

IONIC INTERACTIONS IN NON-AQUEOUS SYSTEMS

A spectroscopic study of the iodide ion under conditions of ion-pairing and pure solvation, and the effects of temperature and pressure on the spectra so observed

by

00000

R.H. Wijayanayake B.Sc., A.R.I.C.

ST
11
18
11/05
10/1/68

F108/2009/21E2

This thesis is presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy

80

242

University of Leeds

1968

56363

ABSTRACT

A comparison of current theories on C.T.T.S. spectra, with particular reference to basic assumptions and related phenomena, is considered. The influence of various factors including static dielectric constant, dipole moments of solvents and the electronic structure of ions on ion-solvent interactions is examined and the utility of solvent polarity scales is discussed. A review of the present concept of ion-pair formation is also given.

The combined effects of temperature and added salts on aqueous iodide spectra have been examined and the results are discussed in terms of the structure of the medium. The spectra of various iodides in several non-aqueous solvents of both high and low polarities have been investigated. The results show that iodides in solvents with static dielectric constant $(D) > 23$ are solvated. If D is < 5 but > 11 solvent shared ion-pairs are formed: between $D=11$ and $D=23$ iodide solutions contain various proportions of free ions and ion-pairs. A mathematical model is considered in order to evaluate the distances separating the charges in ion-pairs. The identity of the solvent shared ion-pair is substantiated.

A correlation between the static dielectric constant and various solvent polarity scales is obtained and the interesting inferences are discussed.

Pressure effects were also studied and the results are tentatively discussed in terms of increased ion-solvent and solvent-solvent interactions. At high temperatures and under pressure, ion-pair formation was detected in good solvating solvents.

1. Charge Transfer to Solvent	1
1.1 Theoretical Interpretation	2
1.1.1 'Confined' and 'Expanded' models	4
(a) 'Confined' model	
(b) 'Expanded' model	
1.2 Comparison of the 'Confined' and 'Expanded' models	8
1.2.1 Basic assumptions of the two models	9
1.2.2 The experimental observations and their agreement with the two models	10
(a) Solvent dependence	
(b) Temperature dependence	
(c) Pressure dependence	
(d) Effects of added salts	
(e) Oscillator strength calculations	
(f) Spectroscopic and solvated electrons	

CONTENTS

	Page
List of figures	i
List of tables	vii
CHAPTER ONE	
1: Charge Transfer to Solvent spectra	1
1.1 Theoretical interpretations	2
1.1.1 'Confined' and 'Expanded' models	4
(a) 'Confined' model	
(b) 'Expanded' model	
1.2 Comparison of the 'Confined' and 'Expanded' models	8
1.2.1 Basic assumptions of the treatments	8
1.2.2 The experimental observation and their agreement with the two models	10
(a) Solvent dependence	
(b) Temperature dependence	
(c) Pressure dependence	
(d) Effects of added salts	
(e) Oscillator strength calculations	
(f) F-centres and solvated electrons	

CHAPTER TWO

2: Ion-solvent interaction	22
2.1 Participation of solvents	22
2.1.1 Solvent structure	23
2.1.2 Influence of static dielectric constant	24
2.2 Behaviour of ions in solution	26
2.3 Generatization of solvent behaviour	28
(a) 'Solvent System Concept'	
(b) 'Cordination' model	
2.4 Solvent polarity scales	34
2.4.1 Rate constant determinations	37
(a) Y-values	
(b) K_S -values	
2.4.2 Spectrophotometric measurements	39
(a) Z-values	
(b) E_T scales	
2.5 Theories on solvent shifts	45
2.6 The structure of water	47
2.7 Effects of added ions on the structure of water	49

CHAPTER THREE

3: Ionic association	53
3.1 Effect of dielectric constant on ionic association	53
3.2 The concept of ion-pairs	54

3.2.1	From conductometric studies	54
3.2.2	A comparison of theory and experimental data	59
3.2.3	Thermodynamic approach	61
3.2.4	Other definitions	63

CHAPTER FOUR

4:	Scope of the present work	66
4.1	A further examination of the 'Confined' model	66
4.2	Use of the pressure cell	67
4.3	Ion-pair formation	67
4.4	Classification of solvents	67

CHAPTER FIVE

5:	Experimental Procedure	69
5.1	Apparatus	69
5.1.1	Spectrophotometers	69
	(a) Cary 14 H	
	(b) Unicam SP 500	
5.1.2	Pressure cell	71
	(a) Cell design	
	(b) Windows and the method of sealing	
	(c) Pressure transmission	
5.1.3	Other cells	74
	(a) Standard cells	
	(b) Variable path length cells	

	(c) A cell for high melting solvents	
5.1.4.1	Thermostats and temperature controllers	75
5.2	Spectrophotometric techniques	78
5.2.1	Cleaning of cells	78
5.2.2	Optimum operating conditions for the spectrophotometers	78
	(a) Hydrogen lamps	
	(b) Optical density maxima	
	(c) Multipot adjustment	
	(d) Scan speed	
5.2.3	Measurement of spectra	79
5.2.4	On using the pressure cell	80
5.2.5	Analysis of spectrophotometric data	80
	(a) Band profile	
	(b) Program One	
	(c) Program Two	
	(d) Program Three	
5.3	Preparation and purification of solutes	85
5.4	Purification of solvents	87
5.5	Criteria of purity	89
5.6	Preparation of solutions	90

CHAPTER SIX

6: Experimental results	94
6.1 Solvent dependence	95
6.1.1 Solvents showing no cation dependence	95
(a) $2p_{3/2} \longleftarrow 1s_0$	
(b) $2p_{1/2} \longleftarrow 1s_0$	
6.1.2 Solvents showing cation dependence	101
6.2 Effects of added salts	106
6.2.1 In non-aqueous solvents	107
6.2.2 In water	107
(a) Effects due to alkali chlorides and ammonium chloride	
(b) Effects due to tetra- n -alkylammonium chlorides	
6.3 Z-values	116
6.4 Effects of applied pressure	120
6.5 The combined effects of pressure and temperature	121

CHAPTER SEVEN

7: Discussion	124
7.1 'Smith-Symens' line	125
7.2 Structure in aqueous salt solutions	127