Chemical Process Analysis:

Chemometrics; Instrument Control; Applications in Equilibrium and Kinetic Investigations

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by

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Author's Declaration

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'…the best kind of knowledge to have is that which is learned for its own sake'

Dedication

This thesis is dedicated to my family.

Table of Contents

Abstract

This work presents the development and application of modern data acquisition and analysis techniques for the investigations of equilibrium and kinetic reactions. The analytical technique is known as second order global analysis and a background of this relatively novel approach has been given. The theory behind and characteristics of the computer programs developed analysis as part of this research are described in Chapter Two along with descriptions of the instrumentation and programs developed for the acquisition of both potentiometric and spectrophotometric data.

Applications of the developed programs include a potentiometric and spectrophotometric study of the protonation and stability equilibria of a series of polydentate N-donor ligands, as detailed in Chapter Three. The combination of potentiometric and spectrophotometric analysis has been shown to be a powerful analytical tool.

Spectrophotometric titrations were also combined with fast stop-flow experiments in order to elucidate the complex reaction mechanisms associated with helicating ligands. The helication of the ligand '$PepdaH_2$' with copper(II) and nickel(II) is examined in Chapter Four, along with discussions concerning the ability to induce chirality in the helicates from the addition of a chiral counter ion.

Investigations into chirality were further continued in Chapter Five where the stereoselectivity of a benzimidazole-based ligand was investigated with circular dichroism titrations. The synthesis and characterisation of the benzimidazole-based ligands are provided, including a study of the ability of the ligands to form higher order complexes as investigated using electrospray mass spectroscopy.

Chapter Six provides an in-depth discussion concerning the use of combined glass hydrogen selective electrodes for the determination of equilibrium constants, as this was a major focus of this research. Different calibration techniques are discussed and a description of the internal calibration technique developed is provided along with examples of the advantages of performing internal calibration of the electrode.

List of Abbreviations and Definitions

b.p.	Boiling point
Bispidinone	3,7-diazabicyclo[3.3.1]nonan-9-one
CD	Circular Dichroism
DMF	*N, N* –dimethylformamide
DMSO	Dimethyl sulphoxide
Dp-bispidinone	1,5-diphenyl-3,7-diazabicyclo[3.3.1]nonan-9-one
Dpdb-bispidinone	1,5-diphenyl-3,7-dibenzyl-3,7-diazabicyclo[3.3.1]nonan-9-one
EFA	Evolving Factor Analysis
ESMS	Electrospray Mass Spectroscopy
GA	Genetic Algorithm
^{1}H n.m.r.	Proton Nuclear Magnetic Resonance
I	Molar ionic strength ($I = \frac{1}{2} \sum z^2[Z]$) of all species in solution
ICD	Induced Circular Dichroism
IR	Infra-red
K_s	Ionisation constant of a solvent
K_W	Ionisation constant of water
LJP	Liquid Junction Potential
m.p.	Melting point
NBS	National Bureau of Standards
NGL/M	Newton-Gauss-Levenberg/Marquardt
NIST	National Institute of Standards and Technology
NMI	National Metrological Institutes
$PepdaH_2$	*N*,*N*'-bis[2-(2-pyridyl)methyl]pyridine-2,6-dicarboxamide
Piperazine	1,4-diazacyclohexane
Pizda	1-[(2"-hydroxycyclohexyl)-3'-aminopropyl]-4-[3'-aminopropyl]piperazine
Pot_Anal	Analytical Program for Potentiometric Titration Data
ProKII	Pro-Kineticist II
RLJP	Residual Liquid Junction Potential
Spec_Anal	Analytical Program for Spectrophotometric Titration Data
ssq	Sum of squared residuals

UV	Ultra-violet
x	Bold lower case characters for vectors
X	Bold upper case characters for matrices
x	Italic characters for scalars and chemical species
y_Z	Activity coefficient of a ±z charged species
[Z]	Molar concentration of species Z
{Z}	Activity of species Z
δ	Standard Deviation
μ	Ionic Strength (M)