OPTIMIZATION OF SODIUM DODECYL SULPHATE LOADING IN POLY (VINYL ALCOHOL)-WATER COATINGS

Submitted in the partial fulfillment of the requirements for the award of degree

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in

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by

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Certificate

This is to certify that the dissertation work Entitled **"Optimization of Sodium Dodecyl Sulphate Loading in Poly (Vinyl Alcohol)-Water Coatings"** submitted by **Ishita Sharma (301602022)** in partial fulfilment for the award of degree of Master of Science in Chemistry from Thapar Institute of Engineering and Technology, Patiala, Punjab, is a genuine work done under our guidance. This work has not been submitted partially or wholly to any other university or institute for the award of this or any other degree or diploma.

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Declaration

I hereby declare that the dissertation report entitled "**Optimization Of Sodium Dodecyl Sulphate Loading in Poly (Vinyl Alcohol)-Water Coatings**", in the partial fulfilment of the requirements for the award of degree of masters of science in chemistry at School of Chemistry & Biochemistry, T.I.E.T., Patiala, is a record of genuine and independent project work done by me carried under the supervisions of **Dr. Raj Kumar Arya** and **Dr. Sanjeev Kumar Ahuja**, Associate Professors, Department of Chemical Engineering, Thapar Institute of Engineering & Technology, Patiala. The work contained in this report has not been submitted partially or wholly to any other university or institute for the award of this or any other degree or diploma.

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Abstract

The residual solvent study in poly (vinyl) alcohol-water based system has been investigated. The effect of anionic surfactant: sodium dodecyl sulphate (SDS), on the drying behavior of coatings has been investigated. Attempts were made to optimize the surfactant loading in order to minimize the residual solvent and drying time. Surfactant loadings were changed from 0.5% to 2.5% by weight. Residual solvent left was 5.88% in poly (vinyl) alcohol-Water, 4.88% in Poly (vinyl) alcohol-sodium dodecyl sulphate (0.5%)-Water, 4.17% in poly(vinyl) alcohol- sodium dodecyl sulphate (1%)-Water 3.85% in poly(vinyl) alcohol-sodium dodecyl sulphate (1.5%)-Water, 3.27% in poly(vinyl) alcohol- sodium dodecyl sulphate (2%)-Water and 2.54% in poly(vinyl) alcohol- sodium dodecyl sulphate (2.5%)-Water for 0.5 wt.%. Effect of initial coating thickness on residual solvent were also investigated. Optimum surfactant loading becomes out to be independent of initial coating thickness.

Table of Contents

Chapter No.	Title	Page No.
	Certificate	ii
	Declaration	iii
	Acknowledgement	iv
	Abstract	v
	List of Tables	viii
	List of Figures	ix
1	**Introduction**	1
	1.1 Background………………………………………………………	1
	1.2 Type of polymeric coatings………………………………………	1
	1.3 Preparation of polymeric coatings…………………………………	1
	1.4 Drying of polymeric coatings……………………………………	2
	1.5 Green coatings……………………………………………………	2
	1.6 Applications of PVA Coatings……………………………………	3
	1.7 Applications of surfactants in coating……………………………	3
2	**Literature Review**	4
	2.1 Research gaps……………………………………………………	6
	2.2 Objectives…………………………………………………………	6
3	**Materials and Methods**	**7**
	3.1 Materials…………………………………………………………	7
	3.2 Methodology………………………………………………………	8

4 Results and Discussion 11

4.1 Case 1: Coatings of 900 µm Initial Thicknesses……………… 11

4.1.1 Effect of Surfactant Loading on Residual Solvent ……………… 11

4.1.2 Effect of Surfactant Loading on Coating Thickness ……………… 12

4.1.3 Effect of Surfactant Loading on Solid Concentration…………… 13

4.1.4 Effect of Surfactant Loading on Solvent Concentration………… 14

4.2 Case 2: Effect of Coating Thickness on Various Coating Parameters. 15

4.2.1 Effect of Surfactant Loading on Residual Solvent ……………… 15

4.2.2 Effect of Surfactant Loading on Coating Thickness……………… 16

4.2.3 Effect of Surfactant Loading on Solid Concentration …………… 17

4.2.4 Effect of Surfactant Loading on Solvent Concentration………… 17

5 Conclusions…………………………………………………………… 23

References……………………………………………………………… 24

Plagiarism Report……………………………………………………… 26

List of Tables

Table No.	Title	Page No.
1	Solubility parameters of PVA and Water……………………….	7
2	Composition of different coating solutions………………………	8
3	Raw data obtained from the semi micro analytical weighing balance…………………………………………………………	9
4	Summarized drying data of PVA-Water coating with and without surfactant of initial thickness 900 microns…………………………	19
5	Summarized drying data of PVA-Water coating with and without surfactant of initial thickness 900 microns…………………………	20

List of Figures

Figure No.	Caption	Page No
3.1	Schematic representation of drying process of coating solution……………	10
4.1	Residual solvent as a function of time for various SDS loading for 900 µm initial thickness at 25ºC.…………………………………………………	11
4.2	Coating thickness as a function of time for various SDS loading for 900 µm initial thickness at 25ºC………………………………………………	12
4.3	Solid concentration as a function of time for various SDS loading for 900 µm initial thickness at 25ºC……………………………………………	13
4.4	Solvent concentration as a function of time for various SDS loading for 900 µm initial thickness at 25ºC………………………………………………	14
4.5	Residual solvent as a function of time for various SDS loading for 1900 µm initial thickness at 25ºC……………………………………………….	15
4.6	Coating thickness as a function of time for various SDS loading for 1900 µm initial thickness…………………………………………………………	16
4.7	Solid concentration as a function of time for various SDS loading for 1900 µm initial thickness at 25° C……………………………………………	17
4.8	Solvent concentration as a function of time for various SDS loading for 1900 µm initial thickness at 25ºC………………………………………...	18
4.9	Ultimate residual solvent (%) and drying time as a function of surfactant loading (wt.%) ………………………………………………………	21

4.9 Ultimate residual solvent (%) and drying time as a function of surfactant loading (wt.%) ………………………………………………………………. 22

Chapter 1

Introduction

1.1 Background

Polymers are large molecules composed of small repeating units called monomers [1]. Coatings can be made from polymers by dissolving in solvent(s) in organic and/or inorganic. Polymeric coatings are used in various fields like textile industry [2], electronic industry (as mouldable semiconductor), LED [1], food industry, biomaterials [3], magnetic media and photographic films [4]. The main purpose of a polymeric coating is to enhance the lifetime of a material or surface by protecting it from moisture, and cracks. On the basis of the Solution of solvent used, whether organic or inorganic the polymeric coatings can be characterized into two types: water-based polymeric coatings and organic-based polymeric coatings.

1.2 Types of Polymeric Coatings

- **Water Based Polymeric Coatings**

These coatings are seeking the attention of the researchers now-a-days, due to their eco-friendly, cost effective nature and green technique. Water-based polymeric coatings use water as a solvent. These types of coatings are also known as green coatings. The normal boiling point of water is 100ºC which makes the coatings resistant to high temperature and have great thermal stability. These coatings have high tensile strength as compared to other organic coatings [5].

- **Organic Based Polymeric Coatings**

In industry, a huge of amount of organic solvents is used in the preparation of polymeric coatings which is not at all environmental friendly. Organic solvents are highly toxic in nature and during the drying of coatings they readily evaporate and combine with air to form ozone which act as a pollutant to the environment and cause several health problems [6].

1.3 Preparation of Polymeric Coatings

Polymeric coatings can be prepared with and without solvents depending on the requirements. These can be prepared by several methods like solution casting technique [7], Spin coating method [8], drop casting method [9], film casting method [10]. Coating thickness can be controlled precisely in case of solution casting technique as compared to other techniques. This method is easy to operate at laboratory scale as well as on industrial scale. The method is highly useful to get a flat coating of uniform thickness, with maximum optical purity [4, 7].

1.4 Drying of Polymeric Coatings

Drying of polymeric coatings is a complex process due to involvement of simultaneous heat and mass transfer. Coatings are wet in the beginning and solid at the end of drying. The phase of solution also changes during the course of drying. Drying of coatings can be done in natural environment as well as in controlled environment. Controlled drying conditions are required to get in order to get the best polymer coatings. Drying affects the physical as well as chemical behavior of the coatings. Some of the physical changes are like shrinking, puffing, crystallization, glass transition and skinning while the chemical changes are like odour, color or texture [11]. Drying of polymeric coatings are done to minimize the amount of solvent trapped in the dried polymeric coatings.

1.5 Green Coatings

Water based coating(s) are attracting so much of research due to non-hazardous eco-friendly nature. Polyvinyl pyrrolidone(PVP), polyethylene glycol (PEG), polyvinyl alcohol (PVA) are mostly commonly used in water based coatings in biomedical, fibres, and in drug delivery [12]. The energy required for water-based coatings is many times higher as compared to organic solvent(s) based coatings due to very high latent heat of vaporization of water. It is always desirable to develop cheaper water-soluble polymer as well to enhance the drying rate of these coatings in order to cut the formulation cost along with operational costs during the drying operation. The addition of surface active agents can improve the drying rate to great extent and research activities in this are growing day by day.

1.6 Applications of PVA Coatings

PVA coatings used to coat the food supplements hence the coatings has wide applications as food packaging material [13]. PVA hydrogels have been used in various biomedical and pharmaceutical applications [14] and these coatings also used to coat the medicinal tablets. PVA films also used in the drug delivery system and enhances the oral delivery of poorly soluble drugs [15].

1.7 Application of Surfactant in Coatings

Surfactants can be used to modify the various properties of the coating formulations. They can be used to disperse molecules in order to get homogenous solution. They can either be used to phase separate or even to bind the polymer(s) and solvent(s) with surfactant chain. Surfactants are mainly classified in several categories ionic, anionic, cationic, and polymeric. The application of different category of surfactant will totally depends on its compatibility with the coating solution. [16]. Surfactants can either be used to enhance the drying rate or to get flat films at the end of drying operations. In order to obtain a flat polymeric film without any ring formation a new effect was introduced known as Marangoni effect [17]. It was found out that only a small concentration of surfactant would be required to alter the behavior of a polymeric film. Surfactant creates a surface tension gradient between the edges and center of film by lowering the surface tension adjacent to the edges. Hence, a flow will be created which will propel the solute back to the center of film by virtue of Marangoni force. This inward flow will cancel out the outward flow of solute and will make the film profile flatter.

Chapter 2

Literature Review

This chapter comprises literature of polymer-surfactant system and water based polymeric coatings.

Okazaki et al. [18] studied the drying of poly(vinyl alcohol)-water coatings. They measured the diffusion and mutual diffusion coefficients for the lower, medium and higher concentration and temperature over a period of time during drying process**.** They considered the concentration dependent diffusion coefficient, concentration dependent equilibrium vapor pressure and seen the effect of shrinkage by simulation studies. The experimental and calculated values were in a very good agreement with each other.

Kajiya et al. [17] studied on drying behavior and film formation process poly(styrene) – fluorosurfactant (F470 and F489) – Dipropylene glycol methyl ether acetate. They changed the poly(styrene) concentration 5%, 10% and 20% by weight and kept the concentration of both the surfactant (F470 and F489) at 0.05%. They observed that with addition of the fluorosurfactant the large amount of polymer was found to be in the middle portion and the film had a flat profile. The dried coating was concave in shape without the surfactant and become flat with application of surfactant. The surfactant levelled the polymer film.

Kristen and Klitzing [19] studied on the effect of polyelectrolyte-surfactant system and discussed their stability in the foam films. They used poly (diallyl dimethyl ammonium chloride (PDADMAC), Poly (sodium 4-styrene sulphonate) (PSS), Poly (2-Acrylamide-2-Methyl propane sulphonic acid) as electrolytes and dodecyltrimethylammonium bromide ($C_{12}TAB$), tetradecyltrimethylammonium bromide ($C_{14}TAB$), cetyltrimethylammonium bromide($C_{16}TAB$) as cationic surfactants. They compared the polyelectrolytes with oppositely charged surfactants and with equally charged surfactants. There was no adsorption on the surface of equally charged polyelectrolytes and surfactants whereas in oppositely charged polyelectrolytes and surfactants have better adsorption due to the formation of polyelectrolytes/surfactant complex. The stabilization of the foam films was occurred in the oppositely charged polyelectrolytes and surfactant combination due to the decrease in surface tension and surface elasticity.

Shamma and Elkasabgy [15] worked on the preparation of Soluplus/PVA based films using solvent casting method. They also added PEG 400 which acts as a plasticiser and increase the mechanical strength of the film. Soluplus was used as a graft copolymer composed of monomeric units are polyethylene glycol, vinyl caprolactam and vinyl acetate. The prepared films then evaluated for properties like tensile strength, thickness and solubility. They analysed that polymeric film of optimized film formula had 10% polymer concentration and 30% PEG and Soluplus: PVA (0.33:0.66). It was concluded that freeze-drying of optimized film enhances the dissolution properties of film by forming a more porous film. The freeze-dried films also enhance the solubility of poorly soluble drugs and act as a good carrier for their oral delivery and enhances their bioavailability.

Ravichandran and Kumari [5] studied a system of SDS at different concentrations in PVA and water is used as solvent. Parameters like relative density, viscosity and ultrasonic velocity of the system was investigated by ultrasonic velocity measurements. They concluded that at lower concentration of SDS solution remains clear, as the formation of micelles followed by their dissolution. High amount of SDS formed the rod like micelles due to the presence of hydrophilic and hydrophobic parts.

Tam and Dai [20] studied a system of PEG and SDS and their binding behavior using isothermal titration calorimetry (ITC). They used deionised water as solvent. They found that molecular weight of PEG affected the binding interactions between polymer and surfactant and there was no binding at low molecular weight. At intermediate molecular weight surfactant micelle formation initiated by polymer which results in the formation of aggregation complex between SDS and PEG. As the molecular weight of PEG raises, segments of PEG become rehydrated by the micellar region of SDS. This results in the reorganisation of PEG/SDS complex through ion-dipole associations.

Recently, Sharma et al.[21] reported studies on surfactant enhanced drying in water based coating. They used poly (vinyl alcohol) as a polymer and PEG, SDS and CAPSTONE FS-63 as surfactants and water as a solvent. They changed the polymer concentration by keeping the surfactants concentration constant. They observed the appreciable change by the addition of fluorosurfactant rather than other anionic (SDS) and neutral (PEG) surfactant. They concluded that fluorosurfactant reduced the residual solvent upto 0.56% whereas the SDS and PEG had 1.33% and 6.88% respectively. The fluorosurfactant containing system were taking more drying time as compared to another surfactant containing system.

2.1 **Research Gaps**

1. Earlier researchers have mainly focused on the drying behavior, surfactant interaction, micelle formation in the polymer surfactant system [5, 22, 23] .
2. A few studies are reported related to film formation using surfactant based systems [17, 19].
3. Recently, Sharma et al [21] used various surfactant to minimize the residual solvent in polymer – solvent systems.
4. No literature has been reported for optimization of surfactant amount in polymeric coatings.

2.1 Objectives

In the present work, the primary objective is to optimize the amount of SDS surfactant in PVA-water coatings in order to minimize the residual solvent. The following sub-objectives are planned to meet the main objectives:

i. To study the residual solvent in PVA – water coating at different SDS loading.
ii. To study the effect of polymer concentration on SDS loading to reduce the residual solvent.

Chapter 3

Materials and Methods

3.1 Materials

Poly (vinyl alcohol) was purchased from Lobachemie, India. It is a high purity analytical grade anhydrous powder form (density: 1.19 g cm^{-3}, molecular weight: 115,000 g mol^{-1}). Sodium dodecyle sulphate was purchased from Sigma Aldrich, Germany (density:1.01 g $cm^{-3,}$ molecular weight: 288.372 g mol^{-1}). Double distilled water was used as the solvent. All the chemicals used in the study were analytical grade research chemicals and they were used as received without any further purification. The values of solubility parameters for selected polymers and solvents are given in Table 1.

Table 1. Solubility parameter of PVA and Water.

Polymer/Solvent	Dispersion solubility, δd, $MPa^{1/2}$	Polar solubility, δp, $MPa^{1/2}$	Hydrogen bonding, δh, $MPa^{1/2}$
PVA	17.5	12.5	10.0
Water	31.3	12.3	34.2

The solubility of polymer and solvents are checked using Flory-Huggins interaction parameter(χ) and being calculated using Bristow and Watson correlation [24] as given below.

$$\chi_{ij=0.35+}\frac{V\bar{\imath}}{RT}(\partial_{PVA}-\partial_{Water})^2 \quad (1)$$

where, χ_{ij} is interaction parameter, $V\bar{i}$ is partial molar volume of solvent (cm^3/mol), δi and δj are solubility parameters of the solvent and polymer, respectively, and T is temperature in K.

the value of χ_{ij} is comes out to be 0.35 which is less than 0.5 which indicates that the system is compatible with each other and hence miscible [25].

3.2 Methodology

Six different concentration of PVA-SDS-Water solutions were prepared. Known amount of polymer, surfactant and water were weighed using semi-micro analytical weighing balance (222SM DR, Precisa) having least count ±0.0001g. All weighed constituents were poured into leak proof Schott Duran reagent bottles and tightened carefully. Now, the sample bottles were kept in hot digital water bath (LWB 311D, Diahann labtech Pvt. Ltd, India) at 90º C for 2 hours followed by mechanical shaking in shaker at 200 rpm for 5 hours to get the homogeneous solution. The shaking time may be more depending upon the requirement.

Solution casting technique is used to prepare polymeric films. The known amount of solution is taken from sample bottles and poured into the stainless steel circular sample holder (12.24 mm diameter and was 2000 microns in depth) using micropipette. The poured solution spread instantaneously into the sample holder due to its dilute nature. The mass of poured sample that is coating is recorded using semi micro analytical weighing balance at 5 s interval until no further change was recorded in two consecutive readings for sufficient long-time gap, i.e., 20 min. The typical drying time was around 5-7 hours and these coatings are considered dried for practical purposes. Figure 3.1 shows the schematic representation of drying process of coating solution. Various coating parameters like coating thickness, residual solvent, average concentration of solid (polymer plus surfactant), and solvent were calculated using standard volumetric methods. These formulas are very well given in earlier literature [21] research work of our group. The sample calculations are as follows.

Table 2. Composition of different coating solutions.

Solution No.	PVA (wt.%)	SDS (wt.%)	Distilled water (wt.%)
1	5.02	0	94.98
2	4.94	0.5	94.56
3	4.98	1	94.02
4	5.02	1.5	93.41
5	5.0	2	93
6	5.18	2.5	92.34

Table 3. Raw data obtained from the semi micro analytical weighing balance

Time(hrs.)	Time(min)	Time(sec)	Mass(mg)
12	3	24	3776.08
12	3	29	3776.05
12	3	34	3776.02
12	3	39	3775.99
12	3	44	3775.95
12	3	49	3775.9
12	3	54	3775.86
12	3	59	3775.81
12	4	4	3775.76
12	4	9	3775.71

Calculations:

Let the initial mass of polymer solution is "*m*", in which 5% PVA and 95% of Water.

Weight of empty sample holder = 3550.93 mg

m = Mass(mg)-sample holder = 3776.08-3550.93= 225.15 mg = 0.22515 g.

Initial mass of polymer, Mp = *m* × 5/100 = 0.22515*5/100= 0.0112 g.

Initial mass of water, M_S = m × 95/100 = 0.22515*95/100= 0.2138 g.

Volume of the polymer, $V_P = \frac{M_P}{Density}$

Volume of the solvent, $V_S = \frac{M_P}{Density}$

Total volume, $V_T = V_P + Vs$

Concentration of the polymer = $\frac{M_P}{V_T}$

Concentration of the solvent = $\frac{M_S}{V_T}$

Coating thickness, $L = \frac{total\ volume}{area\ of\ sample\ holder}$

Residual solvent % = $\frac{mass\ of\ water\ final\ (g)}{mass\ of\ water\ initial\ (g)}$

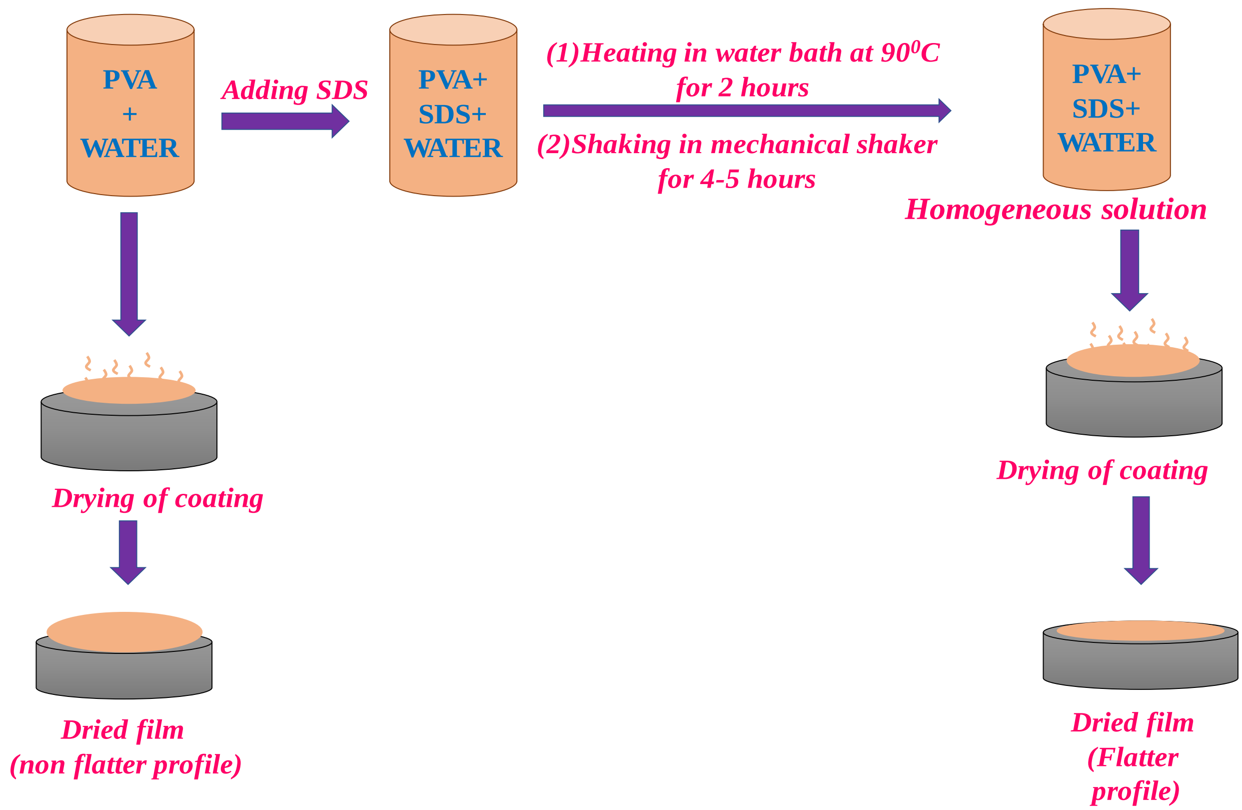

Figure 3.1. Schematic representation of preparation of coating with and without surfactant.

Chapter 4

Results and Discussion

4.1 Case 1: Coatings of 900 µm Initial Thicknesses

4.1.1 Effect of Surfactant Loading on Residual Solvent

Figure 4.1 shows the residual solvent as a function of time in Poly (vinyl alcohol) -water coatings. These are prepared using six different types of solutions. Solution 1 Coating has initial thickness 960 µm, Solution 2 Coating has 941 µm, Solution 3 Coating has 919 µm, Solution 4 Coating has 908 µm, Solution 5 Coating has 945 µm and Solution 6 Coating has 988 µm. Residual solvent left in solution 1 is 5.88%, Solution 2 is 4.88%, Solution 3 is 4.17%, Solution 4 is 3.85%, Solution 5 is 3.27%, and Solution 6 is 2.54%. These results show that amount of residual solvent is decreasing with increasing surfactant (wt. %). Therefore, the optimum value of SDS for this system is 1.5% beyond that the surfactant might be interacting with the polymer and solvent in such a way that the diffusion coefficient of solvent is decreasing to a value slightly higher than pure water system but lower than 1.5% SDS system.

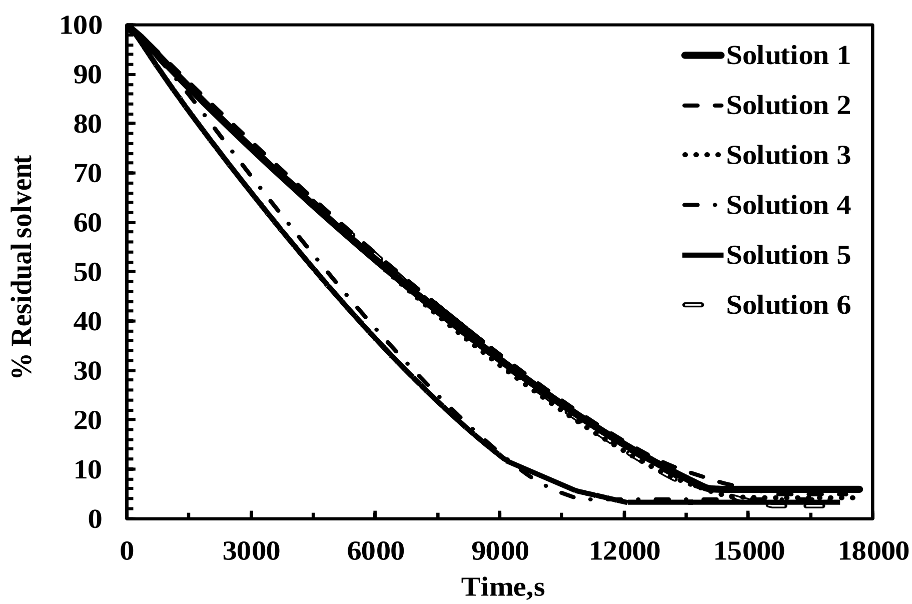

Figure 4.1. Residual solvent as a function of time for various SDS loading for 900 µm initial thickness at 25ºC.

4.1.2 Effect of Surfactant Loading on Coating Thickness

Figure 4.2 shows the coating thickness with time of PVA-Water coatings. Solution 1 has initial coating thickness 960 µm, Solution 2 has 941 µm, Solution 3 has 919 µm, Solution 4 has 908 µm, Solution 5 has 945 µm and Solution 6 has 988 µm. Thicknesses of coatings are decreasing during the course of drying due to evaporation of solvent from the coating – air interface into surrounding air. The coating thickness is decreasing linearly for sufficiently longer time in all of the cases. This proves that mass transfer process in completely externally controlled for this much time duration. The dried coating thickness for Solution 1 is 96 µm, Solution 2 is 91 µm, Solution 3 is 87 µm, Solution 4 is 86 µm, Solution 5 is 88 µm and Solution 6 is 91 µm. These values show that coating thickness is decreasing with increasing surfactant upto 1.5 wt.%. The higher percentage of surfactant makes the solution viscous which slows down the diffusion of solvent. Therefore, there was further increase in coating thickness at 2.5% (wt.%) of SDS but this value is still lower than PVA- Water system having no surfactant.

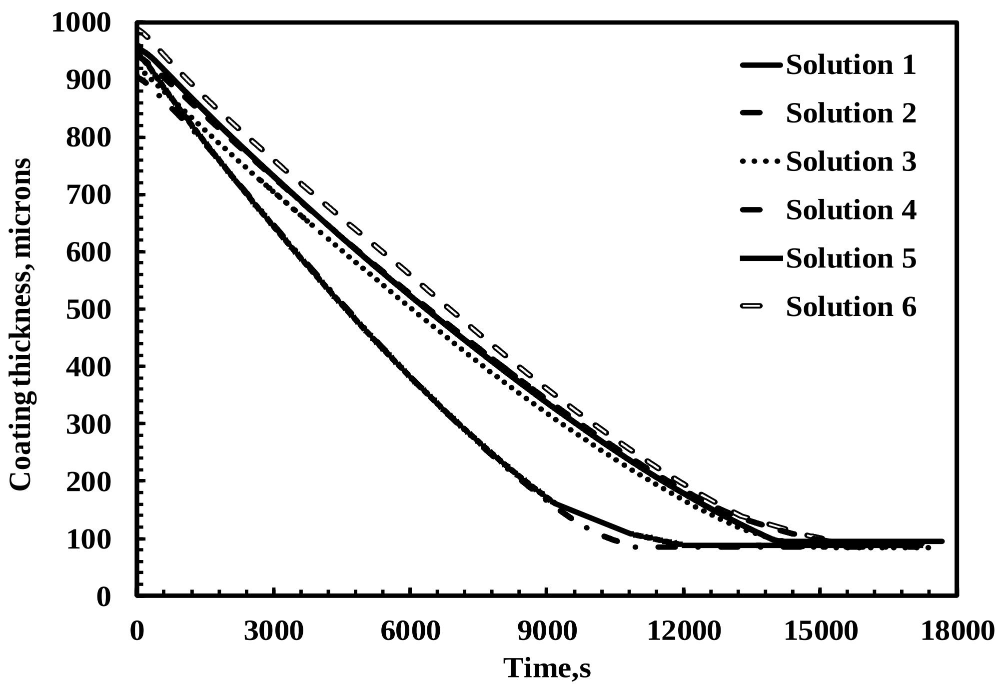

Figure 4.2. Coating thickness as a function of time for various SDS loading for 900 µm initial thickness at 25ºC.

4.1.3 Effect of Surfactant Loading on Solid Concentration

Figure 4.3 shows the solid (PVA+SDS) concentration as a function of time in PVA-Water coatings. These are prepared using six different types of solutions. Solution 1 has initial coating thickness 960 µm, Solution 2 has 941 µm, Solution 3 has 919 µm, Solution 4 has 908 µm, Solution 5 has 945 µm and Solution 6 has 988 µm. Initial concentrations of poly (vinyl alcohol) were 0.050 g cm^{-3}, 0.049 g cm^{-3}, 0.050 g cm^{-3}, 0.050 g cm^{-3}, 0.050 g cm^{-3} and 0.052 g cm^{-3} respectively. The final concentrations of poly (vinyl alcohol) in Solution 1, Solution 2, Solution 3, Solution 4, Solution 5 and Solution 6 coatings are 0.51 g cm^{-3}, 0.53 g cm^{-3}, 0.54 g cm^{-3}, 0.53g cm^{-3}, 0.54 g cm^{-3} and 0.56 g cm^{-3} respectively. These results show that polymer concentration is exponentially increasing with increasing surfactant (wt.%). The polymer concentration is approximately having the same trend in all the coatings prepared from Solution 1 to Solution 6. The highest Solid concentration was achieved in solution 6 coating having 2.5 wt.% SDS.

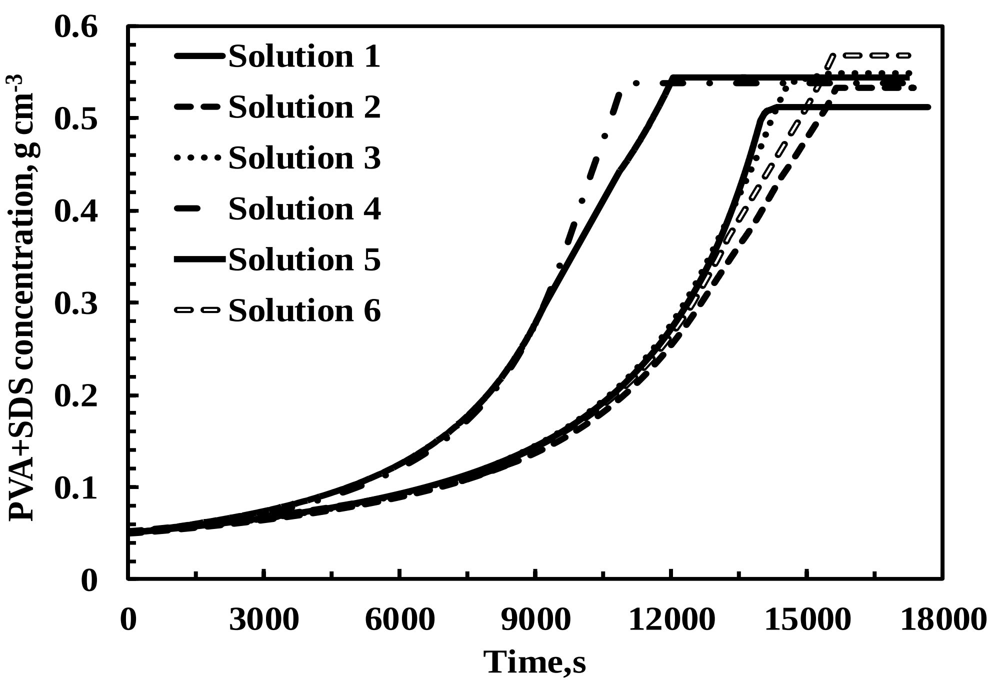

Figure 4.3. Solid concentration as a function of time for various SDS loading for 900 µm initial thickness at 25ºC.

4.1.4 Effect of Surfactant Loading on Solvent Concentration

Figure 4.4 shows the solvent concentration with time in PVA-water coatings. These are prepared using six different types of solutions. In the beginning, the solvent concentrations were 0.95 g cm^{-3}, 0.95 g cm^{-3}, 0.94 g cm^{-3}, 0.94 g cm^{-3}, 0.94 g cm^{-3}, 0.93 g cm^{-3} and 0.93 g cm^{-3} respectively. The solvent concentrations are decreasing exponentially in all the cases which shows typical Fickian diffusion of solvent. The final concentration of solvent left in these coatings are 0.56 g cm^{-3}, 0.54 g cm^{-3}, 0.43 g cm^{-3}, 0.38 g cm^{-3}, 0.33 g cm^{-3} and 0.25 g cm^{-3} respectively. These results show that solvent concentration is exponentially decreasing with increasing surfactant (wt.%). The maximum amount of solvent was removed in case of Solution 6 Coating having 2.5 wt.% SDS which results the lowest solvent concentration.

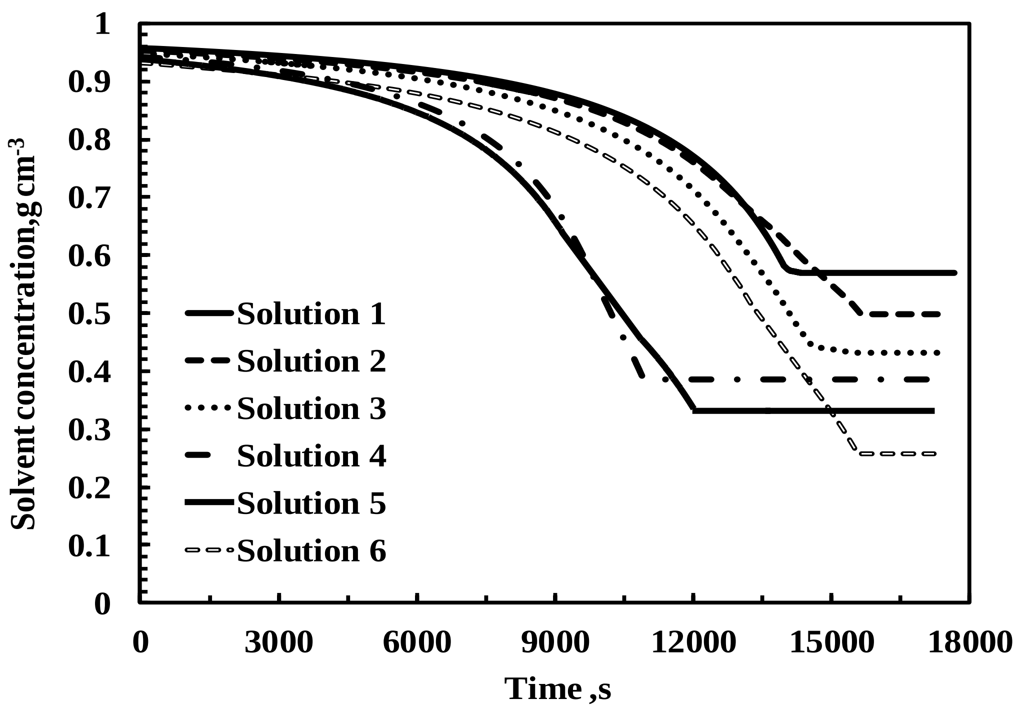

Figure 4.4: Solvent concentration as a function of time for various SDS loading for 900 µm initial thickness at 25ºC.

4.2 Case 2: Effect of Coating Thickness on Various Coating Parameters.

4.2.1 Effect of Surfactant Loading on Residual Solvent

In this case, initial coating thickness was nearly doubled i.e. 1900 µm, to study its effect on residual solvent, coating thickness and concentration of solid and solvent. Figure 4.5 shows the residual solvent as a function of time in Poly (vinyl alcohol) -water coatings. These are prepared using six different types of solutions. Solution 1 has initial coating thickness 1897 µm, Solution 2 has 1959 µm, Solution 3 has 1906 µm, Solution 4 has 1962 µm, Solution 5 has 1936 µm and Solution 6 has 1922 µm. Residual solvent left in Solution 1 is 6.96%, Solution 2 is 5.09%, Solution 3 is 5.49%, Solution 4 is 4.44%, Solution 5 is 4.21%, and Solution 6 is 4.18%. These results show that amount of residual solvent is decreasing with increasing surfactant (wt. %). In the previous system also, the residual solvent also decreasing with the increase in surfactant loadings.

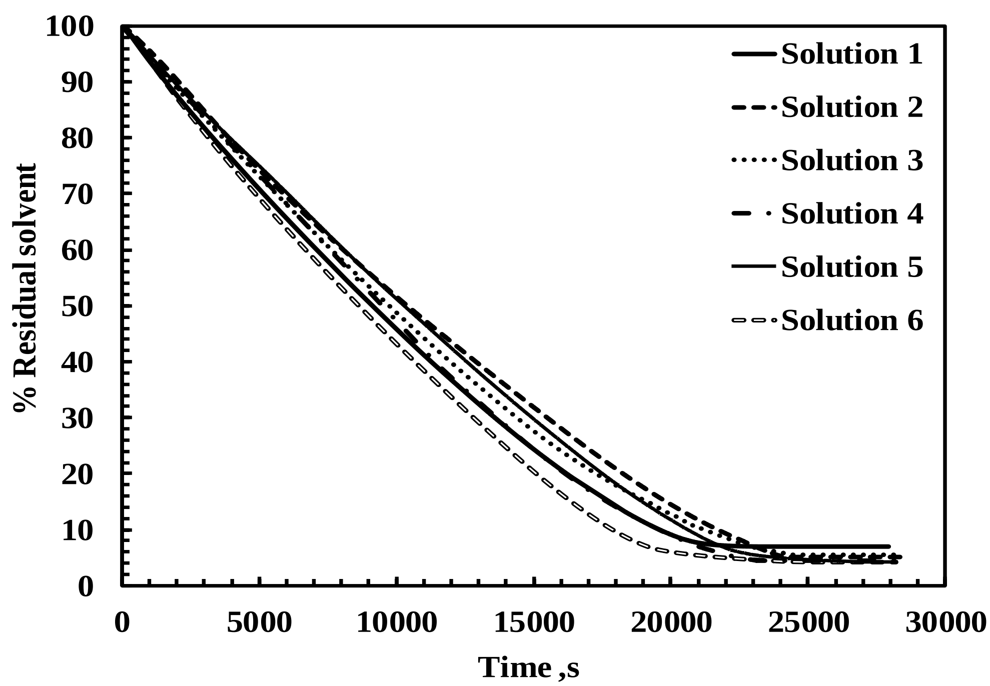

Figure 4.5: Residual solvent as a function of time for various SDS loading for 1900 µm initial thickness at 25ºC**.**

4.2.2 Effect of Surfactant Loading on Coating Thickness

Figure 4.6 shows the coating thickness with time of PVA-Water coatings. Solution 1 has initial coating thickness 1897 µm, Solution 2 has 1959 µm, Solution 3 has 1906 µm, Solution 4 has 1962 µm, Solution 5 has 1936 µm and Solution 6 has 1922 µm. Thicknesses of coatings are decreasing during the course of drying due to evaporation of solvent from the coating – air interface into surrounding air. The coating thickness is decreasing linearly for sufficiently longer time in all of the cases. This proves that mass transfer process in completely externally controlled for this much time duration. The dried coating thickness for Solution 1 is 207 µm, Solution 2 is 187 µm, Solution 3 is 198 µm, Solution 4 is 194 µm, Solution 5 is 196 µm, Solution 6 is 206 µm. These values show that coating thickness is decreasing with increasing surfactant upto 1.5 wt.%. With the higher percentage of surfactant makes the solution viscous which slows down the diffusion of solvent and hence increasing coating thickness. Therefore, there was further increase in coating thickness at 2.5% (wt.%) of SDS but this value is still lower than PVA- Water system having no surfactant i.e. 207 µm.

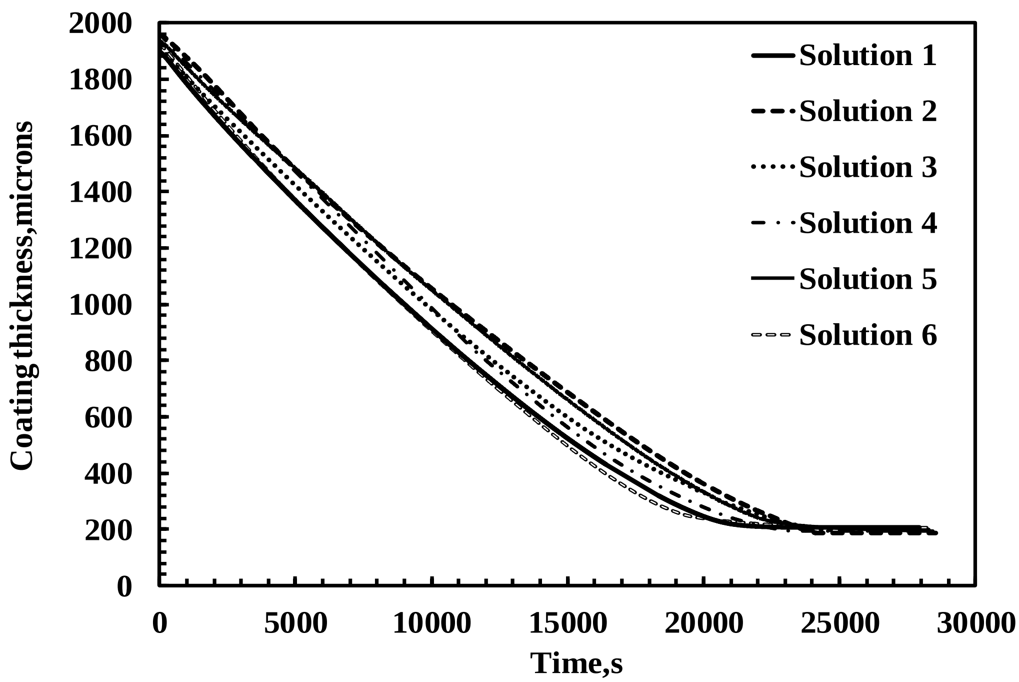

Figure 4.6: Coating thickness as a function of time for various SDS loading for 1900 µm initial thickness.

4.2.3 Effect of Surfactant Loading on Solid Concentration

Figure 4.7 shows the solid (PVA+SDS) concentration as a function of time in PVA-Water coatings. Solution 1 has initial coating thickness 1897 µm, Solution 2 has 1959 µm, Solution 3 has 1906 µm, Solution 4 has 1962 µm, Solution 5 has 1936 µm and Solution 6 has 1922 µm. Initial concentrations of poly (vinyl alcohol) were 0.050 g cm^{-3}, 0.049 g cm^{-3}, 0.050 g cm^{-3}, 0.050 g cm^{-3}, 0.050 g cm^{-3}, and 0.052 g cm^{-3}, respectively. The final concentrations of Solution 1, Solution 2, Solution 3, Solution 4, Solution 5, Solution 6 coatings are 0.46 g cm^{-3}, 0.52 g cm^{-3}, 0.48 g cm^{-3}, 0.51 g cm^{-3}, 0.49 g cm^{-3} and 0.48 g cm^{-3} respectively. As compared from system of initial thickness 900 µm the final concentrations of Solution 1, Solution 2, Solution 3, Solution 4, Solution 5, Solution 6 coatings are 0.51 g cm^{-3}, 0.53 g cm^{-3}, 0.54 g cm^{-3}, 0.53g cm^{-3}, 0.54 g cm^{-3} and 0.56 g cm^{-3} respectively.

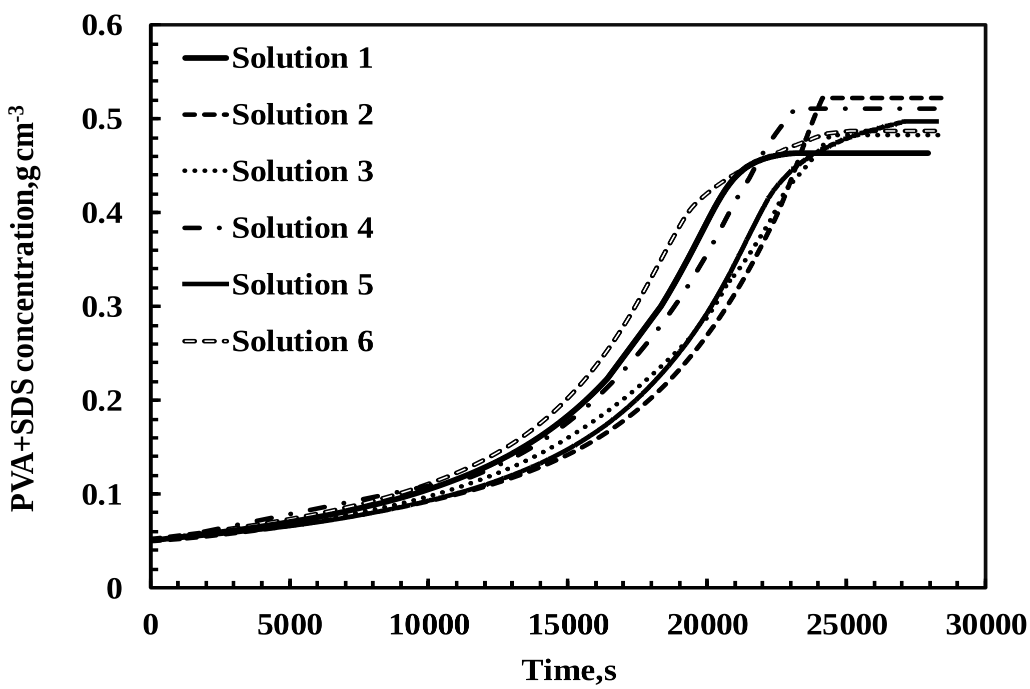

Figure 4.7. Solid concentration as a function of time for various SDS loading for 1900 µm initial thickness at 25° C.

4.2.4 Effect of surfactant loading on solvent concentration

Figure 4.8 shows the solvent concentration with time in PVA-water coatings prepared from Solution 1, Solution 2, Solution 3, Solution 4, Solution 5, and Solution 6. In the beginning, the solvent concentrations were 0.95 g cm^{-3}, 0.95 g cm^{-3}, 0.94 g cm^{-3}, 0.94 g cm^{-3}, 0.94 g cm^{-3}, 0.93 g cm^{-3} and 0.93 g cm^{-3} respectively. The solvent concentrations are decreasing exponentially in all the cases which shows typical Fickian diffusion of solvent. The final concentration of solvent left in these coatings are 0.61 g cm^{-3}, 0.50 g cm^{-3}, 0.50 g cm^{-3}, 0.42 g cm^{-3}, 0.38 g cm^{-3} and 0.36 g cm^{-3} respectively. These results show that solvent concentration is exponentially decreasing with increasing surfactant (wt.%).

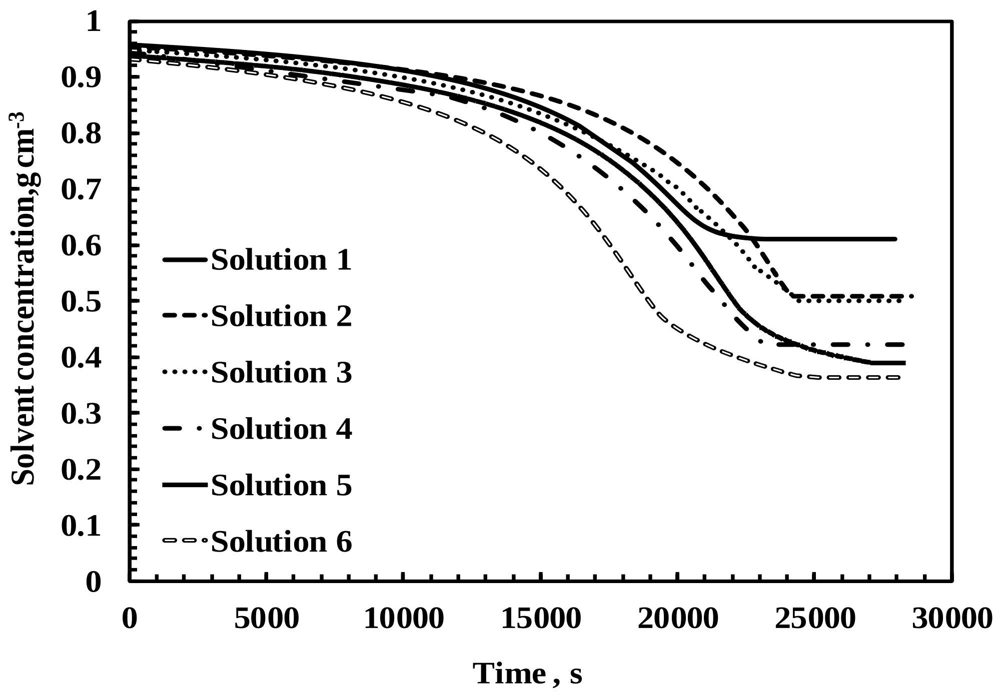

Figure 4.8: Solvent concentration as a function of time for various SDS loading for 1900 μm initial thickness at 25ºC**.**

The residual solvent is the amount of solvent trapped in the dry polymeric coating. It is greatly influenced by the presence of surfactant in polymeric coatings. The amount of solvent is highly dependent on the concentration of surfactant which in general reduces the amount of residual solvent with the increase in its concentration. The reduction in the residual solvent percentage is mainly due to the lowering of surface tension by the surfactant. The residual solvent is decreased from 5.88% to 2.54 % in case of 900 μm initial thickness from Solution 1 to Solution 6 in Table 4 row 1 and row 6 respectively. Solution 1 is the PVA-Water coating with no surfactant whereas from Solution 2 to Solution 6 surfactant has following concentrations 0.5%, 1%, 1.5%, 2% and 2.5 respectively. The optimum value of SDS comes out to be 1.5% as it diminishes the residual solvent as well as it has less drying time among all the Solutions. Similarly, when the initial coating thickness has been changed to 1900 microns. The residual solvent decreases with the increase in surfactant concentration. The residual solvent is decreased from 6.96% to 4.18% in case of 1900 μm initial thickness from Solution 1 to Solution 6 in Table 5 row 1 and row 6 respectively. The coating solution with SDS concentration 1.5% by weight comes out to be the optimum value as it reduces the residual solvent as well as it has less drying time among all the Solutions.

Table 4: Summarized drying data of PVA-Water coating with and without surfactant of initial thickness – 900 microns.

Solution No.	Composition	Initial thickness (microns)	Final thickness (microns)	Ultimate residual solvent (%)	Drying time (s)			
					Falling rate		Constant rate	
					Time (s)	% Solvent left	Time (s)	% Solvent left
Solution 1	PVA (%)-Water (%)	960	95	5.88	0-14138	5.95	14138-17674	5.88
Solution 2	PVA (%)-Water (%)-SDS (0.5%)	941	88	4.88	0-15473	5.21	15473-17323	4.88
Solution 3	PVA (%)-Water (%)-SDS (1%)	919	84	4.17	0-14543	4.45	14543-17534	4.17
Solution 4	PVA (%)-Water (%)-SDS (1.5%)	908	85	3.85	0-10900	3.93	10900-17116	3.85
Solution 5	PVA (%)-Water (%)-SDS (2%)	945	88	3.27	0-11999	3.36	11999-17199	3.27
Solution 6	PVA (%)-Water (%)-SDS (2.5%)	988	91	2.54	0-15599	2.54	15599-17234	2.54

Table 5: Summarized drying data of PVA-Water coating with and without surfactant of initial thickness 1900 microns.

Solution No.	Composition	Initial thickness (microns)	Final thickness (microns)	Ultimate residual solvent (%)	Drying time (s)			
					Falling rate (s)		Constant rate (s)	
					Falling time (s)	% solvent left	Constant time (s)	% solvent left
Solution 1	PVA (%)-Water (%)	1897	207	6.96	0-21536	7.25	21536-27932	6.96
Solution 2	PVA (%)-Water (%)-SDS (0.5%)	1959	187	5.09	0-24161	5.09	24161-28537	5.09
Solution 3	PVA (%)-Water (%)-SDS (1%)	1906	198	5.49	0-24533	5.49	24533-28428	5.49
Solution 4	PVA (%)-Water (%)-SDS (1.5%)	1962	194	4.44	0-23078	4.5	23078-28509	4.44
Solution 5	PVA (%)-Water (%)-SDS (2%)	1936	196	4.21	0-25546	4.49	25546-28236	4.21
Solution 6	PVA (%)-Water (%)-SDS (2.5%)	1922	206	4.18	0-23646	4.43	23646-28201	4.18

Figure 4.9 shows variation of ultimate residual solvent with surfactant loading. Primary y-axis and Secondary y-axis shows the drying time (s) with surfactant loading(wt.%). The drying

time increases to small extent from Solution 1 to Solution 2 and then decreases upto Solution 4. Then with further increased in surfactant concentration increased the drying time. The result indicated that the optimum value of SDS is 1.5 wt.% in PVA-Water system which not only reduces the residual solvent percentage but also decrease the drying time very significantly. Hence Solution 4 i.e. coating solution having 1.5 wt.% SDS is the optimum value of SDS loading for this system having initial thickness 900 µm. The optimum SDS loading for this system is 1.5 wt.% which gives minimum residual solvent as well as the least drying time beyond this value residual solvent decreases but there is sharp increase in the drying time.

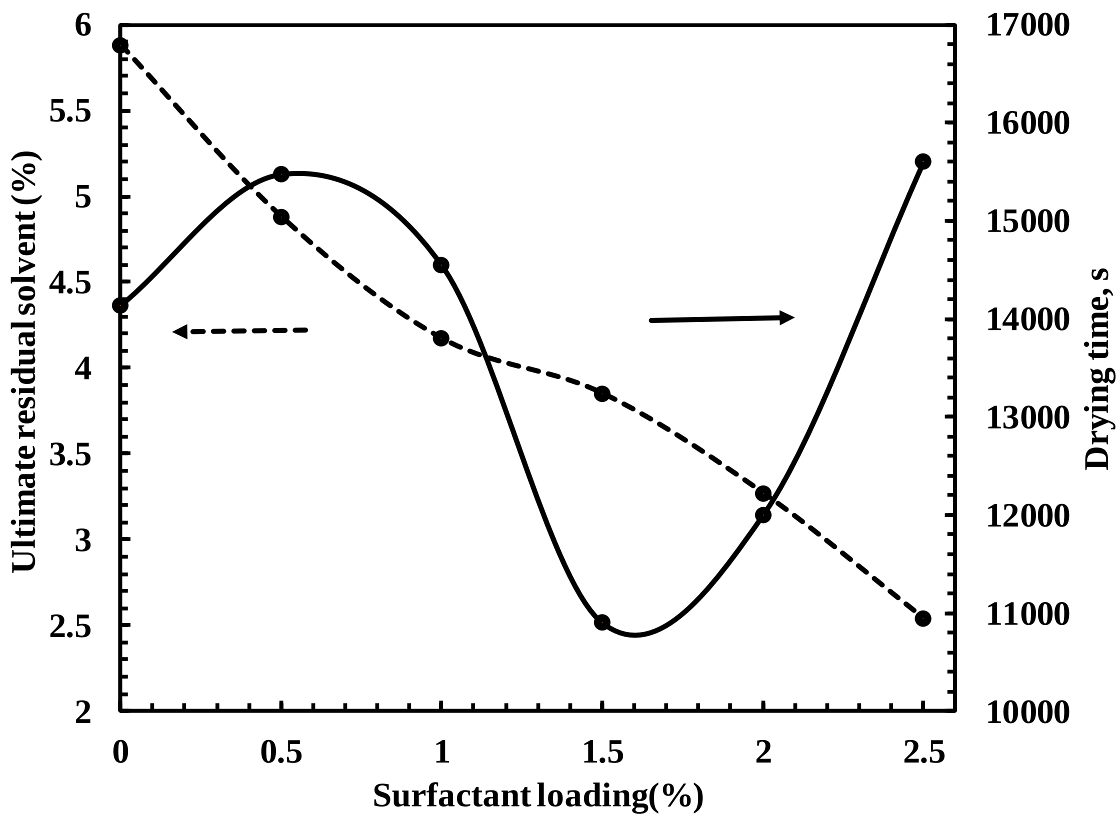

Figure 4.9: Ultimate residual solvent (%) and drying time as a function of surfactant loading (wt.%).

Figure 4.10 shows the variation of residual solvent (%) with surfactant loading (wt.%) of 1900 µm thick coatings. Residual solvent follows the same trend as it was in the case of 900 µm thickness. The residual solvent decreases with increase in surfactant loading. However, there is slight increase in residual solvent from Solution 2 Solution 3 i.e. from 5.09 to 5.49 % which is not much significant. Otherwise the residual solvent decreases with increase in surfactant. Figure 4.10 also shows variation of drying time with surfactant loading (wt.%). The drying time increases with increasing surfactant loading in general. The results show decrease in drying time in case of 1.5% of SDS. Then again at high concentration of SDS drying time increases and little decrease in case of 2.5 wt.% of SDS but still higher from PVA +Water without surfactant. Hence results indicated that 1.5% SDS is the optimum value of SDS loading for this system at 1900 µm thickness also. This shows that optimum SDS loading is independent of coating thickness which in agreement of solution thermodynamics. Physical variables like initial coating cannot affect the diffusion mechanism and system internal properties and thermodynamic interaction parameter, activities i.e., the diffusion rate. It may only take higher drying time due to thick coating i.e. high amount of solvent to be removed at same diffusion and convective mass transfer rates.

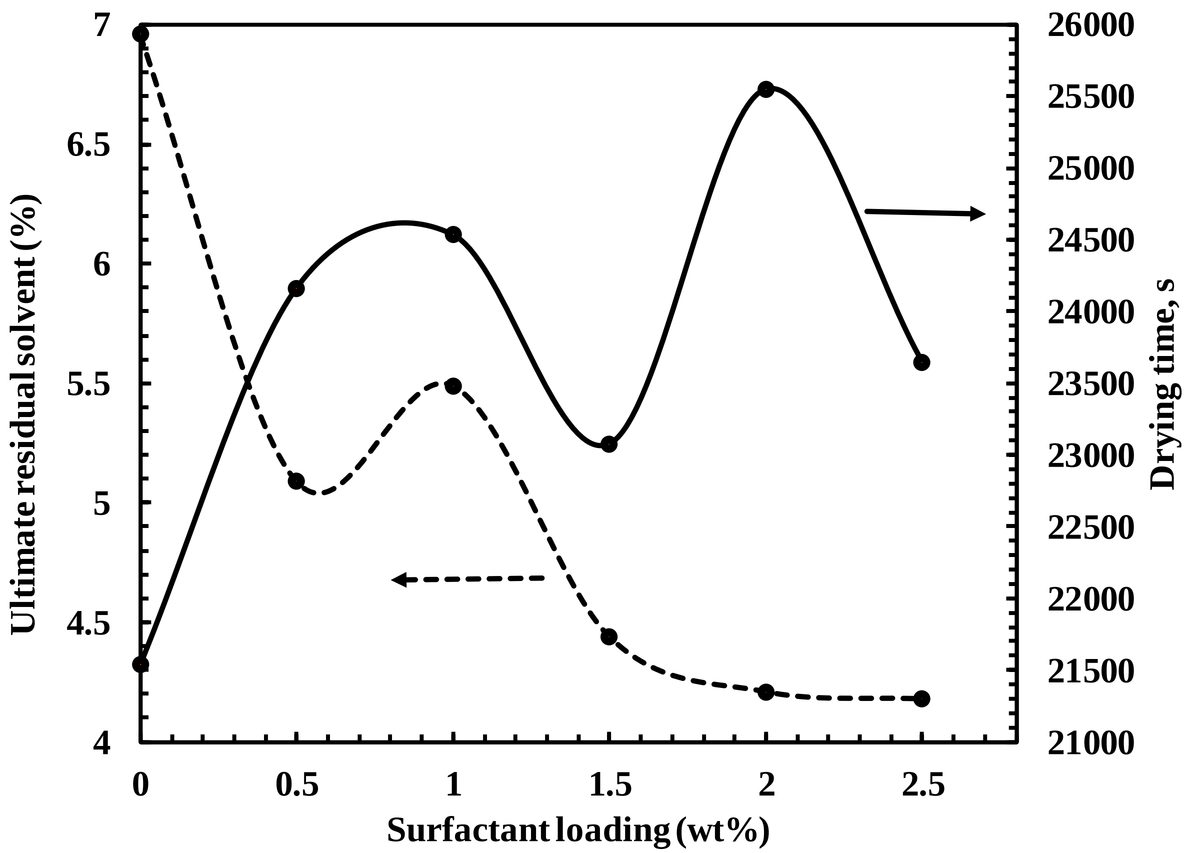

Figure 4.10: Ultimate residual solvent (%) and drying time (s) as a function of SDS loading (wt.%) in case of initial thickness 1900 µm at 25ºC.

Chapter 5

Conclusions

Sodium dodecyl sulphate has influenced the drying behavior to a large extent. Residual solvent decreased with increase in surfactant loading. The drying time required for drying has also decreased with surfactant loading and increases after a particular amount of loading. For the system studied, the optimum loading comes out to be 1.5 wt.% which was independent of initial coating thickness. The initial coating thickness is not able to change the diffusion and convective mass transfer due to independency of polymer solution thermodynamics on initial coating thickness, coating geometry etc.

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