Comparison of the Interactions Between Anionic Surfactants and Polyacrylonitrile

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Abstract  Viscosity and specific electrical conductivity of polyacrylonitrile (PAN) in N,N-dimethylformamide (DMF) medium are studied in the presence and absence of anionic surfactants as sodium oleate, sodium dodecyl sulfate and palmitic. Critical micelle concentrations of these surfactants are determined in DMF medium. Thermodynamic functions \(\Delta H_m^\circ\), \(\Delta G_m^\circ\) and \(\Delta S_m^\circ\) of micelle formation of sodium dodecylbenzene sulfonate and sodium dodecyl sulfate are determined. Curves of X-ray diffraction and differential thermal analysis showed that the PAN samples containing SDS lead to the development of the crystalline structure of PAN, and the initiation temperature decreases of the cyclization reaction of nitrile groups of PAN by 8.5 °C, respectively.

Keywords  Polyacrylonitrile · Viscosity · Conductivity · Fiber · Mechanical and structural properties · Surfactants

1 Introduction

Since the invention of PAN-based carbon fibers in the 1950s by Shindo and Watt have attracted the world’s attention as high-performance materials [1]. The PAN used in the textile industry is considered copolymers and has hardness linear chains [2–4].

Viscosity of PAN solution plays a significant role in the studying of mechanical and structural properties of produced fiber. A study of the relationship between viscosity of PAN solutions and concentration in DMF medium shows strong associations of PAN molecules, and this is because of the interactions between dipoles [5–7].
2. Instruments

2.2.1 Differential Thermal Analysis

The differential thermal analysis (DTA) is carried out in Linseis PT-1600 at heating rate of 10°C/min from ambient temperature to 400°C in a Helium environment.

2.2.2 X-ray Diffractometer

The patterns of X-ray diffraction (XRD) of PAN are obtained using a STOE transmission STADI diffractometer, with copper as target and nickel as filter (λ = 1.5408 Å) at 30 kV and 30 mA. The scanning speed was 3.7 min⁻¹ in the range 2θ = 10°–90° at 298 K.

2.2.3 Conductometer

Specific electrical conductivity is measured by SANXIN–MP 513 Lab Conductivity Meter.

2.2.4 Falling Ball Viscometer

The falling ball viscometer (HAAKE Co.) corresponds to the requirements of many international standards (ISO 12058 and the German standard DIN 53015). The measuring tube is jacketed by means of an outer glass tube, to control the solution temperature (±0.03°C for test temperatures between 10 up to 80°C). This device can measure the viscosity ranging between 0.3–75,000 mPas. Every value was measured three times and then averaged.

2.3 Preparation of PAN Solutions

PAN solutions are prepared in range 0.5–10 wt%. PAN fibers are dissolved in DMF by continuous stirring at laboratory temperature, and then, transparent polymeric solutions are obtained. Also, PAN solutions are prepared in the presence of different concentrations of surfactant. Then, viscosity and specific electrical conductivity of prepared solutions are studied.
2.4 Preparation of PAN Solid Samples

The solid samples of PAN are prepared in order to study their structural and thermal properties in the following way. PAN solutions are prepared in the presence of surfactant and its absence, then poured in Petri dishes, put in dryer at 50 °C until the complete vaporization of DMF, where solid samples are obtained, these samples are examined by XRD and DTA.

3 Results and Discussion

Viscosity (η) of PAN solutions are measured at 298, 308, 318, 328 K, and specific electrical conductivity (SEC) is measured at 298, 308 K. Viscosity of PAN solutions is estimated through the following equation:

\[ \eta = K(d_1 - d_2)t \]  \hspace{1cm} (1)

where \( K \) ball constant, \( d_1 \) ball density, \( d_2 \) solution density, \( t \) falling time of the ball.

Then, a specific viscosity (\( \eta_{sp} \)) calculated through the following equation [6]:

\[ \eta_{sp} = \eta - \eta_0 \]  \hspace{1cm} (2)

\( \eta_0 \) solvent viscosity.

Tables 1, 2 and 3 show the results of measuring the viscosity and the SEC respectively.

Figures 3 and 4 show the dependence of specific viscosity and SEC on PAN concentration, respectively.

Figure 3 shows that \( \eta_{sp} = f(C) \) is an exponential relationship. Specific viscosity increases in an almost straight line

**Table 1** Viscosity of PAN solutions

| \( T \) (K) | PAN concentration \( C \) (wt %) |
|------------|----------------------------------|
|            | 1  | 2  | 3  | 4  | 6  | 8  | 10 |
| \( \eta \) (mPas) |
| 298        | 0.473 | 1.495 | 3.210 | 8.831 | 15.813 | 46.338 | 109.333 | 264.968 |
| 308        | 0.420 | 1.221 | 2.751 | 7.359 | 12.876 | 37.971 | 90.210 | 224.973 |
| 318        | 0.375 | 1.097 | 2.293 | 6.227 | 10.843 | 30.892 | 70.102 | 164.980 |
| 328        | 0.339 | 0.955 | 2.030 | 5.321 | 9.261 | 25.743 | 56.234 | 129.980 |

**Table 2** Specific viscosity of PAN solutions

| \( T \) (K) | PAN concentration \( C \) (wt %) |
|------------|----------------------------------|
|            | 1  | 2  | 3  | 4  | 6  | 8  | 10 |
| \( \eta_{sp} \) |
| 298        | 2.160 | 5.786 | 17.670 | 32.431 | 96.966 | 230.147 | 559.186 |
| 308        | 1.907 | 5.547 | 16.521 | 29.657 | 89.407 | 213.785 | 534.650 |
| 318        | 1.925 | 5.114 | 15.605 | 27.914 | 81.378 | 185.938 | 438.946 |
| 328        | 1.817 | 4.988 | 14.696 | 26.318 | 74.938 | 164.882 | 382.421 |

**Table 3** SEC of PAN solutions

| \( T \) (K) | PAN concentration \( C \) (wt %) |
|------------|----------------------------------|
|            | 0  | 0.5 | 1  | 2  | 3  | 4  | 6  | 8  | 10 |
| \( \chi \) (µS cm\(^{-1}\)) |
| 298        | 0.7 | 12.3 | 23.0 | 39.1 | 52.8 | 64.0 | 82.6 | 92.1 | 97.5 |
| 308        | 0.8 | 14.5 | 27.8 | 44.0 | 59.8 | 70.9 | 88.9 | 102.0 | 111.4 |
Fig. 4 SEC dependence on PAN concentration at 298, 308 K

at low concentrations, and then markedly increases starting with the percolation threshold of a crystalline structural formation (5 wt% approximately). This refers to the interaction between dipoles of PAN which leads to the occurrence of strong associations of macromolecules. Figure 3 also shows that temperature change does not affect the mechanism of crystalline structure formation; this may be due to the hardness of polymer chains [2, 6, 9].

Figure 4 shows that $\chi = f(C)$ is a logarithmic relationship. SEC increases with increasing of PAN concentration, then after a concentration of 5 wt%, conductivity becomes practically independent of concentration. This happens because of the completion of crystal structure [19].

The CMCs of anionic surfactants are determined by the SEC in DMF medium at 298 K. The results are listed in Table 4.

The CMC of anionic surfactant in DMF medium is determined by using the following equation $\log \chi = f(C)$. Figure 5 shows that.

Figure 5 also shows that the SEC increases at the beginning of the curve sharply, until the start of micelles formation then slowdown. This may be due to the partial link of counter ions with ionized micelles [13, 20, 21].

Values of CMCs are listed in Table 5.

Table 4 SEC of anionic surfactants solutions at different concentrations

| Surfactant       | CMC $\times 10^4$ (mol l$^{-1}$) |
|------------------|----------------------------------|
| SO (C$_{17}$H$_{33}$COONa) | 1.6                              |
| PA (C$_{15}$H$_{31}$COOH)   | 12.5                             |
| SDS (C$_{12}$H$_{25}$SO$_4$Na) | 80                              |
| SDBS (C$_{12}$H$_{25}$C$_6$H$_4$SO$_3$Na) | 7.7                           |

Table 5 Values of CMCs of anionic surfactants at 298 K

| Surfactant       | CMC $\times 10^4$ (mol l$^{-1}$) |
|------------------|----------------------------------|
| SO (C$_{17}$H$_{33}$COONa) | 1.6                              |
| PA (C$_{15}$H$_{31}$COOH)   | 12.5                             |
| SDS (C$_{12}$H$_{25}$SO$_4$Na) | 80                              |
| SDBS (C$_{12}$H$_{25}$C$_6$H$_4$SO$_3$Na) | 7.7                           |
Table 5 shows that CMC value of SDBS lower by about ten times that of SDS, which both has the same of dodecyl group \((C_{12}H_{25})\). This is due to a link of benzene group which has a strong hydrophobic nature with the dodecyl group of SDBS. The disparity in the value of CMC for each of SO and PA is attributable to the difference of the chemical composition.

Thermodynamic functions of micelle formation of SDS and SDBS are studied because they have the same dodecyl group. The CMCs for each of them in DMF are identified at different temperatures.

CMCs values of SDS and SDBS at different temperatures are listed in Table 6.

Table 6 shows that with increasing temperature the CMC values of SDS and SDBS increase. This happens because when temperature increases the solubility of surfactant increases, therefore formation of surfactant micelle needs to a greater concentration.

The effect of temperature on micelle formation was investigated through the following Arrhenius equation:

\[
\text{CMC} = A \exp \frac{\Delta H_m^o}{RT}
\]  

\(\Delta H_m^o\) enthalpy of micelle formation, \(A\) constant related to the nature of the solution, \(R\) universal gas constant, \(T\) absolute temperature.

Equation (3) can be expressed in the logarithm form as:

\[
\log \text{CMC} = \log A + \frac{\Delta H_m^o}{2.303R} \frac{1}{T}
\]  

(4)

The relationship (4) takes the following format in case we use anionic surfactants [22]:

\[
\log \text{CMC} = \log A + \frac{\Delta H_m^o}{4.606R} \frac{1}{T}
\]  

(5)

The plot of log CMC against \(1/T\) yields a straight line, the slope of which gives \(\Delta H_m^o\). Then, Gibbs energy \(\Delta G_m^o\) and entropy \(\Delta S_m^o\) of micelle formation are determined from the following equations at 298 K, respectively [23]:

\[
\Delta G_m^o = 2.303RT \log \text{CMC}
\]  

(6)

\[
\Delta S_m^o = \frac{\Delta H_m^o - \Delta G_m^o}{T}
\]  

(7)

Values of thermodynamic functions are listed in Table 7.

Table 7 shows that \(\Delta G_m^o < 0\) is compatible with the fact that operation of micelle formation is spontaneous, \(\Delta S_m^o < 0\) is because that a system becomes more regular when micelle formation. Also, we find that the leading force for the process of micelle formation is decrease of enthalpy. Additionally, Table 7 shows that decrease of entropy of SDS larger by six times than decrease of entropy of SDBS. This is due to the fact that hydrocarbon root length of SDS is shorter and therefore greater regularity of the system occurs when micelles are formed [12, 23].

In order to investigate the effect of anionic surfactants on the hydrodynamic properties of PAN, we studied the viscosity and specific electrical conductivity of PAN solutions containing surfactants.

The results of measuring the viscosity of PAN solutions 1, 10 wt \% containing different concentrations of anionic surfactants at 298 K are showed in Tables 8 and 9, respectively.
Table 9  Viscosity of PAN solutions 10 wt % containing different concentrations of anionic surfactants

| SO solutions | PA solutions | SDS solutions |
|--------------|--------------|--------------|
| C × 10^4 (mol l⁻¹) | η (mPa s) | C × 10^4 (mol l⁻¹) | η (mPa s) | C × 10^3 (mol l⁻¹) | η (mPa s) |
| 0.12 | 267.320 | 1.56 | 271.052 | 1.56 | 304.963 |
| 0.25 | 270.345 | 3.12 | 274.967 | 3.12 | 274.967 |
| 0.50 | 272.332 | 6.25 | 273.865 | 6.25 | 254.969 |
| 1.00 | 255.326 | 12.50 | 274.977 | 12.50 | 174.979 |
| 2.00 | 155.198 | 25.00 | 269.768 | 25.00 | 159.980 |
| 4.00 | 144.211 | 50.00 | 289.965 | 37.50 | 160.121 |
| 6.00 | 144.533 | 75.00 | 287.125 | 50.00 | 164.980 |
| 8.00 | 145.204 | 100.00 | 284.965 | -- | -- |

Figure 6  Viscosity dependence of PAN solutions 1, 10 wt% on the anionic surfactant concentration.

Figure 6 shows the viscosity dependence of PAN solutions 1, 10 wt% on the anionic surfactant concentration. Figure 6 shows that the viscosity of PAN solutions 1, 10 wt% in the presence of SO, SDS and PA, starts decreasing at the field of CMC for each of them, but this decline will be sharp for both solutions PAN (10% + SO) and PAN (10% + SDS). Whereas the effect of SO and SDS on the viscosity of PAN solutions (1 wt%) is almost insignificant. Also, from Fig. 6 we find that the relationship between viscosity of PAN solutions and PA concen-
tration becomes complicated; the reason of this may be due to an acidity characteristic of PA and possibility of forming Louis salts with DMF. We conclude from above that effec-
tiveness of the effect of anionic surfactants on the viscosity is determined by the concentration of polymer significantly [7, 17].

The results of measuring the SEC of PAN solutions 1, 10 wt% containing different concentrations of anionic surfactants at 298K are showed in Tables 10 and 11, respectively.

Figure 7 shows the SEC dependence of PAN solutions 1, 10 wt% on the anionic surfactant concentration.

Figure 7 shows that the SEC of PAN solutions 1, 10 wt% in the presence of SO and SDS increases at the beginning of the curve until the start of CMC then slow down, thus the conductivity becomes practically constant at the large concentrations for each of the SO and SDS. Additionally, conductivity of PAN/SO solutions increases with increasing of PAN concentration at all concentrations of SO, whereas conductivity of PAN/SDS solutions decreases with increasing of PAN concentration and this just at concentrations of SDS higher than CMC. Decrease of conductivity of the system (PAN 10 % + SDS) from conductivity of the system (PAN 1 % + SDS) due to the occurrence of more associative points between PAN and SDS in the first system. This is because of the large concentration of PAN that leads to a decrease in the concentration of SDS micelles capable of transmitting electrical current. Figure 7 also shows that the presence of PA in the PAN solutions 1, 10 wt% does not affect on the conductivity significantly [17, 24].

Structural and thermal properties of PAN in the presence of SDS are studied, because of its efficient effect on both vis-

Table 10  SEC of PAN solutions 1 wt% containing different concentrations of anionic surfactants

| SO solutions C × 10^4 (mol l^-1) | PA solutions C × 10^4 (mol l^-1) | SDS solutions C × 10^3 (mol l^-1) |
|----------------------------------|----------------------------------|----------------------------------|
|                                 | χ (µS cm^-1)                     |                                 |
| 0.12                            | 24.4                             | 22.7                             |
| 0.25                            | 25.0                             | 22.4                             |
| 0.50                            | 26.8                             | 22.3                             |
| 1.00                            | 29.9                             | 22.4                             |
| 2.00                            | 38.2                             | 22.5                             |
| 4.00                            | 41.0                             | 22.4                             |
| 6.00                            | 45.6                             | 22.0                             |
| 8.00                            | 47.0                             | 21.3                             |

Table 11  SEC of PAN solutions 10 wt% containing different concentrations of anionic surfactants

| SO solutions C × 10^4 (mol l^-1) | PA solutions C × 10^4 (mol l^-1) | SDS solutions C × 10^3 (mol l^-1) |
|----------------------------------|----------------------------------|----------------------------------|
|                                 | χ (µS cm^-1)                     |                                 |
| 0.12                            | 107.0                            | 101.1                            |
| 0.25                            | 107.9                            | 102.8                            |
| 0.50                            | 109.6                            | 103.3                            |
| 1.00                            | 111.9                            | 103.0                            |
| 2.00                            | 117.2                            | 103.5                            |
| 4.00                            | 121.1                            | 104.0                            |
| 6.00                            | 126.7                            | 104.0                            |
| 8.00                            | 132.0                            | 103.8                            |

Fig. 7 SEC dependence of PAN solutions 1, 10 wt% on the anionic surfactant concentration
cosity and conductivity. Therefore, two solid samples were prepared, as described in the experimental section, the first one is PAN 10 wt%, and the second one is PAN 10 wt% containing $25 \times 10^{-3}$ mol l$^{-1}$ of SDS. Then, these samples are tested by XRD and DTA. The X-ray diffractometer has software to evaluate crystalline structure. Figure 8 shows the X-ray diffraction patterns.

Figure 8 shows that X-ray diffraction patterns have two peaks; the first one has a strong intensity, while the second is weak and broad, the first peak indicates to a crystalline structure, while the second peak indicates that there is still some kind of amorphous structure [25]. Figure 8b also shows that the intensity of the first peak increases, in comparison with the first peak in Fig. 8a, which proves that the crystalline structure has developed in the presence of SDS.

Figure 9 shows the DTA curves.

Figure 9 shows that the DTA curve of two samples have an exothermic peak indicates to a cyclization of nitrile groups of PAN. Figure 9a shows that the initiation temperature of DTA curve started at 295.2°C with a peak maximum at 301.8°C, while Fig. 9b shows that the initiation temperature of DTA curve started at 286.7°C with a peak maximum at 297.6°C, this means that the start of the cyclization reaction of nitrile groups of a sample containing SDS is a lower by 8.5°C. Additionally, Fig. 9b shows that the peak intensity is rises in comparison with the peak intensity in Fig. 9a; this refers to increasing the cyclization reaction of nitrile groups and regularity of PAN structure in the presence of SDS [26,27].

4 Conclusions

- We have found that the specific viscosity and the specific electrical conductivity dependence on PAN concentration is an exponential and logarithmic relationship, respectively, where the specific viscosity increases dramatically after the crystalline structural formation, whereas conductivity becomes practically independent of concentration after the crystalline structural formation.
- The CMC of anionic Surfactants (SO, PA, SDS and SDBS) in DMF medium has been determined.
- The leading force for the process of micelle formation of SDS and SDBS is the decrease of enthalpy.
- Effectiveness of the effect of SO, PA and SDS on viscosity is determined by the concentration of polymer significantly.
- Conductivity of PAN solutions is strongly influenced in the presence of SDS and SO, while conductivity of PAN solutions containing PA practically dose not affected.
- The foundations of changes of hydrodynamic properties of PAN solutions in the presence of SO, PA and SDS and its absence have been laid.
- We have found that the crystalline structure of PAN has developed in the presence of SDS.
- The initiation temperature decreases of the cyclization reaction of nitrile groups of PAN in the presence of SDS by 8.5°C.
Fig. 9  DTA curves.  a PAN 10 wt %,  b PAN 10 wt % containing $25 \times 10^{-3}$ mol l$^{-1}$ of SDS

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