the possibility that structures similar to one or more of the ice polymorphs exist in the liquid. In exactly the same way, the structures of clathrate hydrates and related systems arouse speculation that similar organisations exist in the corresponding aqueous solutions.[59,60] Groups of hydrogen-bonded water molecules can form pentagonal dodecahedra[59] (Fig. 5). These structures could occur in liquid water.[6]

In the solid state, dodecahedra cannot fill space regularly, and so voids are formed in which guest molecules are trapped; e.g. chlorine. Simple clathrate hydrates are either structure I or II systems. The unit cell of a structure I hydrate comprises 46 water molecules forming two small and six large holes (Fig. 6). If these eight sites are filled by guest
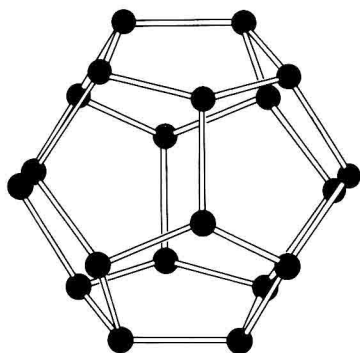

FIG. 5. Oxygen positions in a pentagonal dodecahedron formed by water molecules; oxygen atoms at the vertices; redrawn from Ref. 2.