

Contents

Contents of Volume 1	xv
Contents of Volume 3	xvi
Contents of Volume 4	xvii

Chapter 1

The Solvent Properties of Water

F. Franks

1. Water, the Universal Solvent—the Study of Aqueous Solutions	1
2. Aqueous Solutions of Nonelectrolytes	5
2.1. Apolar Solutes	6
2.2. Polar Solutes	19
2.3. Ionic Solutes Containing Alkyl Residues—“Apolar Electrolytes”	38
3. Aqueous Solutions of Electrolytes	42
3.1. Single Ion Properties	42
3.2. Ion–Water Interactions	43
3.3. Interionic Effects	47
4. Complex Aqueous Mixtures	48

Chapter 2

Water in Stoichiometric Hydrates

M. Falk and O. Knop

1. Introduction	55
2. Symmetry and Types of Environment of the H ₂ O Molecule in Crystals	57

2.1.	Site Symmetry	57
2.2.	Consequences of the Low Symmetry of the H ₂ O Molecule	57
2.3.	Types of Environment	59
2.4.	Water Networks in Hydrates	61
3.	Information from X-Ray and Neutron Diffraction	63
3.1.	Quality of the Data	63
3.2.	Hydrogen Bonding	70
3.3.	Electron-Acceptor Coordination	80
3.4.	Internal Geometry of the H ₂ O Molecule	84
4.	Information from Vibrational Spectroscopy	88
4.1.	Vibrations of Water Molecules in Crystals	88
4.2.	Site Symmetry of the Water Molecules and Their Equivalence	95
4.3.	OH and OD Stretching Frequencies	102
4.4.	Bending Frequencies	107
4.5.	Librational Frequencies	108
4.6.	Translational Frequencies and the Cation-Water Interaction	109
4.7.	Band Intensities	110
4.8.	Bandwidths and Orientational Disorder	110
4.9.	Single-Crystal Spectra and the Orientation of Water Molecules in the Crystal	111
5.	Pseudohydrates	111
6.	Summary	112

Chapter 3

Clathrate Hydrates

D. W. Davidson

1.	Introduction	115
1.1.	Gas Hydrates: Historical Survey	115
1.2.	Gas Hydrates as Clathrates	119
1.3.	Classification of Clathrate Hydrates	120
1.4.	Tabulation of Clathrate Hydrate Properties	122
2.	Structures of the Lattices	128
2.1.	Hydrates of Structures I and II	128
2.2.	Hydrates I and II as Ices	132

2.3.	Bromine Hydrate	133
2.4.	“Ice VIII”	134
2.5.	Amine Hydrates	136
2.6.	Semiclathrate Hydrates of Peralkyl Ammonium and Other Salts	140
2.7.	Comparison of Clathrate and Semiclathrate Structures	145
3.	Thermodynamic Properties	146
3.1.	The Ideal Solution Model	146
3.2.	Determination of Hydrate Compositions	149
3.3.	Free Energies of the Lattices of Structures I and II	154
3.4.	Mixed Hydrates	156
3.5.	Enthalpies of Encagement and of the Empty Lattices	160
3.6.	Spherical Cell Models	161
3.7.	Lennard-Jones Model with Discrete Water Molecules	168
3.8.	Effect of Pressure on Hydrate Stability	171
3.9.	Lower Critical Decomposition Temperature	172
4.	Kinetic Properties of the Water Molecules	172
4.1.	Dielectric Properties of Ice Ih	173
4.2.	Dielectric Properties of Structure II Hydrates	174
4.3.	Relaxation Times of the Water Molecules in Structure II	178
4.4.	Dielectric Properties of Structure I Hydrates	179
4.5.	Relaxation Times of Water Molecules in Structure I	181
4.6.	Comparison with Dielectric Relaxation of the Ices Proper	182
4.7.	Outline of a Molecular Model of Relaxation of Ices and Hydrates	184
4.8.	Resolution of Structure II Dielectric Spectra into Discrete Relaxation Times	189
4.9.	Dielectric Properties of Amine Hydrates	191
4.10.	Dielectric Properties of Tetraalkyl Ammonium Salt Hydrates	195
4.11.	NMR Spectra of the Protons of the Water Lattices	195
4.12.	Infrared Spectra	201
5.	Motion of the Guest Molecules	201
5.1.	Contribution of Guest Molecules to the Static Per- mittivities (ϵ_{02})	202
5.2.	Behavior of ϵ_{02} at Low Temperatures	204
5.3.	Dielectric Relaxation of Guest Molecules	206

5.4.	Limiting Permittivities at Very Low Temperatures ..	210
5.5.	Electrostatic Fields of the Water Molecules	212
5.6.	Effect of Electrostatic Fields on Reorientation of Polar Guest Molecules	216
5.7.	Dipole–Dipole Interactions between Guest Molecules	217
5.8.	NMR Spectra of Guest Molecules	218
5.9.	Infrared Spectra	227
6.	Other Aspects of Clathrate Hydrates	228
6.1.	Preparation and Kinetics of Formation	228
6.2.	Natural Gas Hydrates	228
6.3.	Natural Occurrence of Clathrate Hydrates	229
6.4.	Uses of Clathrate Hydrates	230
6.5.	Related Structures	233
6.6.	Models of Liquid Water Structure	234

Chapter 4

Infrared Studies of Hydrogen Bonding in Pure Liquids and Solutions

W. A. P. Luck

1.	Introduction	235
2.	Methods of Infrared Spectroscopy for the Determination of Hydrogen Bonds	239
2.1.	Investigation of Hydrogen Bonds in Solution	245
2.2.	The Badger–Bauer Rule	264
2.3.	Distance Dependence of Hydrogen Bonds	270
2.4.	Angle Dependence of Hydrogen Bonds	272
2.5.	Matrix Technique	275
2.6.	Intramolecular Hydrogen Bonds	282
2.7.	Comparison of Hydrogen Bond Studies in the Fundamental Frequency Range and in the Overtone Regions	287
2.8.	Overtone Frequencies of Alcohols	293
2.9.	Assignment of the Side Bands of the Alcohols	297
2.10.	Alcohol Bands Due to Hydrogen Bonds	300
2.11.	Toward a Theory of the Hydrogen Bond	305
2.12.	Hydrogen Bonds in Pure Liquids	309
2.13.	Determination of Free OH Groups in Alcohols and in Water	314

*Chapter 5***Thermodynamic Properties**

F. Franks and D. S. Reid

1.	Introduction.....	323
1.1.	Classification of Solutes.....	328
2.	Binary Systems.....	330
2.1.	Infinitely Dilute Solutions.....	330
2.2.	Aqueous Solutions at Finite Concentration.....	356
2.3.	Dilute Solutions of Water in Nonelectrolytes.....	371
2.4.	Summary of Binary Systems.....	372
3.	Ternary Solutions.....	375
3.1.	Ternary Solutions Containing Both H ₂ O and an Apolar Solute.....	375
3.2.	Ternary Solutions Containing an Electrolyte.....	377
4.	Relevance to Biological Systems.....	380

*Chapter 6***Phase Behavior of Aqueous Solutions at High Pressures**

G. M. Schneider

1.	Introduction.....	381
2.	Liquid–Gas Equilibria.....	382
3.	Liquid–Liquid Equilibria.....	384
3.1.	Pressure Dependence of Critical Solution Temperatures in Binary Systems.....	384
3.2.	Extension to Ternary Systems and Influence of Added Salts.....	389
3.3.	Effect of Solid Phases.....	392
4.	Gas–Gas Equilibria.....	393
5.	Phase-Theoretical Aspects.....	398
6.	Thermodynamic Description.....	400
7.	Conclusions.....	403

*Chapter 7***Dielectric Properties**

J. B. Hasted

1.	The Static Dielectric Constants of Polar Liquids	405
2.	The Static Dielectric Constants of Nonelectrolytic Aqueous Solutions	412
3.	Calculation of Dipole Moments of Solutes	427
4.	Some Discussion of Experimental Techniques	431
5.	Dielectric Relaxation of Polar Liquids	436
6.	Dielectric Relaxation of Aqueous Mixtures.....	441
	6.1. Hydration Sheaths of Long Lifetime	455
7.	Conclusions	456

*Chapter 8***Spectroscopic Properties**

M. J. Blandamer and M. F. Fox

1.	Introduction.....	459
2.	Experimental Investigations	462
	2.1. Spectra of Water in Aqueous Solutions.....	462
	2.2. Spectra of Solutes in Aqueous Solutions	465
	2.3. Spectra of Probes in Aqueous Solutions	466
	2.4. Electron Spin Resonance Spectra of Radicals in Aqueous Solutions	471
3.	Interpretation of Experimental Data	474
	3.1. Typically Aqueous Mixtures	476
	3.2. Typically Nonaqueous Mixtures	492

*Chapter 9***Acoustic Properties**

M. J. Blandamer

1.	General Introduction	495
2.	Experimental Techniques	499
3.	Presentation of Experimental Results	502

4.	General Survey of Acoustic Properties of Liquid Mixtures	504
5.	Water	507
6.	Aqueous Solutions Containing Urea	507
7.	General Features in the Absorption Properties of Typically Aqueous Mixtures	509
	7.1. Low Cosolvent Mole Fractions	509
	7.2. Region of Excess Absorption: PSAC Region	510
	7.3. Temperature Dependence: PSAC Region.....	514
	7.4. Frequency Dependence: PSAC Region.....	514
8.	Typically Nonaqueous Mixtures	515
9.	Interpretation of Ultrasonic Data	516
	9.1. Low Cosolvent Mole Fractions	516
	9.2. The PSAC Region	518

Chapter 10

NMR Spectroscopic Studies

M. D. Zeidler

1.	Theoretical Background for the Interpretation of NMR Parameters	529
	1.1. Relaxation Rates	529
	1.2. Spin-Echo Self-Diffusion Constants	537
	1.3. Chemical Shifts.....	538
2.	Experimental Results and Interpretation of Data	540
	2.1. Aqueous Solutions of Nonelectrolytes	540
	2.2. Aqueous Solutions of Electrolytes with Alkyl Groups	567
3.	General Conclusions Obtained from NMR Spectroscopic Studies	573

Chapter 11

Molecular Theories and Models of Water and of Dilute Aqueous Solutions

A. Ben-Naim

1.	Introduction.....	585
2.	The Mixture Model Approach	587
	2.1. Introduction.....	587
	2.2. A Discrete Mixture Model	588

2.3. A Continuous Mixture Model	594
2.4. An Exact Two-Structure Model	598
2.5. Embedding Existing Models into a General Framework	600
3. Structure of Water and Structural Changes	604
3.1. Possible Definitions of the “Structure of Water”..	604
3.2. Structural Changes and Thermodynamics	605
3.3. Distribution of Local Structure around a Solute....	611
4. Example of a Simple Solvable Two-Structure Model.....	613
4.1. Motivation	613
4.2. Description of the Model and Its Solution.....	615
5. Conclusion	622
References	625
Subject Index	663
Compound Index	675
Formula Index	683