INVESTIGATION OF THE POLYMERIZATION AND COPOLYMERIZATION OF VINYLIMIDAZOLE

THESIS

Submitted for the Degree of Doctor of Philosoply

In

" **Physical Chemistry**"

By

SAKINA MOHAMED MOHAMED ABDEL_AZIZ

(B.Sc. 1982 , M.Sc. 1987)

S. 393

S. 1

Presented to

Chemistry Departement

Universty College for Girls

Ain Shams University

AIN SHAMS UNIVERSITY

1993

Central Library - Ain Shams University

INVESTIGATION OF THE POLYMERIZATION AND COPOLYMERIZATION OF VINYLIMIDAZOLE

THESIS ADVISORS

Prof. Dr. Essam Mohamed Ezzo.

Prof. Dr. Maher Zaki ElSabee

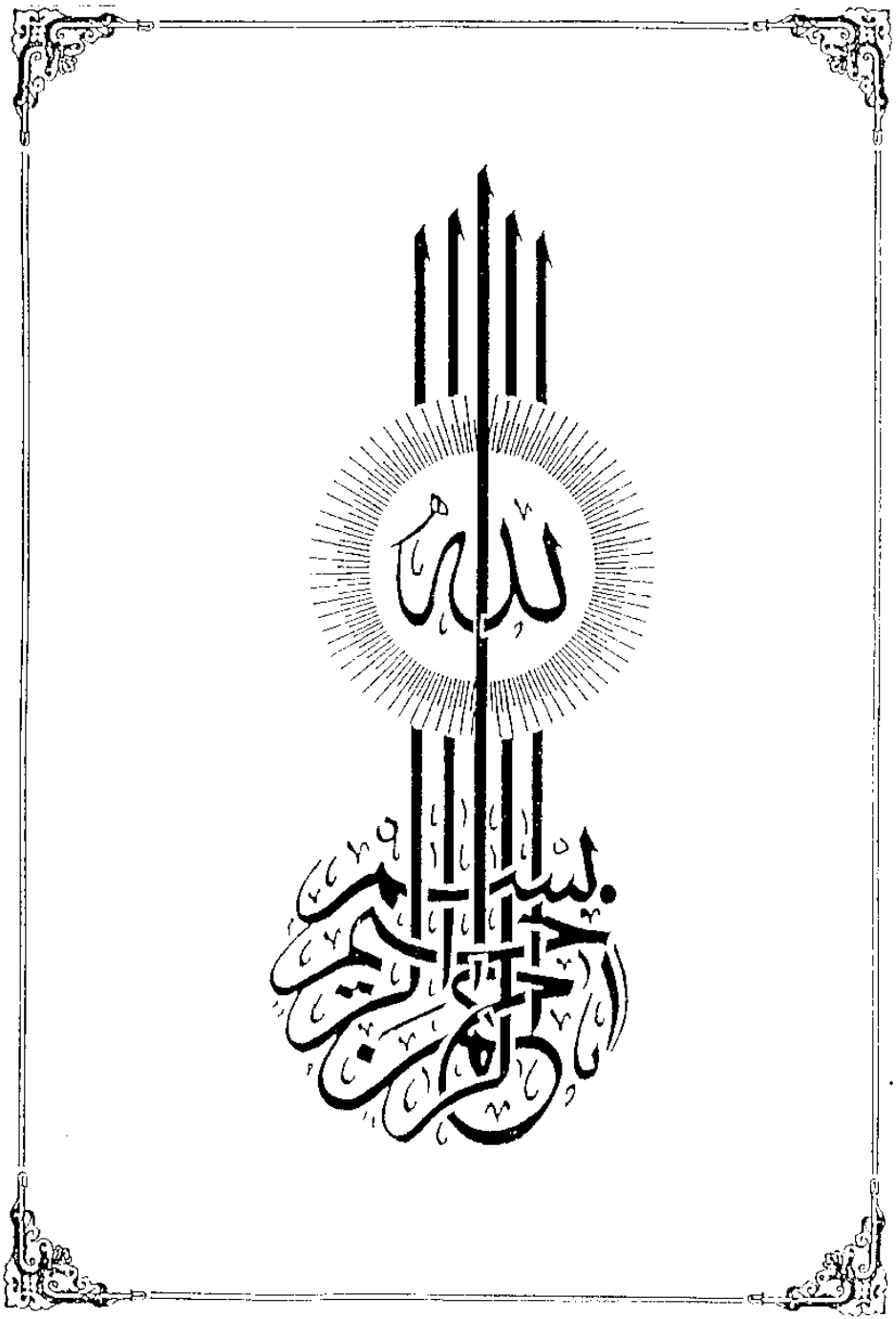
APPROVED

E.M.Ezzo

Head Of Chemistry Department

Marguerite A. Wassef

Central Library - Ain Shams University



Central Library - Ain Shams University

ACKNOWLEDGEMENT

The author is deeply thankful to ***Prof. Dr. Essam Mohamed Ezzo*** *Professor of Physical Chemistry, University College for Girls, Ain Shams University, and also* ***Prof. Dr. Maher Zaki Elsabee****, Professor of Physical Chemistry, Faculty of Science, Cairo University, not only for suggesting and directing the research project but also for their continuous guidance, advice, help, valuable criticism and for discussing the results.*

The author thanks ***Prof. Dr. Saleh Awad****, Professor of Physical Chemistry, University College for Girls, Ain Shams University for the offering of his laboratory and measure the conductivity and for the discussing and the revising of this part.*

The author also appreciates the full co-operation and kindness of her husband and her sister during the preparation of the thesis.

The author will remember with gratitude the co-operation of the head of the chemistry Department and all the members of the chemistry Department .

Central Library - Ain Shams University

ABSTRACT

The kinetics were studied of polymerization and copolymerization of vinylimidazole, acrylamide, N-phenylmaleimide and acrylonitrile. The rate of polymerization was determined in different solvents. The intrinsic viscosity and UV studied were carried out to solutions of polymer and copolymer. The corrosion capability of vinylimidazole, acrylamide and acrylonitrile and their copolymers were studied for aluminium in alkaline medium.

Central Library - Ain Shams University

CONTENTS

Page

AIM OF THE WORK.....1

CHAPTER I

INTRODUCTION.....2

I-A. POLYMERIZATION BEHAVIOUR.....2

I-B. ELECTROCHEMICAL BEHAVIOUR.....18

CHAPTER II

EXPERIMENTAL.....26

II-A. MATERIALS.....26

II-B. POLYMERIZATION PROCESS 33

II-C. COPOLYMERIZATION PROCESS 34

II-C-a. The Dilatometric method for the Determination of the copolymerization rate.....34

II-C-b. Characterization of the copolymers.....35

II-C-b-i Viscosity measurements.....35

II-C-b-ii Copolymer Analysis..... 35

II-C-c. Methods of calculation of reactivity ratios..... 39

II-C-c-i Fineman - Ross (F-R) method..... 39

II-C-c.ii Kelen-Tudõs (K-T) method..... 40

II-C-d. UV Spectroscope..... 43

II-D. ELECTROCHEMICAL MEASUREMENTS.....43

II-D-a. Potential Measurement.....43

II-D-b. Electrode Vessel..... 43

II-D-c. Corrosion Rate Measurements.....44

II-D-d. Calulation of corrosion (V_{corr}).....44

II-D-e. Calculation of potential (E_h).....45

Central Library - Ain Shams University

Page

CHAPTER III

RESULTS AND DISCUSSION.....50
III-A. POLYMERIZATION BEHAVIOUR.....50
III-A-a. Polymerization behaviour of the monomer.....50
III-A-a-i. Determination of the rate of free-radical polymerization of the investigated monomers.....50
III-A-a-ii. Dependence of the rate of polymerization on the initiator concentration.....51
III-A-a-iii. Dependence of the rate of polymerization on the monomer concentration.....54
III-A-a-iv. Determination of the polymerization activation energy..... 57
III-A-a-v. Effect of solvent polarity on the polymerization rate..... 60
III-B. COPOLYMERIZATION BEHAVIOR OF VINYLIMIDAZOLE..... 62
III-B-a. Copolymerization behavior of vinylimidazole (VI) with acrylamide (AA).....62
III-B-b. Copolymerization behavior of vinylimidazole (VI) with N-phenylmaleimide (NPMI).....69
III-B-c. Copolymerization behavior of vinylinidazole (VI) with acrylonitrile (AN).....78
III-C. ElECTROCHEMICAL BEHAVIOUR.....96
III-C-a. Corrosion Measurements.....96
III-C-b. Potential Measurements.....129

CHAPTER IV

CONCLUSIONS. 141

CHAPTER V

REFERNCES.....145

CHAPTER VI

ARABIC SUMMARY.....

Central Library - Ain Shams University

LIST OF TABLES

No.		Page
(1)	The values of overall rate of copolymerization of vinylimidazole with acrylamide	65
(2)	The intrinsic viscosity of some samples of the copolymer [VI : AA]	68
(3)	Copolymerization data for the vinylimidazole $VI(M_1)$ _ acrylamide AA (M_2) system in distilled water at 60°C by $K_2S_2O_8$	71
(4)	Analysis of the copolymerization data of the $VI(M_1)$-AA (M_2) in dist. H_2O at 60°C by $K_2S_2O_8$ by the F-R and K-T methods	72
(5)	The values of overall rate of copolymerization of vinylimidazole with N-Phenylmaleimide	77
(6)	The intrinsic viscosity of some samples of the copolymer [VI : NPMI]	79
(7)	Copolymerization data for the vinylimidazole $VI(M_1)$ - N-phenylmaleimide (NPMI) (M_2) system in dioxane at 60°C by azobisisobutyronitrile	82
(8)	Analysis of the copolymerization data of the VI (M_1) - NPMI (M_2) in dioxane at 60°C by azobisisobutyronitrile by the F-R and K-T methods	84
(9)	Copolymerization data for the vinylimidazole VI (M_1) _ acrylonitrile AN (M_2) system in dioxane at 60°C by azobisisobutyronitrile	87
(10)	Analysis of the copolymerization data of the VI (M_1) - AN (M_2) in dioxane at 60°C by azobisisobutyronitrile by the F-R and K-T methods	89
(11)	Vinylimidazole with reactivity ratios calculated by different methods	93
(12)	Q and e Values for Free-Radical-Initiated Copolymerization of 1-vinylimidazole (M_1)	95

Central Library - Ain Shams University

No. Page

(13) Rate of corrosion of aluminium in 0.1, 0.2, 0.3, and 0.4 M NaOH.....97

(14) Rate of corrosion of aluminium in 0.1, 0.2, 0.3, and 0.4M NaOH, containing different concentrations of monomer (a): vinylimidazole (VI).....99

(15) Rate of corrosion of aluminium in 0.1, 0.2, 0.3, and 0.4 M NaOH, containing different concentrations of monomer (b): Acrylamide (AA).....103

(16) Rate of corrosion of aluminium in 0.1, 0.2, 0.3, and 0.4 M NaOH, containing different concentrations of monomer (c): Acrylonitrile (AN).....106

(17) Rate of corrosion of aluminium in 0.1, 0.2, 0.3, and 0.4 M NaOH, containing different concentrations of copolymer (I): [VI] : [AA] 20 : 80.....110

(18) Rate of corrosion of aluminium in 0.1, 0.2, 0.3, and 0.4 M NaOH, containing different concentrations of copolymer (II): [VI] : [AA] 40 : 60.....112

(19) Rate of corrosion of aluminium in 0.1, 0.2, 0.3, and 0.4 M NaOH, containing different concentrations of copolymer (III): [VI] : [AA] 50 : 50.....114

(20) Rate of corrosion of aluminium in 0.1, 0.2, 0.3, and 0.4 M NaOH, containing different concentrations of copolymer (IV): [VI] : [AA] 70 : 30.....117

(21) Rate of corrosion of aluminium in 0.1, 0.2, 0.3, and 0.4 M NaOH, containing different concentrations of copolymer (V): [VI] : [AA] 90 : 10.....119

Central Library - Ain Shams University

No. Page

(22) Rate of corrosion of aluminium in 0.1, 0.2, 0.3, and 0.4 M NaOH, containing different concentrations of copolymer (I): [VI] : [AN] 20 : 80.....121

(23) Rate of corrosion of aluminium in 0.1, 0.2, 0.3, and 0.4 M NaOH, containing different concentrations of copolymer (II): [VI] : [AN] 40 : 60.....124

(24) Rate of corrosion of aluminium in 0.1, 0.2, 0.3, and 0.4 M NaOH, containing different concentrations of copolymer (III): [VI] : [AN] 90 : 10.....126

(25) The effect of the rate of corrosion of aluminium by macromolecules.....128

(26) Effect of monomer concentrations on the potentials of aluminium in 0.2 and 0.4M NaOH at steady state.....131

(27) Effect of copolymer concentrations on the potentials of aluminium in 0.2 and 0.4M NaOH at steady state.....134

(28) Effect of copolymer concentrations on the potentials of aluminium in 0.2 and 0.4M NaOH at steady state.....138

Central Library - Ain Shams University

LIST OF FIGURES

No.		Page
(1)	The electrode vessel and the prepared aluminium electrode	46
(2)	Apparatus for the distillation of water	47
(3)	Cell for Pre-electrolysis of NaOH	48
(4)	Capillary viscometer commonly used for measurement of polymer solution viscosities (Ubbelohde)	49
(5)	Conversion-time curves for VI at 60°C and [M] = 4.00 mol./L in DMF	52
(6)	Dependence of the rate of polymerization of VI on the initiator concentration in DMF at 60°C and [M] = 4.00 mol./L	53
(7)	Conversion-time curves for VI at 60°C and [AIBN]=$1X10^{-2}$ mol./L in DMF	55
(8)	Dependence of the rate of polymerization for VI on the monomer concentration [M] at constant [AIBN] = $1X10^{-2}$ mol./L in DMF at 60°C	56
(9)	Conversion-time curves for VI [AIBN]=$1X10^{-2}$ mol./L , [M] = 4.00 mol./L in DMF	58
(10)	The logarithm of polymerization rate versus 1/T in DMF at [M] = 4.00 mol./L , [AIBN]=1×10^{-2} mol./L	59
(11)	Relation between the volume contraction and the polymerization time of VI in different solvents , [M] = 4.00 mol./L and [AIBN] = 1×10^{-2} mol./L	61

Central Library - Ain Shams University

No. Page

(12) Volume contraction-time curves for the solution copolymerization of VI with AA using $K_2S_2O_8$ as an initiator 5 X 10^{-2} mol./L, solvent distilled H_2O at 60°C.....63

(13) Initial overall rate of copolymerization of the VI [M_1]-AA [M_2] system versus monomer feed molar ratios at 60°C , $K_2S_2O_8$ = 5 X 10^{-2} mol./L, total monomer concentration = 2 mol./L in distilled H_2.....64

(14) Intrinsic viscosity concentration measurement for VI- AA copolymer.....66

(15) Intrinsic viscosity of copolymerization ofVI[M_1] - AA[M_2] system versus monomer feed molar ratio at 30°C.....67

(16) Plots of copolymer composition versus monomer composition for VI and AA using $K_2S_2O_8$ as an initiator 5 X 10^{-2} mol./L at 60°C.....70

(17) Fineman - Ross plots for VI(M_1) with AA (M_2).....73

(18) Kelen - Tudös plots for VI(M_1) with AA(M_2).....74

(19) Volume contraction-time curves for the solution copolymerization of VI with NPMI using [AIBN] = 5 X 10^{-2} mol./L, solvent dioxane.....75

(20) Initial overall rate of copolymerization of the VI [M_1]-NPMI [M_2] system versus monomer feed molar ratios at 60°C , AIBN = 5 X 10^{-2} mol./L, total monomer concentration = 2 mol./L in dioxane.....76

(21) Intrinsic viscosity concentration measurement for VI- NPMI copolymer.....80

(22) Intrinsic viscosity of copolymerization ofVI[M_1] - NPMI[M_2] system versus monomer feed molar ratio at 30°C.....81

Central Library - Ain Shams University

No. Page

(23) Plots of copolymer composition versus monomer composition for VI and NPMI using AIBN as an initiator 5 X 10^{-2} mol./L at 60°C.....83

(24) Fineman - Ross plots for VI(M_1) with NPMI (M_2).....85

(25) Kelen - Tudõs plots for VI(M_1) with NPMI(M_2).....86

(26) Plots of copolymer composition versus monomer composition for VI and AN using AIBN as an initiator 5 X 10^{-2} mol./L at 60°C.....88

(27) Fineman - Ross plots for VI(M_1) with AN (M_2).....91

(28) Kelen - Tudõs plots for VI(M_1) with AN(M_2).....92

(29) UV spectra of (a) Pure VI , (b) Pure AA, (c) Mix. VI and AA.....94

(30) Effect of concentration of NaOH on the corrosion of aluminium at 30°C.....98

(31) Effect of monomer concentration (VI) on the corrosion rate of aluminium in different concentrations of NaOH solutions at 30°C.....100

(32) Effect of monomer concentration (AA) on the corrosion rate of aluminium in different concentrations of NaOH solutions at 30°C.....102

(33) Effect of monomer concentration (AN) on the corrosion rate of aluminium in different concentrations of NaOH solutions at 30°C.....105

(34) Effect of copolymer concentration on the corrosion rate of aluminium in different concentrations of NaOH solutions
(I) [VI : AA] 20 : 80 109

Central Library - Ain Shams University

No. Page

(35) Effect of copolymer concentration on the corrosion rate of aluminium in different concentrations of NaOH solutions (II) [VI : AA] 40 : 60 111

(36) Effect of copolymer concentration on the corrosion rate of aluminium in different concentrations of NaOH solutions (III) [VI : AA] 50 : 50 113

(37) Effect of copolymer concentration on the corrosion rate of aluminium in different concentrations of NaOH solutions (IV) [VI : AA] 70 : 30 116

(38) Effect of copolymer concentration on the corrosion rate of aluminium in different concentrations of NaOH solutions (V) [VI : AA] 90 : 10 118

(39) Effect of copolymer concentration on the corrosion rate of aluminium in different concentrations of NaOH solutions (I) [VI : AN] 20 : 80 122

(40) Effect of copolymer concentration on the corrosion rate of aluminium in different concentrations of NaOH solutions (II) [VI : AN] 40 : 60 125

(41) Effect of copolymer concentration on the corrosion rate of aluminium in different concentrations of NaOH solutions (III) [VI : AN] 90 : 10 127

(42) Effect of monomer concentration on corrosion potentials of aluminium in 0.2 M NaOH solution 132

(43) Effect of monomer concentration on corrosion potentials of aluminium in 0.4 M NaOH solution 133

Central Library - Ain Shams University

No. Page

(44) Effect of copolymer concentration [VI : AA] on corrosion potentials of aluminium in 0.2 M NaOH solution 136

(45) Effect of copolymer concentration [VI : AA] on corrosion potentials of aluminium in 0.4 M NaOH solution 137

(46) Effect of copolymer concentration [VI : AN] on corrosion potentials of aluminium in 0.2 M NaOH solution 139

(47) Effect of copolymer concentration [VI : AN] on corrosion potentials of aluminium in 0.4 M NaOH solution 140

Central Library - Ain Shams University