

Contents

1	Introduction	1
2	Solute-Solvent Interactions	7
2.1	Solutions	7
2.2	Intermolecular Forces	12
2.2.1	Ion-Dipole Forces	13
2.2.2	Dipole-Dipole Forces	14
2.2.3	Dipole-Induced Dipole Forces	15
2.2.4	Instantaneous Dipole-Induced Dipole Forces	16
2.2.5	Hydrogen Bonding	17
2.2.6	Electron-Pair Donor/Electron-Pair Acceptor Interactions (EPD/EPA Interactions)	23
2.2.7	Solvophobic Interactions	31
2.3	Solvation	34
2.4	Preferential Solvation	43
2.5	Micellar Solvation (Solubilization)	48
2.6	Ionization and Dissociation	52
3	Classification of Solvents	65
3.1	Classification of Solvents according to Chemical Constitution	65
3.2	Classification of Solvents using Physical Constants	75
3.3	Classification of Solvents in Terms of Acid-Base Behaviour	88
3.3.1	Brønsted-Lowry Theory of Acids and Bases	88
3.3.2	Lewis Theory of Acids and Bases	93
3.4	Classification of Solvents in Terms of Specific Solute/Solvent Interactions	96
3.5	Classification of Solvents using Multivariate Statistical Methods	99
4	Solvent Effects on the Position of Homogeneous Chemical Equilibria	107
4.1	General Remarks	107
4.2	Solvent Effects on Acid/Base Equilibria	109
4.2.1	Brønsted Acids and Bases in Solution	109
4.2.2	Gas-Phase Acidities and Basicities	114
4.3	Solvent Effects on Tautomeric Equilibria	121
4.3.1	Solvent Effects on Keto/Enol Equilibria	121
4.3.2	Solvent Effects on Other Tautomeric Equilibria	128
4.4	Solvent Effects on Other Equilibria	136
4.4.1	Solvent Effects on Brønsted Acid/Base Equilibria	136
4.4.2	Solvent Effects on Lewis Acid/Base Equilibria	138
4.4.3	Solvent Effects on Conformational Equilibria	142
4.4.4	Solvent Effects on <i>cis/trans</i> or <i>E/Z</i> Isomerization Equilibria	148
4.4.5	Solvent Effects on Valence Isomerization Equilibria	150
4.4.6	Solvent Effects on Electron-Transfer Equilibria	153
4.4.7	Solvent Effects on Host/Guest Complexation Equilibria	156

5 Solvent Effects on the Rates of Homogeneous Chemical Reactions	165
5.1 General Remarks	165
5.2 Gas-Phase Reactivities	173
5.3 Qualitative Theory of Solvent Effects on Reaction Rates	180
5.3.1 The Hughes–Ingold Rules	181
5.3.2 Solvent Effects on Dipolar Transition State Reactions	192
5.3.3 Solvent Effects on Isopolar Transition State Reactions	206
5.3.4 Solvent Effects on Free-Radical Transition State Reactions	220
5.3.5 Limitations of the Hughes–Ingold Rules	235
5.4 Quantitative Theories of Solvent Effects on Reaction Rates	239
5.4.1 General Remarks	239
5.4.2 Reactions between Neutral, Apolar Molecules	240
5.4.3 Reactions between Neutral, Dipolar Molecules	246
5.4.4 Reactions between Neutral Molecules and Ions	254
5.4.5 Reactions between Ions	255
5.5 Specific Solvation Effects on Reaction Rates	259
5.5.1 Influence of Specific Anion Solvation on the Rates of S _N and other Reactions	259
5.5.2 Protic and Dipolar Aprotic Solvent Effects on the Rates of S _N Reactions	265
5.5.3 Quantitative Separation of Protic and Dipolar Aprotic Solvent Effects for Reaction Rates by Means of Solvent-Transfer Activity Coefficients	277
5.5.4 Acceleration of Base-Catalysed Reactions in Dipolar Aprotic Solvents	282
5.5.5 Influence of Specific Cation Solvation on the Rates of S _N Reactions	285
5.5.6 Solvent Influence on the Reactivity of Ambident Anions	292
5.5.7 Solvent Effects on Mechanisms and Stereochemistry of Organic Reactions	298
5.5.8 Influence of Micellar and Solvophobic Interactions on Reaction Rates and Mechanisms	317
5.5.9 Liquid Crystals as Reaction Media	326
5.5.10 Solvent Cage Effects	331
5.5.11 External Pressure and Solvent Effects on Reaction Rates	336
5.5.12 Solvent Isotope Effects	343
5.5.13 Reactions in Biphasic Solvent Systems and in Neoteric Solvents	345
6 Solvent Effects on the Absorption Spectra of Organic Compounds	359
6.1 General Remarks	359
6.2 Solvent Effects on UV/Vis Spectra	360
6.2.1 Solvatochromic Compounds	360
6.2.2 Theory of Solvent Effects on UV/Vis Absorption Spectra	371
6.2.3 Specific Solvent Effects on UV/Vis Absorption Spectra	380
6.2.4 Solvent Effects on Fluorescence Spectra	384
6.2.5 Solvent Effects on ORD and CD Spectra	393
6.3 Solvent Effects on Infrared Spectra	397
6.4 Solvent Effects on Electron Spin Resonance Spectra	403
6.5 Solvent Effects on Nuclear Magnetic Resonance Spectra	410

6.5.1	Nonspecific Solvent Effects on NMR Chemical Shifts	410
6.5.2	Specific Solvent Effects on NMR Chemical Shifts	417
6.5.3	Solvent Effects on Spin-Spin Coupling Constants	422
7	Empirical Parameters of Solvent Polarity	425
7.1	Linear Gibbs Energy Relationships.....	425
7.2	Empirical Parameters of Solvent Polarity from Equilibrium Measurements.....	432
7.3	Empirical Parameters of Solvent Polarity from Kinetic Measurements ..	438
7.4	Empirical Parameters of Solvent Polarity from Spectroscopic Measurements.....	448
7.5	Empirical Parameters of Solvent Polarity from Other Measurements ...	481
7.6	Interrelation and Application of Solvent Polarity Parameters	483
7.7	Multiparameter Approaches	490
8	Solvents and Green Chemistry	509
8.1	Green Chemistry	509
8.2	Reduction of Solvent Use.....	511
8.3	Green Solvent Selection	513
8.4	Non-Traditional Solvents.....	514
8.4.1	Water	514
8.4.2	Supercritical Carbon Dioxide (sc-CO ₂)	529
8.4.3	Ionic Liquids.....	534
8.4.4	Polyethylene Glycols (PEGs).....	543
8.4.5	Biomass-Derived Solvents	544
8.5	Outlook	548
Appendix	549
A.	Properties, Purification, and Use of Organic Solvents.....	549
A.1	Physical Properties	549
A.2	Purification of Organic Solvents.....	556
A.3	Spectroscopic Solvents.....	557
A.4	Solvents as Reaction Media.....	562
A.5	Solvents for Recrystallization	563
A.6	Solvents for Extraction and Partitioning (Distribution)	570
A.7	Solvents for Adsorption Chromatography	572
A.8	Solvents for Acid/Base Titrations in Non-Aqueous Media.....	574
A.9	Solvents for Electrochemistry	578
A.10	Toxicity of Organic Solvents	578
References	587
Figure and Table Credits	675
Subject Index	677

