International Journal of Applied Sciences: Current and Future Research Trends
(IJASCFRT)
ISSN (Print) , ISSN (Online)

https://ijascfrtjournal.isrra.org/index.php/Applied_Sciences_Journal

Electrospinning Polyacrylonitrile Nanofibers

Alia M Hindi[a]*, Mohammad Yahia Masri[b]

[a]*Postgraduate Studies (PhD)*
[b]*Pro, Faculty of Science, University of Aleppo*
[a]*Email: allyfirst1@hotmail.com*

Abstract

Polyacrylonitrile (PAN) solutions were prepared at a constant concentration in dimethylformamide (DMF) medium with different concentrations of octadecylamine (ODA) colloidal surfactant. (ODA). The studied solutions were spun with an electric spinning device, with a voltage of 30 kV, the collector cylinder is 10 cm from the injector, the pumping rate is 0.5 ml/hr, the diameter of the injector needle is 0.5 mm, and the diameter of the injection needle is 0.5 mm. The accumulator rotation speed is 100 c/min. We examined the spun fibers using SEM scanning electron microscopy, and found a decrease in the diameter of these fibers from 280 nm to 115 nm due to the increase in the surface active substance (ODA) concentration. The X-ray diffraction spectrum was examined for the as-prepared fibers, and we observed an evolution of the crystal structure of PAN in the presence of ODA.

Keywords: Electrospinning; Nanofiber; Polyacrylonitrile; Surfactants.

1. Introduction

Since the beginning of the eighties, the technology of electrospinning has begun to acquire a very large interest, and this can be attributed to the boom that occurred in the field of nanotechnology and its applications, as the number of universities, institutes and research centers interested in this technology exceeded more than two hundred [1,2], and many of Scientific articles on this topic, and several patents related to this technology have also been granted [3]. It is worth noting that electrospinning is the only technique that uses electrostatic force in the production of nanofibers from polymer solutions or smelters with diameters that may reach up to 2 nm and with a very large specific surface [4,5]. Although electrospinning is the simplest method for fabricating nanofibers, there are some important factors that can have a significant impact on the nanofiber structure, its diameter, these factors are classified into [6].

---

* Corresponding author.

Variables influencing the various factors

Factors affecting polymer solution viscosity, solution concentration, polymer molecular weight, Solvent properties, surface tension, and electrical conductivity

Factors affecting electrospinning technique Applied voltage, distance between injector head and collector, flow rate

External factors temperature, relative humidity

Each of the previous factors greatly affects the shape and structure of the resulting fibers, so it is necessary to find an appropriate combination between all these factors to obtain the fibers of the required diameter [7-10].

Surface-active colloidal materials strongly affect the structural and mechanical properties of polymeric solutions, because the effectiveness of the mutual effects between the molecules of the polymer itself, is greatly affected by the presence of these materials, and these materials also affect the shape and dimensions of the nanofibers formed from them [11,12]. Research and studies on the effect of surfactant colloids on the structural properties of the dispersed systems of polymer solutions are still few and rare [13,14].

There are two types of reciprocal effects between the surfactant colloid and polymers, the first is an electrostatic reciprocal effect of Figure (1) [15] and the second: a hydrophobic reciprocal effect of Figure (2) [16] This is due to the nature of the chemical structure of each of them.

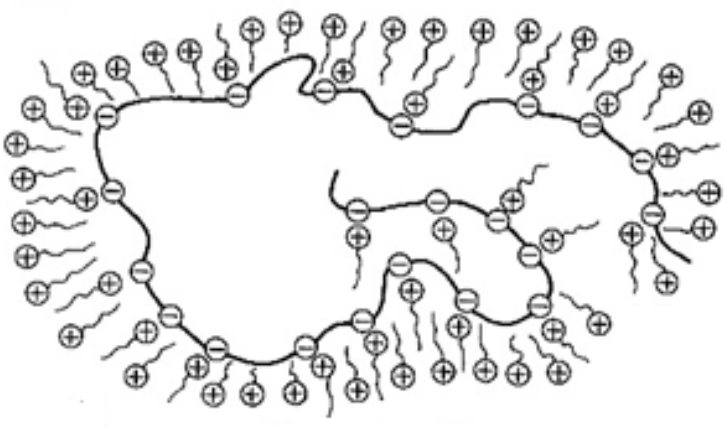

Figure 1: Electro-static interaction.

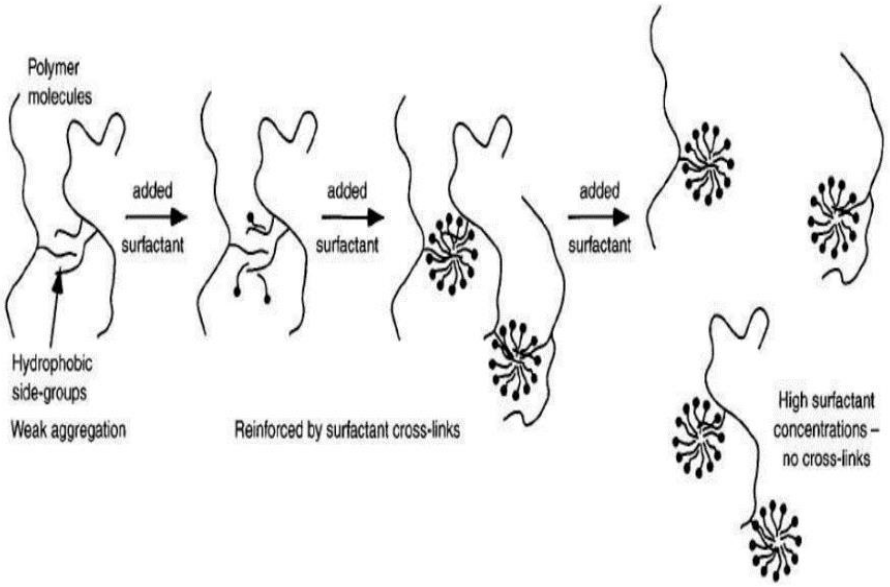

Figure 2: Hydrophobic interaction**.**

Sodium dodosylbenzene sulfonate SDBS surface-active colloid was used in PAN/DMF polyacrylonitrile solutions. A decrease in the diameters of the resulting nanofibers and an increase in the smoothness and quality of their surface was observed [17].

The effect of the colloidal surface-active substance octadecylamine on the electrospun nanofibers of polyphenols coated with urea was studied. An increase in the rate of urea release was observed, due to a decrease in the diameter of the fibers in the presence of octadecylamine [18].

He also investigated the effect of the surface-active colloidal octadecylamine ODA on polyvinyl alcohol and found a decrease in the surface tension of the studied polymeric solutions and in the radii of electrically spun nanofibers [19].

2. The practical section

1-Materials used:

1- Polyacrylonitrile synthetic fibers with a known molecular mass of 100,000 g/mol [20].

2- Dimethylformamide DMF with purity (GC) (99.5%) from MERCK

3- Octadesylamine ($C_{18}H_{37}NH_2$) ODA from Alfa Aesar

2- Devices used:

1- The German-made ball drop viscosity device from HAAKE company, which complies with ISO 12058. This device is equipped with a water shirt to keep the temperature with an accuracy of ±0.03°C and measures with

this accuracy up to 80°C. This device enables us to measure the viscosity within the range (0.3 - 75000) mPa S, according to the ball used.

2- French-made WTW-Inolab-Level-1 electrical conductivity device with an accuracy of 0.01 ±

3- An electric spinning device designed and produced by us [21]

4- X-ray diffraction device (X-ray diffraction "XRD")

5- Scanning Electron Microscopy "SEM".

3. Practical results and their discussion

1- A pure solution of polyacrylonitrile was prepared with a concentration of 10% by weight. The sample was dissolved in a dimethylformamide solution by continuous stirring at the laboratory temperature. Thus, we obtained a transparent polymeric solution. Then we prepared solutions of PAN 10%W in the presence of different concentrations of ODA. Taking into account the stability of the polymer concentration in each studied sample, then it was left for the next day to study its viscosity and electrical conductivity.

2- The prepared solutions were spun with an electrospinning device

3- The spun fibers (SEM) and (XRD) tests were carried out.

In order to determine the marginal concentration of CMC of ODA taken in its salt form, we studied its specific electrical conductivity in DMF at different concentrations of it and at a temperature of 298 K, and the results are presented in Table (1)

Table 1: The specific electrical conductivity of ODA solutions at different concentrations of it and at a temperature of 298K.

ODA C×10^5,mol/L	1.2	2.4	4.8	9.6	19.2	38.4
$\mathcal{K}$,µs/cm	580	588.9	606	608	613.8	622.3
Log $\mathcal{K}$	2.763	2.770	2.782	2.784	2.788	2.794

The marginal concentration of liquefied formation (CMC) of ODA surface-active colloid was determined, by studying the relationship between the logarithm of specific electrical conductivity log k and the concentration of ODA. Figure (3) shows:

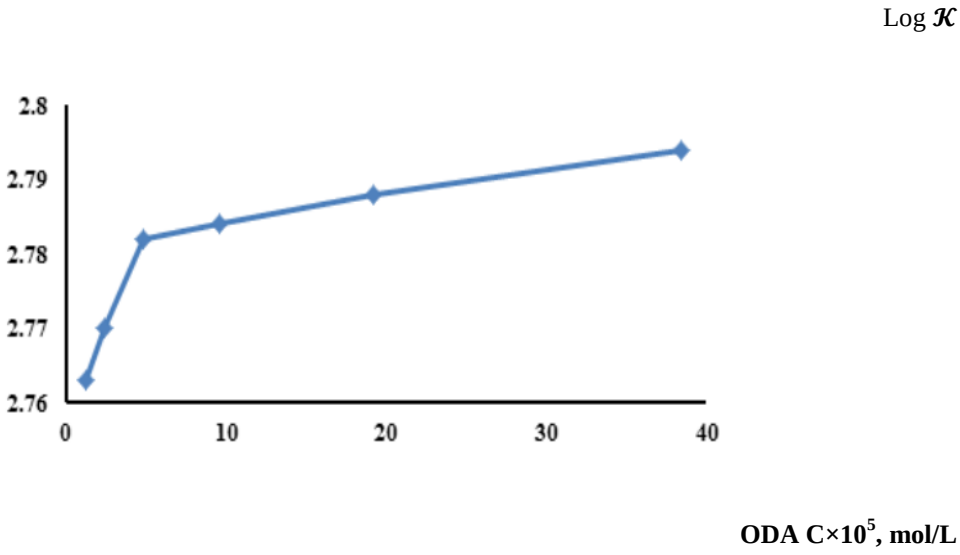

Figure 3: The relationship of log K with the ODA concentration function at 298K.

We find in Figure (3) that there is a breaking point in the graph and we consider that this point represents the CMC and is equal to 4.8X10-5 mol/L [22]

The viscosity of the solutions prepared from PAN 10% by weight was calculated in the presence of different concentrations of ODA according to the following relationship [23]:

$\eta=(d1-d2)\ t$

where: ***k*** the sphere constant, d1 the density of the sphere, d2 the density of the solution, t the time of the ball falling.

We show in Table (2) the results of measuring the viscosity of the prepared solutions at a temperature of 298 K.

Table 2: The viscosity of PAN solutions 10% by weight in the presence of different concentrations of ODA at a temperature of 298K.

SAMPLE	Viscosity η, mPas
PAN 10% Pure	264.968
PAN 10% + ODA 1.25×10^{-5} mol/L	238.537
PAN 10% + ODA 2.5 ×10^{-5} mol/L	231.932
PAN 10% + ODA 5×10^{-5} mol/L	228.012
PAN 10% + ODA 8 ×10^{-5} mol/L	226.705
PAN 10% + ODA 10×10^{-5} mol/L	225.967
PAN 10% + ODA 20×10^{-5} mol/L	224.676

Figure (4) shows the relationship of viscosity of PAN 10%W solutions in the presence of different concentrations of ODA at a temperature of 298K.

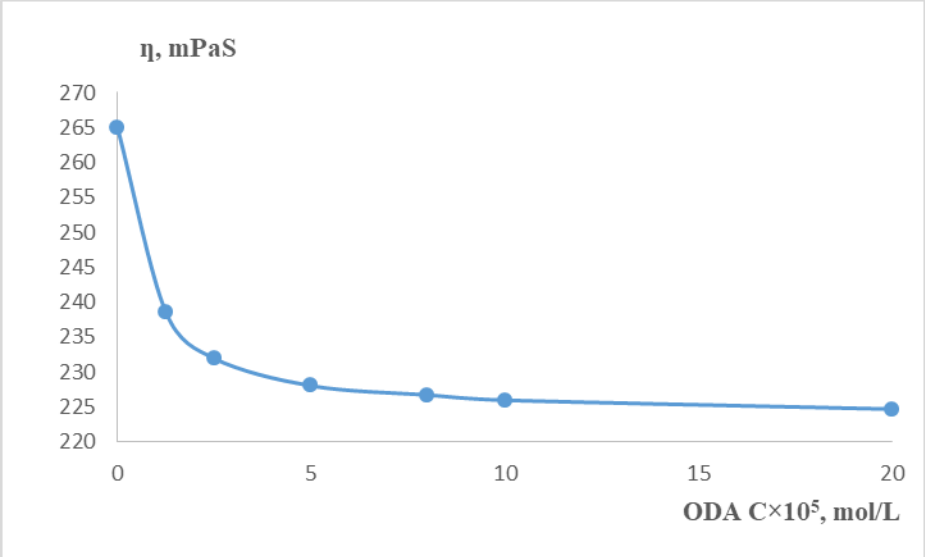

Figure 4: Relationship of the viscosity of PAN 10%W solutions in the presence of different concentrations of ODA and that at a temperature of 298K**.**

We find in Figure (4) that the viscosity of PAN solutions in the presence of different concentrations of ODA decreases sharply with the increase of ODA concentration up to the limiting concentration of CMC, then the viscosity is not related to the ODA concentration and this is due to the effect of ODA on the conformation of the polyacrylonitrile macromolecules. and weaken the mutual influences between them. [16, 24]

We also studied the relationship of the specific electrical conductivity of PAN solutions in the presence of different concentrations of ODA at the temperature of 298K. We present in Table (3) the values of the specific electrical conductivity of the prepared PAN solutions at a temperature of 298K.

Table 3: The specific electrical conductivity of PAN solutions 10% by weight in the presence of different concentrations of ODA at a temperature of 298K.

SAMPLE	specific electrical conductivity κ, µs/cm	Log κ
PAN 10% Pure	97.5	1.989
PAN 10% + ODA 1.25×10^{-5} mol/L	165	2.22
PAN 10% + ODA 2.5×10^{-5} mol/L	229	2.36
PAN 10% + ODA 5×10^{-5} mol/L	318.4	2.503
PAN 10% + ODA 8×10^{-5} mol/L	399	2.601
PAN 10% + ODA 10×10^{-5} mol/L	439.5	2.643
PAN 10% + ODA 20×10^{-5} mol/L	677.6	2.831

We show in Figure (5) the relationship of the specific electrical conductivity of PAN 10% W solutions in the presence of different concentrations of ODA at a temperature of 298 K

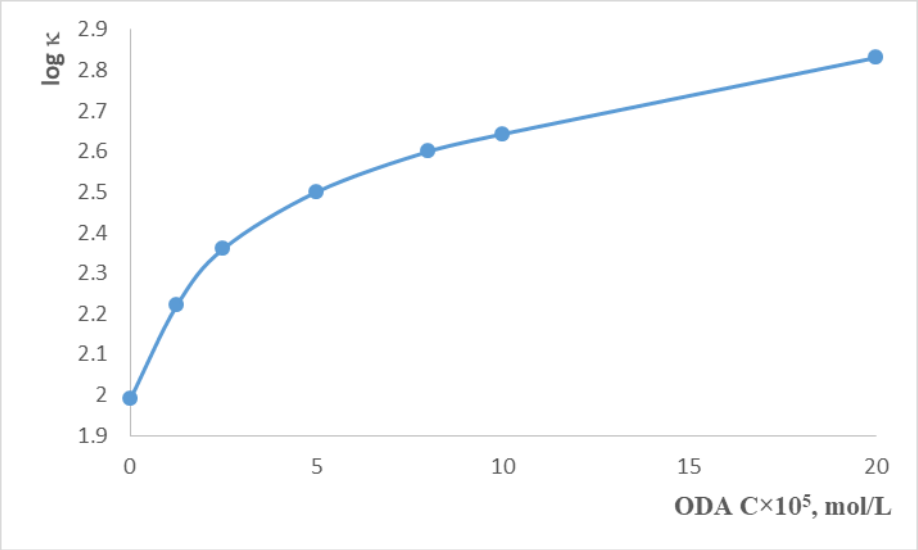

Figure 5: Relationship of the specific electrical conductivity of PAN 10%W solutions in the presence of different concentrations of ODA and that at a temperature of 298K.

We find in Figure (5) that the specific electrical conductivity of PAN/ODA solutions increased with the increase in ODA concentration, sharply at small concentrations and a less sharp increase for concentrations greater than 10×10-5 mol/L of ODA.

The previously prepared solutions were spun with an electrospinning device to prepare the nanofibers, when the following variables were fixed:

- Solution flow rate: 0.5 ml/h., Voltage riser: 30 kv.
- Collector rotation speed: .100 cy/min, collector distance from the injector: 10 cm.
- Collector type: Rotary cylindrical, injection needle diameter 0.5 mm.

Scanning electron microscope images were taken for the resulting fibers to calculate their average diameter. Figure (6) shows that:

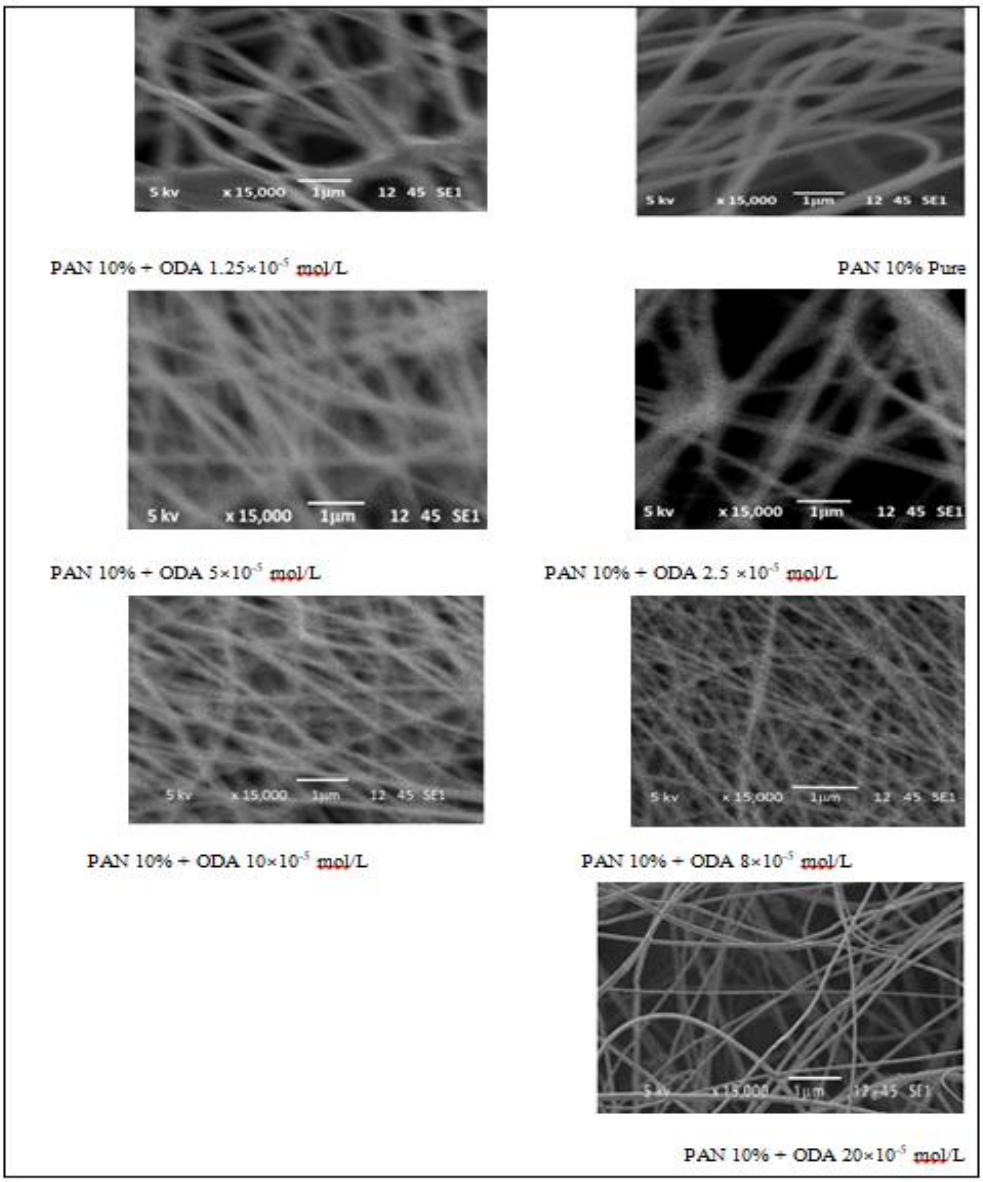

Figure 6: SEM images with different concentrations of ODA.

In Table (4) we show the diameter of the fibers measured by means of SEM

Table 4: shows the diameter of the fibers measured by a device**.**

spun solution	average diameter (nm)
PAN 10% Pure	280
PAN 10% + ODA 1.25×10^{-5} mol/L	225
PAN 10% + ODA 2.5 ×10^{-5} mol/L	190
PAN 10% + ODA 5×10^{-5} mol/L	145
PAN 10% + ODA 8 ×10^{-5} mol/L	130
PAN 10% + ODA 10×10^{-5} mol/L	125
PAN 10% + ODA 20×10^{-5} mol/L	115

Figure (7) shows the relationship of the average diameter of the polyacrylonitrile nanofibers to the increase in the concentration of ODA.

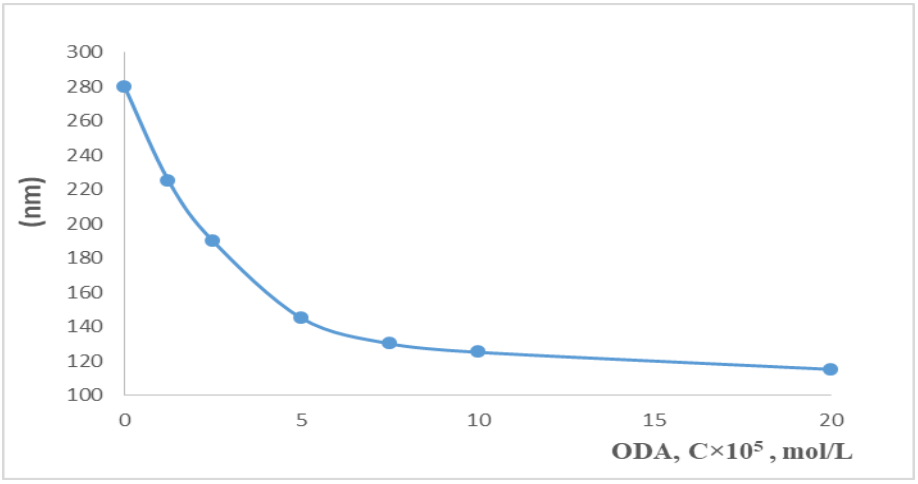

Figure 7: Relationship of the average diameter of the PAN nanofibers to the increase in the concentration of ODA . Surfactant Colloid.

We notice from Table (4) and Figure (6) a sharp decrease in the average radii of the PAN in the presence of ODA, due to the mutual effects between the PAN and ODA [11,15,16]

We studied the previous samples using X-ray diffraction, which is connected to a computer to assess the degree of crystallization. Figure (7) shows the XRD graphs of the previous samples.

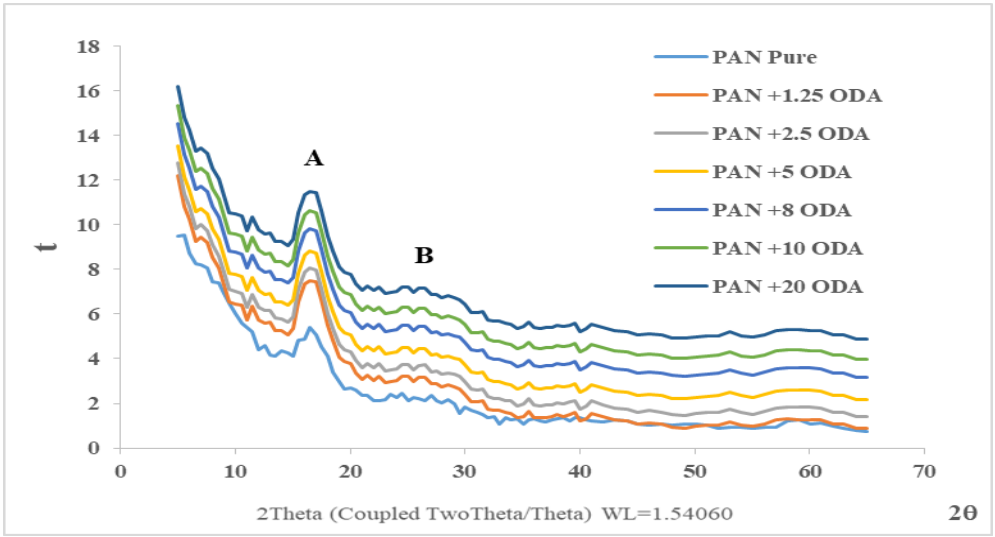

Figure 7: XRD spectra of the prepared PAN samples.

We find from Figure (7) that the X-ray diffraction patterns of the previous samples contain two main peaks, the

first peak is strong (A), and the second is weak and broad (B), where the first peak indicates the formation of the crystal structure, while the second peak indicates that there is still a glass structure [25]. In Figure (7), we see the evolution of the structure in the presence of ODA from the pure PAN structure.

4. Conclusions

We noticed that the relationship of viscosity and specific electrical conductivity of PAN/ODA solutions is non-linear,We found that the viscosity of PAN/ODA solutions decreases sharply up to the threshold concentration of mycelite formation, then the viscosity is no longer correlated with the ODA concentration,We found that the specific electrical conductivity of PAN/ODA solutions increased with increasing ODA concentration, It was found by using scanning electron microscope (SEM) that the average diameters of the PAN nanofibers decreased sharply with increasing ODA concentration up to the marginal concentration of flocculants, then this decrease becomes not significant,Using the XRD device, it was found that the structure of PAN10%W developed with an increase in the concentration of ODA due to the mutual effects between PAN and ODA.

References

[1]. Li, Z., & Wang, C., 2013, One-dimensional Nanostructures: Electrospinning Technique and Unique Nanofibers, j Springer.

[2]. A. Greiner, J.H. Wendorff,2007, Electrospinning: a fascinating method for the preparation of ultrathin fibers, Angewandte Chemie International Edition, 46 (2007) 5670-5703.

[3]. Tlili, Tawfeeq Abdullah Alkanhal, 2019, Nanotechnology for water purification: electrospun nanofibrous membrane in water and wastewater treatment, Journal of Water Reuse and Desalination | 09.3 | 2019, p 232-248

[4]. Yuan Gao, Yen Bach Truong, Yonggang Zhu, Ilias Louis Kyratzis ,2014, Electrospun Antibacterial Nanofibers: Production, Activity,and In Vivo Applications, J. APPL. POLYM. SCI. 2014, DOI: 10.1002/APP.40797.

[5]. Al-Jallad, Mazen; Al-Atassi, Yemen; 2016; Preparation of carrier compounds (polymer-polymer carrier): Preparation of nanowoven and electrically conductive mats from polymeric lactic acid (PLLA) and polyaniline PANI, Higher Institute of Applied Sciences and Technology, Department of Applied Physics, Damascus.

[6]. Saikat Sinha Ray, Shiao-Shing Chen, Nguyen Cong Nguyen†, Hau Thi Nguyen, 2019, Electrospinning: a versatile fabrication technique for nanofibrous membranes for use in desalination, Nanoscale Materials in Water Purification, chapter 9, p (247-273

[7]. Jaydevsinh M. Gohil, Rikarani R. Choudhury,2019, Introduction to nanostructured and nano-enhanced polymeric membranes: preparation, function, and application for water purification, Nanoscale Materials in Water Purification, chapter 2, p (25-57).

[8]. Yana Bagbi, Arvind Pandey, Pratima R. Solanki, 2019, Electro spun nanofibers for air filtration, Nanoscale Materials in Water Purification, chapter 10, p (275-288).

[9]. Shichao Zhang, Nadir Ali Rind, Ning Tang, Hui Liu, Xia Yin, Jianyong Yu, Bin Ding ,2019, Electro spun nanofibers for air filtration, Nanoscale Materials in Water Purification, chapter 12, p (365-389).

[10]. Blesson Isaac, Robert M. Taylor, and Kenneth Reifsnider, 2021, Mechanical and Dielectric Properties of Aligned Electrospun Fibers, journal MDPI, fibers 2021,9,4.

[11]. Voyutsky S., 1978- Colloid Chemistry. Mir Publisher, Moscow.

[12]. Fralov Y.G., 1982- Course of colloidal chemistry. Kimya, Moscow.

[13]. Lipatov Y. S., 1984- Colloid Chemistry of Polymers. Doumca, Keav.

[14]. Kienskaya K. I, 1994- The Interplay between Hydrodynamic and Structural Characterstics in Surfactant –Polyacrylonitrile Systems. Polymer Science, 36(1),91-94

[15]. NAGARJAN R, 1981- On nature interaction between polymers and surfactants in dilute aqueous solution. *American Chemical society, 2, 33- 38.*

[16]. ODEH F, 2006- Polymer- surfactant interaction. Clarkson university, 49.

[17]. Deng-Guang Yu, Gareth R. William, Li-Dong Ga, S.W. Annie Bligh, Jun-He Yang, Xia Wang, 2011, Coaxial electrospinning with sodium dodecylbenzene sulfonate solution for high quality polyacrylonitrile nanofibers, Colloids and Surfaces A: Physicochem. Eng. Aspects 396 (2012) 161–168.

[18]. Meizhou Sun a,1, Heling Guo a,1, Jiliang Zheng b, Yu Wang a, Xinghuan Liu, Qian Li Rongjie Wang, Xin Jia, Hydrophobic octadecylamine polyphenol film coated slow released urea via one-step spraying co-deposition, j. polymertesting. Volume 91,106831 (2020).

[19]. Murat Şimşek, Zakir M O Rzayev and Ulviya Bunyatova ,2016, Multifunctional electroactive electro spun nanofiber structures from water solution blends of PVA/ODA–MMT and poly (maleic acid-alt-acrylic acid): effects of Ag, organoclay, structural rearrangement and NaOH doping factors, Adv. Nat. Sci.: Nanosci. Nanotechnology. 7, 025009 (13pp).

[20]. ABDUL NOUR, S., 2014- Study of the intermolecular interaction between Polyacrylonitrile and amphoteric surfactant (Betaine) in dimethyl formamide. Asian *Journal of Chemistry, 26, 4810- 4814.*

[21]. Hindi, Alia, Abdul Noor, Said, Al-Haj Omar, Salah, 2021, Design of an electrospinning device to produce of polyacrylonitrile nanofibers, Aleppo University Research Journal, Issue 149

[22]. Bahrami H.,2007- Dynamic Adsorption of Gemini and Conventional Cationic Surfactants onto Polyacrylonitrile. Colloids and Surfaces, 307(13), 121-127.

[23]. Hindi, Alia; 2016, Study the interactions between surfactant colloid (octadecylamine) and polyacrylonitrile macromolecules, Master's thesis, University of Aleppo

[24]. Tager A, 1978– Physical chemistry of polymers. Mir Publisher, 2nd Ed, Moscow.

[25]. Xiao H, 2008, Interior structure of polyacrylonitrile nanofibers with LiCl., Materials Letters, 62(8-9), 1325-1327