

11-21-2020

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Recommended Citation

Eissa, A.; Radwan, M.; Bader, S.; El Hefnawy, M.; and Deef Allah, M. (2020) "Synthesis of Anionic Polymeric Surfactants with Expected Surface Properties.," *Mansoura Engineering Journal*: Vol. 35 : Iss. 2 , Article 11. Available at: <https://doi.org/10.21608/bfemu.2020.124656>

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SYNTHESIS OF ANIONIC POLYMERIC SURFACTANTS WITH EXPECTED SURFACE PROPERTIES

تحضير بعض البوليمرات الأيونية المتوقعة لها نشاط سطحي

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ملخص

في هذا البحث تم تحضير بوليمرات أيونية بيلمره الأستيرين المكبرت مع استرات الأليل المختلفه لكلوريدات الأحماض (ديكانويل ولايوريل والبالميتويل) بنسب مختلفة ثم معادلتها بواسطة الصودا الكاوية وذلك للحصول على بوليمرات أيونية ذات نشاط سطحي. وتم اثبات تركيب هذه البوليمرات بواسطة طيف الأشعة تحت الحمراء والرنين النووي المغناطيسي. وتم تقييم الخواص السطحية لهذه المركبات من ناحية النوبانية والتوتر السطحي والتوتر السطحي البيئي والنقطة الحرجة للميسلات وقوة الرغوة والقدرة على الاستحلاب وكذلك قدرتها على البلل. وتم قياس قوة ثبات هذه المركبات في الأوساط الحامضية والقاعدية. وتم تطبيق هذه البوليمرات في مجال الصباغة على نوعين من الصبغات ثنوبان بصعوبه في الماء وملاحظة نوبانية هذه الاصبغ في درجة حرارة الغرفة وكذلك قدرتها على التثبيت عند ارتفاع درجة الحرارة حتى 130°م.

ABSTRACT:

A novel three series of anionic polymeric surfactants were prepared by polymerization of sulfonated styrene and allyl ester of long chain fatty acid chloride (decanoyl, lauroyl and palmitoyl chloride). The unique structural features of these surfactants were confirmed by different spectroscopic tools (IR and ¹HNMR). The surface properties of these compounds such as surface tension, interfacial tension, emulsion stability, wetting power, foam height, solubilization and dispersant properties in disperse dye systems were determined and evaluated. A comparison studies were done between the chemical structures and surface properties of such compounds. Biodegradability and stability to hydrolysis in acidic and alkaline medium were determined and evaluated.

Keywords: surfactant, surface tension, CMC, biodegradability

1. INTRODUCTION :

Many water-soluble polymers are used as surfactants because of their amphipathic structure and surface activities-similar to those of traditional surfactants⁽¹⁾. Also, surfactants are widely used as dispersing and leveling agents in the disperse dyeing process^(2,3). A few surfactants have aliphatic double chains that aggregate themselves in aqueous solution to form bilayer structures. These aggregates, generally referred as vesicles, have high entrapping efficiency for small molecules and are being studied as drug carriers.

Disperse dyeing of polyester is usually carried out in the presence of dispersants. These dispersants are added to increase the dispersion stability solubility, leveling and fastness properties of the dyes^(4,5). However, they may cause staining on the fabric and

have a reductive effect on dyes, they are also discharged as effluent with the residual dyeing liquor, increasing the COD and BOD values of the effluent and causing environmental problems⁽⁶⁾.

There is increasing interest in the synthesis of tailor-made polymeric surfactants. Although necessarily less well-defined than small-molecule surfactants, polymeric surfactants probably offer greater opportunities in terms of flexibility, diversity and functionality. This is especially true in the light of recent advances in controlled/ living radical polymerisation chemistry⁽⁷⁾.

In present work, we study the preparation of three series of anionic polymeric surfactants to obtain water-soluble copolymer.

2. Experimental:

2.1. Materials:

Styrene, chlorosulfonic acid, trimethylamine and allyl alcohol were Merck (Darmstadt) products. Fatty acid chloride (decanoyl, lauroyl and palmitoyl chloride) and benzoyl peroxide were obtained from Aldrich (Steinheim, Germany). All other chemicals were of analytical grade. The water used was doubly distilled. Two disperse dyes used were Dispersol Yellow (Disp yellow HG 80) and Dispersol Blue (Blue FBL 150). These dyes were supplied by BASF Co. (Germany).

2.2 Methods:

2.2.1. Preparation of sulfonated styrene:

A 10% (w/v) solution of styrene (50g), in methylene chloride (500 ml) was prepared and the solution was stirred. Chlorosulfonic acid in methylene chloride was prepared by cooling 150 ml of methylene chloride in an ice bath for approximately 10 min. The specified amount of chlorosulfonic acid in methylene chloride was slowly added with stirring to begin the sulfonation reaction⁽⁸⁾.

2.2.2. Preparation of allyl fatty esters:

Allyl alcohol (30 mmol) was dissolved in chloroform (25ml) under stirring and a drop of trimethyl amine was added as a catalyst. Equal mole amount of fatty acid chloride (decanoyl or lauroyl or palmitoyl chloride) was added dropwise over a period of 3 min at 0-5°C. Continued stirring at this temperature for 24 hr. Upon completion of the reaction, the solvent was evaporated under vacuum⁽⁹⁾.

2.2.3. Preparation of anionic polymeric surfactants (copolymerization reaction):

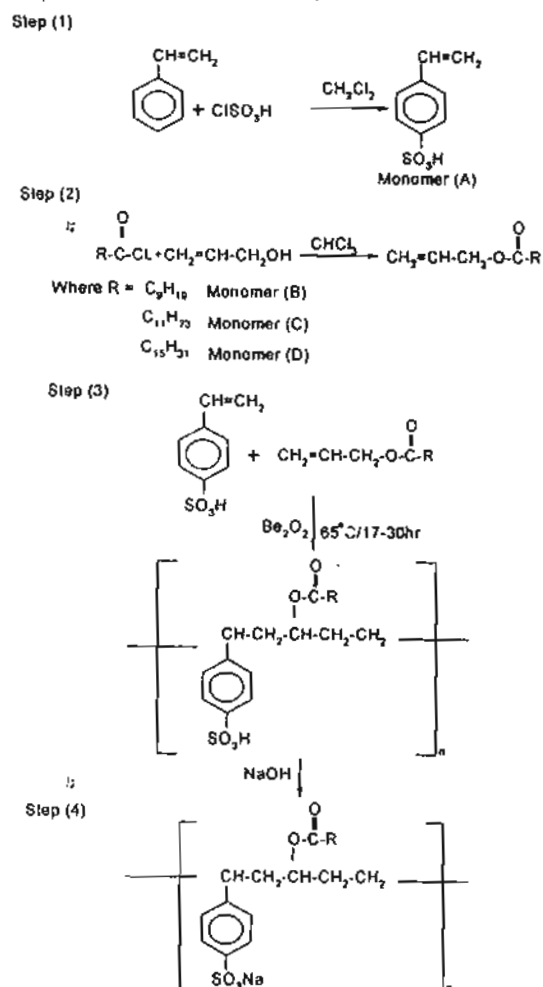
The copolymers were obtained by the solution polymerization techniques shown in scheme 1. The monomers were placed in polymerization tubes and diluted with dimethylformamide [sulfonated styrene placed with each allyl fatty ester derived from (decanoyl, lauroyl and

palmitoyl chloride)] respectively according to the percents in the tables.

The polymerization was initiated by adding 1 mol % benzoyl peroxide as a free radical initiator. The tubes were flushed with nitrogen gas for about 20 min then sealed and thermostated at 65 °C for about 17-30hr depending on the monomer pairs and composition.

The copolymers were obtained by reprecipitation from petroleum ether (40-60) and finally vacuum at 60°C. Then the product polymer was cooled and neutralized with sodium hydroxide solution⁽¹⁰⁾.

The following scheme describes the preparation of novel three series of anionic polymeric surfactants.



Scheme 1 preparation of the novel three series of anionic polymeric surfactants

3. Analysis :

IR spectra were obtained with a Shimadzu (Kyoto, Japan) IR 470, and ¹H-NMR spectra were obtained with a Varian USA EM 390 spectrometer at 90 MHz with dimethylsulfoxide (DMSO) as a solvent and tetramethylsilane (TMS) as a zero reference.

4. Measurements :

Surface tension was determined at room temperature with a Du-Nouy international tensiometer⁽¹¹⁾ (Fisher, Germany).

Foaming properties were determined by the Ross-Mile method with a foam accumulate measuring system whereas the foaming production was measured by the height of the foam initially produced. The foaming stability was measured by the height after 3 min⁽¹²⁾.

Solubilization was measured by a common method, in which a 50-mL solution was shaken with 40 mg of purified dispersed dye and various concentrations of anionic polymeric surfactant for 48 hr. at 30°C. The insoluble dyes were filtered off through a glass filter, solubilized dyes were extracted from the filtrate by toluene, and their concentrations were determined spectrophotometrically⁽¹³⁾.

Dispersing properties were determined by the following method: A 100 mL solution of 0.1 g of commercial dispersed dye and 0.1 g of dispersing agent was adjusted to pH 5.0 by the addition of an appropriate amount of acetic acid. Then, the solution was heated to 130°C by a computer-controlled dyeing system for 1h. After this treatment, the solution was cooled to 90 - 95°C and vacuum filtered immediately with a Buchner funnel. The filtrate was diluted with acetone, and the concentration was determined spectrophotometrically. The dispersability was calculated as follows:⁽¹⁴⁾

$$\text{Dispersability (\%)} = \frac{\text{Dye concentration of Filtrate}}{\text{Dye concentration of Original solution}} \times 100$$

Table (1): physical properties of anionic polymeric surfactants

Polymer	Monomer's Ratios	color	form	yield %
	I A : B II A : C III A : D			
Ip ₁	0.8 : 0.2	Brown	Viscous	79.52
Ip ₂	0.5 : 0.5	Brown	Viscous	76.02
Ip ₃	0.2 : 0.8	Brown	Viscous	57.62
IIp ₁	0.8:0.2	Brown	Viscous	78.8
IIp ₂	0.5:0.5	Brown	Viscous	75.72
IIp ₃	0.2:0.8	Brown	Viscous	59.32
IIIp ₁	0.8:0.2	Brown	Viscous	82.7
IIIp ₂	0.5:0.5	Brown	Viscous	85.12
IIIp ₃	0.2:0.8	Brown	Viscous	54.37

5. Results and discussion

Scheme 1 describes the preparation of the novel three series of water-soluble anionic polymeric surfactant. The analytical data and physical properties of prepared surfactants are shown in table (1).

The IR spectra of the prepared sulfonated styrene shows broad band at 3407 cm⁻¹ caused by the νOH, band at 3037 cm⁻¹ caused by the νCH of aromatic chain and band at 1628 cm⁻¹ characteristic of νC=C as in figure (1).

The IR spectra of the prepared allyl ester shows band at 2923 cm⁻¹ caused by the νCH of aliphatic chain, band at 1741 cm⁻¹ caused by the νC=O of ester group, band at 1380 cm⁻¹ characteristic of ν-CH₃ and band at 724 cm⁻¹ caused by ν-CH₂- as in figure (2).

The IR spectra of the surfactants shows band at 3427 cm⁻¹ caused by the νOH, a strong band at 2923 cm⁻¹ caused by the νCH of aliphatic chain, a band at 1740cm⁻¹ characteristic of the νC=O ester group and band at 1464 cm⁻¹ characteristic of ν-CH₃ as in figure (3).

The ¹H-NMR spectra of prepared sulfonated styrene was shown in figure (4). It gives signal at δ=6.281 ppm (CH₂=CH-) and signal at δ = 7.166-7.53 ppm (C₆H₄) (Ar).

The ¹H-NMR spectra of prepared allyl ester was shown in figure (5). It gives signal at δ=0.743 ppm (-CH₃), signal at δ=1.137-1.36 ppm (-CH₂-) and signal at δ = 4.275 ppm(-CH₂-COO-).

The ¹H-NMR spectra of prepared surfactant was shown in figure (6). It give signal at $\delta = 0.8$ ppm (-CH₃), signal at $\delta = 1.2 - 1.27$ ppm (-CH₂-), signal at $\delta = 3.9$ ppm (-CH₂-O), signal at $\delta = 4.41 - 4.44$ ppm (-CH₂-COO-) and signal at $\delta = 7.56$ ppm (C₆H₄) (Ar).

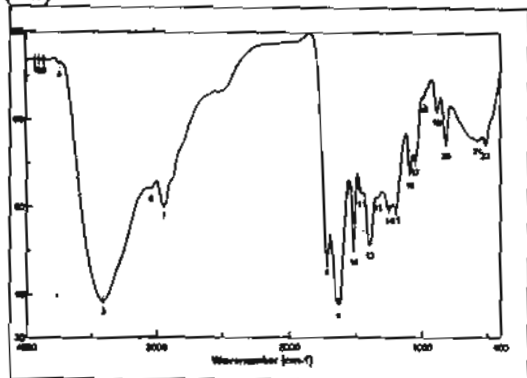


Figure (1): IR- spectra of prepared sulfonated styrene

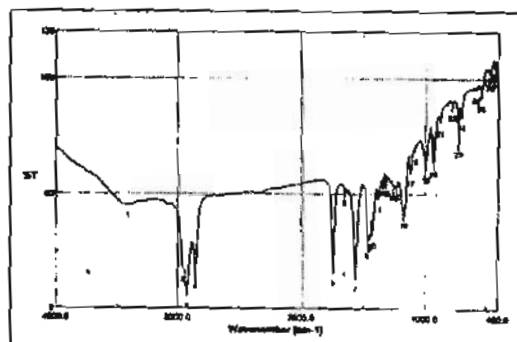


Figure (2) IR spectra of the prepared allyl ester

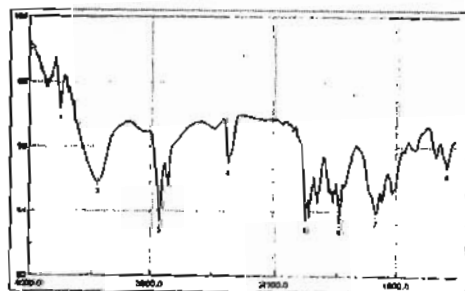


Figure (3): IR- spectra of prepared anionic polymeric surfactant

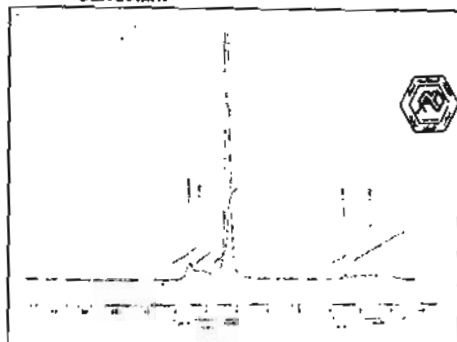


Figure (4) ¹H-NMR spectra of prepared sulfonated styrene

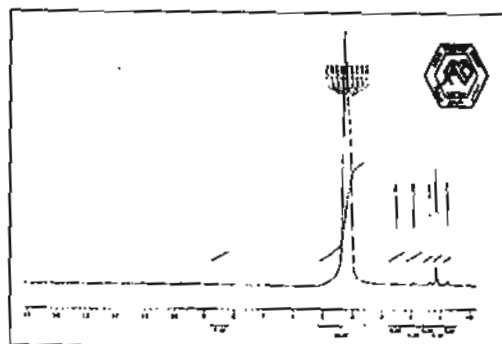


Figure (5): ¹H-NMR spectra of prepared allyl ester

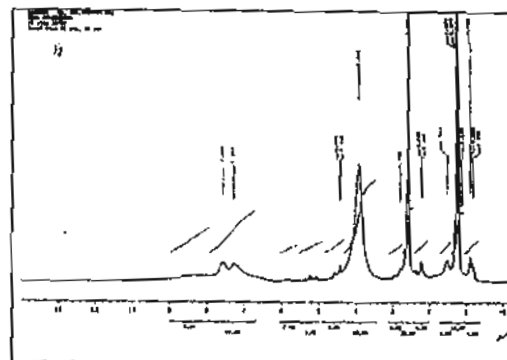


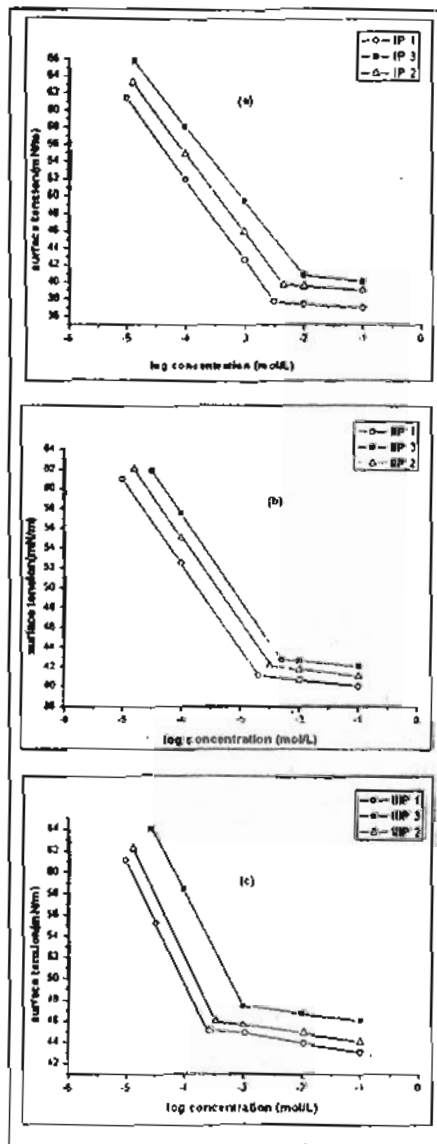
Figure (6): ¹H-NMR spectra of prepared anionic polymeric surfactant.

5.1. Surface properties:

The water - soluble polymeric surfactants prepared in this study were evidently of an amphipathic structure similar to the structures of traditional surfactants. The aromatic and saturated aliphatic residues were the hydrophobic portion; the sulfonate group (anionic) was the hydrophilic portion. The surface activities of these water - soluble polymeric surfactants are shown in table (2). The surface tensions of the solutions were reduced by the addition of the surfactants because of the amphipathic structure , which caused the concentration of the surfactant molecules at the surface and reduction of surface tension .⁽¹⁵⁻¹⁷⁾

Inflection points were observed in the curves as shown in figure (7). The concentration at the inflection point corresponds to the critical micelle concentration (cmc) in the cases of traditional surfactants⁽¹⁸⁾. The values found were smaller than the values of traditional surfactants because of the high MWs and large hydrophobic chains of polymeric

surfactants. The increase in the length of saturated aliphatic fatty chain as shown in table (2) lead to decrease in surface activity⁽¹⁹⁾.



Figure(7) : Plots of surface tension versus log molar concentration of water soluble anionic polymeric surfactants at 25°C ; (a) polymer IP1 - IP3, (b) IIP1-IIP3 and (C) IIP1-IIP3.

5.2. Wetting properties

The prepared water-soluble polymeric surfactants exhibited good wetting properties, as shown in table (2). A change in saturated aliphatic fatty chain led to increase in wetting time with increasing length of aliphatic fatty chain⁽²⁰⁾.

5.3. Stability to Hydrolysis :

All the prepared water-soluble anionic polymeric surfactants exhibited good stability, especially in acidic medium, but slightly lower stability in the basic medium. The presence of the sulfonate group probably protected the ester linkage through steric hindrance. The change of the saturated aliphatic fatty chain as shown in table (2) lead to increase in stability in both acidic and basic medium⁽²¹⁾.

5.4. Foaming properties:

The low-foaming tendency of surfactants is important in some applications such as dyeing auxiliaries in the modern textile-dyeing industry. The relative low-foaming properties of water-soluble polymeric surfactants are shown in table (3). All of these polymeric surfactants provided not only low-foaming properties as measured by the height of the foam initially produced but also low-foaming stability. These low-foaming effects were probably caused by (1) the presence of multihydrophilic groups, which caused a considerable increase in the area per molecule and produced less cohesive forces at the surface; (2) The multianionic hydrophilic SO_3Na , which increased the electrostatic repulsion among surfactant molecules counteracting the interchain cohesive forces; and (3) the water-soluble polymers that are believed to coil in the aqueous phase, which decreased the cohesive forces caused by intermolecular and intermolecular bonds⁽²²⁾.

5.5. Emulsifying power:

Emulsification is of immense importance to the technological development of surfactants. The emulsifying ability of water soluble, polymeric surfactant is shown in table (4) which indicates that all polymeric surfactants exhibit good emulsifying power toward liquid paraffin, kerosene, and O-dichlorobenzene, as was expected. The change in saturated aliphatic fatty chain length led to an increase in the separation time between the oil and aqueous phase with increasing length of aliphatic fatty chain⁽²³⁾.

Table (2): surface properties of anionic polymeric surfactants

Polymer	Monomer's Ratios I A : B II A : C III A : D	Surface tension (mN/m) 0.1% at 25°C	Interfacial tension (mN/m) 0.1% at 25°C	Kraft point °C	CMC (mol/L)	φ CMC (mN/m)	Wetting time	Stability to hydrolysis Hr : min : sec	
								A H ⁺ (p)	OH ⁻ (p)
Ip ₁	0.8:0.2	37	11	0	0.003	37.5	37	0:56:12	0:8:15
Ip ₂	0.5:0.5	39	14	0	0.005	39.5	42	1:12:42	0:9:42
Ip ₃	0.2:0.8	40	15	3	0.01	41	47	1:30:22	0:10:56
IIP ₁	0.8:0.2	40	15	0	0.0019	41	41	2:45:35	0:10:45
IIP ₂	0.5:0.5	41	16	2	0.003	42	45	3:36:42	0:11:17
IIP ₃	0.2:0.8	42	17	3	0.005	42.5	48	4:45:32	0:12:32
IIIP ₁	0.8:0.2	43	17	0	0.00025	45	50	5:11:00	0:15:12
IIIP ₂	0.5:0.5	44	19	2	0.0003	46	52	6:34:52	0:25:00
IIIP ₃	0.2:0.8	46	21	6	0.001	47.5	56	8:21:32	0:27:38

Table (3): foaming properties of anionic polymeric surfactants

Polymer	Monomer's Ratios I A : B II A : C III A : D	Foam height (m.m.)			
		25°C		85°C	
		Initial	3min	Initial	3min
Ip ₁	0.8:0.2	88	0	85	0
Ip ₂	0.5:0.5	92	0	89	0
Ip ₃	0.2:0.8	95	0	90	0
IIP ₁	0.8:0.2	104	0	98	0
IIP ₂	0.5:0.5	109	0	105	0
IIP ₃	0.2:0.8	112	0	106	0
IIIP ₁	0.8:0.2	118	0	115	0
IIIP ₂	0.5:0.5	121	0	119	0
IIIP ₃	0.2:0.8	128	0	125	0

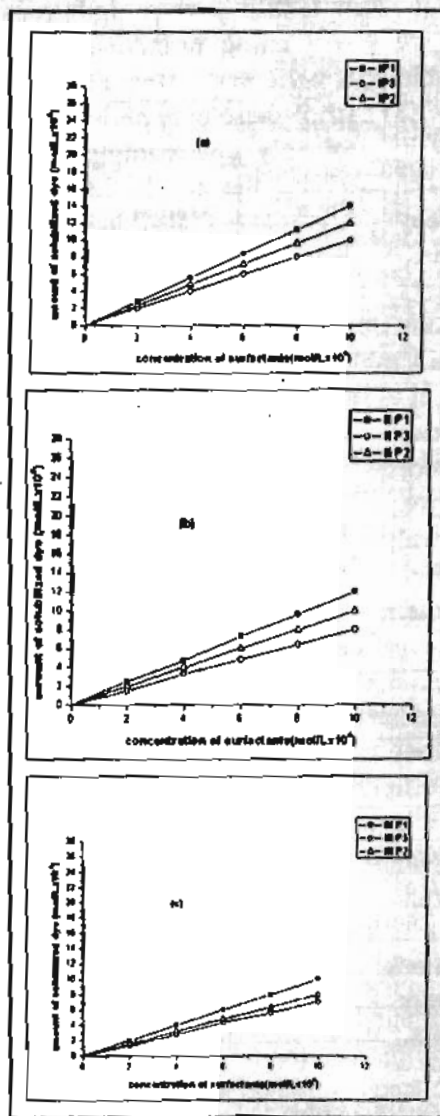
Table (4): Emulsifying properties of anionic polymeric surfactants

Polymer	Monomer's Ratios I A : B II A : C III A : D	separation time hr:min: sec		
		kerosene	Liquid parafin	O-dichlorobenzen
Ip ₁	0.8:0.2	0:2:55	0:19:33	0:25:42
Ip ₂	0.5:0.5	0:3:12	0:30:17	0:29:18
Ip ₃	0.2:0.8	0:4:32	0:32:46	0:30:55
IIP ₁	0.8:0.2	0:9:37	0:40:15	0:34:12
IIP ₂	0.5:0.5	0:10:26	0:44:12	0:37:08
IIP ₃	0.2:0.8	0:12:38	0:44:56	0:38:25
IIIP ₁	0.8:0.2	0:29:45	0:56:13	0:48:19
IIIP ₂	0.5:0.5	0:35:34	1:15:39	1:08:12
IIIP ₃	0.2:0.8	0:45:32	1:35:46	1:16:13

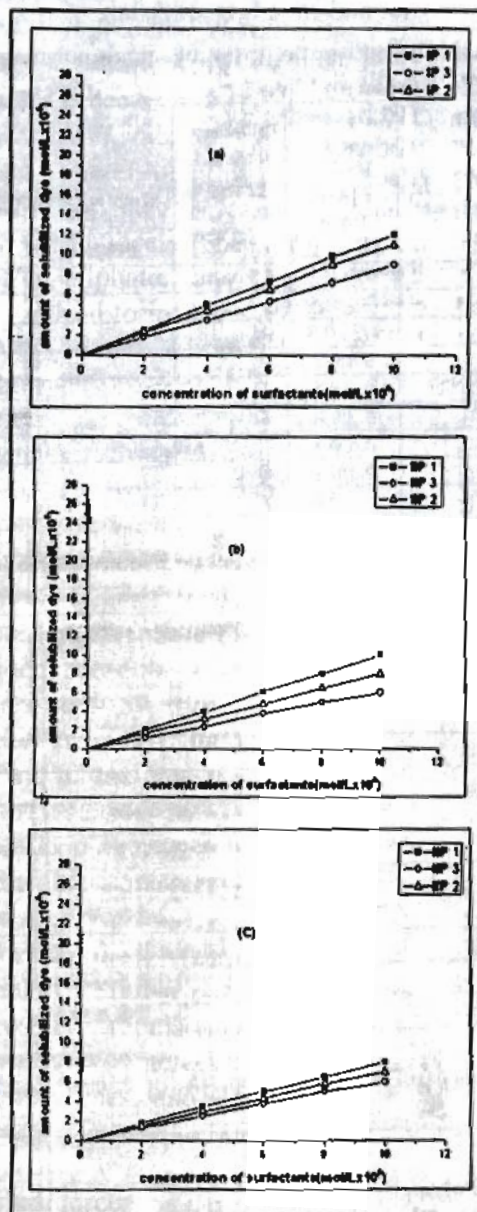
5.6. Solubilization:

The solubilization of the water-soluble anionic polymeric surfactants applied with two dispersant dyes: [dye I] Dispersol Yellow (Disp yellow HG 80) and [dye II] Dispersol Blue (Blue FBL 150) are shown in figure (8,9). A linear relationship was obtained for the solubilization of the applied dyes with the concentration of the water-soluble anionic polymeric surfactants.

The solubilization capacity of surfactants decreases with increasing aliphatic fatty chain length⁽²⁴⁾.



Figure(8): Plots of the amount of solubilized dye as a function of the surfactant concentration for dye (I); (a) polymer IP1 – IP3, (b) IIP1-IIP3 and (C) IIP 1-IIP3.



Figure(9): Plots of the amount of solubilized dye as a function of the surfactant concentration for dye (II); (a) polymer IP1 – IP3, (b) IIP1-IIP3 and (C) IIP 1-IIP3.

5.7. Dispersant Properties(Heat Stability)

Purified dispersed dyes are hydrophobic and almost insoluble in water. Their low aqueous solubility is attributed to hydrophobic bonding, causing aggregation and precipitation when the concentrations are increased. Generally, some surfactants (i.e, the dispersing agent) are incorporated during production of the final dye powder of liquid. Its function is to prevent aggregation and precipitation⁽²⁵⁾. However, in some practical dyeing processes, such as the dyeing of polyester

fibers at high temperatures, the reaggregation of the dye particles will occur at elevated temperatures when the heat stability of the dispersant system is insufficient. To prevent this, an additional dispersing agent with a high heat stability may be introduced into the dye bath initially or during the course of dyeing. The water-soluble surfactants prepared in this study were evaluated for these cases, and their stability at elevated temperature with two dispersant dyes: [dye I] Dispersol Yellow (Disp yellow HG 80) and [dye II] Dispersol Blue (Blue FBL 150).

These systems are shown in table (5), it is clear that in all of the two applied dye systems, The heat stability was improved by the addition of the water-soluble anionic polymeric surfactants.

The high heat stability of the water-soluble polymeric surfactants was probably caused by their unique structural features: (1) high MW, (2) the aromatic structure and ester linkage of the hydrophobic portion, and (3) the multiple ionic groups.

These structural features favor its adsorption on to the surface of dye crystals. The sulfonate group produce strong electrostatic repulsion and, hence, stabilize the dispersion⁽²⁶⁾.

The hydrophobic groups come into contact with the particle surface, leaving the

hydrophilic groups directed toward the aqueous phase and producing solvation protection for dye particles. At an elevated temperature, the separation of the novel dispersing agent from dye particles is minimized because of a strong association between the dispersing agent and dye particles, thus resulting in a high stability of these dispersing systems.

Table (5): Dispersant properties of anionic polymeric surfactants.

Polymer	Monomer's Ratios I A : B II A : C III A : D	Dispersability %	
		Yellow dye(I)	Blue dye(II)
I _{p1}	0.8 : 0.2	59.16	39.16
I _{p2}	0.5 : 0.5	55.2	35.92
I _{p3}	0.2 : 0.8	46.86	26.12
Blank		10.42	9.66
II _{p1}	0.8 : 0.2	45.8	24.53
II _{p2}	0.5 : 0.5	44	24.12
II _{p3}	0.2 : 0.8	42.85	22.3
Blank		10.42	9.66
III _{p1}	0.8 : 0.2	38.9	18.82
III _{p2}	0.5 : 0.5	35.22	17.28
III _{p3}	0.2 : 0.8	27.09	16.20
Blank		10.42	9.66

5.8. Biodegradation

A biodegradation test in ordinary river water⁽²⁷⁾ gave satisfactory results, as shown in table (6).

All the products had a degradation of about 80% after about 6 days

6. Conclusions

From these results and other previous data, we conclude that the introduction of the SO₃Na group in polymer chains moieties and solubility in aqueous media increased their activity.

Table (6): Biodegradability percent of anionic polymeric surfactants

Polymer	Monomer's Ratios I A : B II A : C III A : D	1 st day	2 nd day	3 rd day	4 th day	5 th day	6 th day	7 th day	8 th day
		I _{p1}	0.8 : 0.2	59	62	68	75	84	95
I _{p2}	0.5 : 0.5	55	59	65	73	81	87	92	-
I _{p3}	0.2 : 0.8	50	55	61	68	74	82	87	92
II _{p1}	0.8 : 0.2	52	59	65	72	81	86	93	-
II _{p2}	0.5 : 0.5	50	55	59	63	73	83	86	93
II _{p3}	0.2 : 0.8	48	52	55	61	68	75	82	90
III _{p1}	0.8 : 0.2	48	55	63	67	75	82	87	93
III _{p2}	0.5 : 0.5	45	52	60	65	72	80	83	89
III _{p3}	0.2 : 0.8	42	49	55	61	70	78	80	90

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