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Study the Effect of Phenol on formation of Supramolecular gel

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Abstract

In this work, the cationic surfactant hexacetyl pridinium chloride (*HCPC)* was blended with anionic surfactant Sodium Dodecyl benzene Sulfate (SDBS) by using different concentrations (0.0025 - 0.1M) of phenol and at temperature ranges (20-35 C^o). It was found that the viscosity values for the mixture of SDBS / HCPC at a certain mixing ratios (12/3, 10.5/4.5 and 9/6), were increased in the presence of phenol, due to formation of self-assembled supramolecular. Moreover, the thermodynamic functions as well as the activation energy for the process of self-assembled were calculated. Conductivity measurements were also performed for further support. The results revealed a physical interaction insight intermolecular forces.

Keywords: colloids, effect phenol on micelles, supramolecular gel, intermolecular forces .

Introduction

Supramolecular chemistry refers to the area of chemistry beyond the molecules and focuses on the chemical systems made up from a number of assembled molecular subunits or components[1]. While, traditional chemistry focuses on the covalent bond, supramolecular chemistry examines weaker and reversible non-covalent forces between molecules. These forces include hydrogen bonding, metal coordination, hydrophobic forces, Vander Waals forces, pi-pi interactions, and electrostatic effects. These interactions play a significant role in changing the viscosity of the medium [2,3]. Therefore, supramolecular assemblies are usually less stable than molecular compounds.

The most straightforward method for is syptamolecular formation self-assembly techniques, which is to say that mixing components under given set of conditions (solvent, temperature, pH etc.). One of the major goals for supramolecular chemists is to synthesize a supramolecular assembly with new functions that a single molecule or ion cannot afford. The term supermolecule has sometimes used to describe supramolecular assemblies which are complexes of two or more molecules often macromolecules like (micelles). Supermolecule has also been used in biochemistry to describe complexes of biomolecules ,such as peptides and]oligonucleotides [4,5). The process by which a supramolecular assembly forms is called molecular self-assembly. Supramolecular gel or micelles from surfactants are considered as one of the biggest sizes of supra-molecular structures that formed by self-assembled amphiphilic molecules. The strong intermolecular forces of different surfactants lead to either supramolecular / aggregations or disintegration depending on the type of surfactant. The unique characteristics of supra-molecular gel or aggregate as thermodynamically controlled living polymer (can be broken or reformed), makes special important applications in many fields[6].

There are a numerous studies [7,6] concern studying the effect of additives on the viscosity of the surfactants. These studies give interpretations and understanding to the driving force that enhance supramolecular gel formation.

Kaler et al.[8] studied last decade the case of growth of supramolecular gel by SANS have in SDS solutions with increasing amounts of p-toluidine hydrochloride (PTHC) up to the point when the molar ratio becomes 1:1. Another workers have[9] investigated the effects of ionic strength and small hydrophobic molecules on the viscoelasticity of anionic sodium lauryl ether sulphate supramolecular gel. They indicated that the viscosity increases with increasing the hydrophobic character of the added molecules.

Experimental part

The highly purified surfactants *SDBS* $(CH_3(CH_2)_{10}CH_2(C_6H_6)–SO_3^-Na^+)$ and *HCPC* $(CH_3(CH_2)_{18}CH_2NCl^-)$ were purchased from Aldrich and Fluka companies. Double distilled water was used $KMnO_4$ (1g) and KOH (0.13g) were added for each liter of distilled water that has a conductivity of less then $0.043x10^{-6}$ cm^{-1} range between (3-5µs). Solutions (2%wt) of each surfactant was made to give concentrations of *0.0786* and *0.0745 M* for *SDBS and* HCPC *respectively*.

The dynamic viscosity (η) measurements were carried out using modified Ostwald apparatus. The conductivity measurements were determined by using WTW conductometer with an accuracy ± 0.01µS cm^{-1} In order to control the temperature of the above measured physical properties with ±0.1C^o accuracy, thermostat type Hakke NK22 was used. All measurements were repeated for at least three times for double check the reproducibility of the data.

Results and Discussion

It was using the different temperatures have been taken in order to evaluate ΔG^o, ΔH^o and ΔS^o parameters for thermodynamically controlled living polymers[12,6]. Because we are find the case equilibrium and dealing with

The approximate thermodynamic functions for formation supramolcular gel. And apprehensible modifiability the idea that combination between solutions of high viscosity or a gel-like nature due to the formation of supramolecular gel with that of high molecular polymer[2,3] .

The standard Gibbs free energy (ΔG^o) was estimated using the following empirical equation [10,11] :

$$\Delta G^{o}=-RT\ \mathrm{In}\ \eta\ldots\ldots\ldots\ldots(1)$$

When R is the gas constant, T is the absolute temperature and η is the observed dynamic viscosity. The empirical standard enthalpy (ΔH^{o}) was evaluated graphically using this model [10]:

$$d\ \ln \eta/d(1/T) = -\Delta H^{o}/R \quad \ldots\ldots(2)$$

The standard entropy (ΔS^{o}) was calculated using the following general thermodynamic equation (12):

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} \ldots\ldots\ldots\ldots(3)$$

While the activation energy of solution viscosity (Ea) has been determined according to the following model(11) :

$$\eta \propto e^{Ea/RT} \ldots\ldots\ldots\ldots(4)$$

The effect of adding phenol on the formation of supramolecular gel for a combination of cationic and anionic surfactant SDBS and HCPC at temperatures (20,25,30 and 35 C°) was studied. The obtained results for blending process of with HCPC/SDBS are listed in Table (2).

Fig. : 1 shows the relationship between viscosity and the percentage of the SDBS at different temperatures. The results revealed that the maxium value reported for the viscosity was at 20°C and at ratio of 12/3.

The results in table (2) indicated a significant increase in viscosity values for the HCPC/ SDBS in the presence of phenol particularly when the temperature (20C°) and (0.1 M) concentration. The reason for, that the low temperature is facilitate the process of supramolcular gel formation by providing kinetic energy, which increased the possibility of overlapping between oppositely charged surfactant, because of the presence of strong electrostatic attractive forces as well as the presence of hydrophobic effect [13,14].

At a temperature above (35C°) or more, increasing in the kinetic energy of the surfactant molecules will cause difficulty in gathering it and preventing micelles formation. Moreover, the increas in the kinetic energy will also cause a decrease in viscosity values .This is identical to what was found in the case of SDBS in literature [6].

Results also showed that the viscosity values for HCPC in the presence of SDBS irregularly increase with increasing phenol concentration. This can be attributed to the polar nature of phenol[15]. Phenol tends to be close to the surface of the micelles which will separate the oppositely charged polar heads causing disruption the electrostatic attractive forces by steric effect. Moreover, the ability to form hydrogen bond between hydrogen atom belongs to the hydroxyl of phenol and polar head group ($-OSO_3$ in the case of the SDBS), which again disturb the process of attraction between oppositely charged polar heads and lead to an increase in viscosity values.

The results in table (1) also showed that both HCPC and SDBS revealed a slight decrease in the viscosity values with temperature increase and in the presence or absence of phenol. Nevertheless, the system reports a slight increase in viscosity at temperature value (35C°) without phenol. In general, we notice that the viscosity decreased with increasing temperature [16]. Fig.: 2 shows the relationship between phenol concentration and viscosity at different temperatures. Fig.: 3 show the relationship between viscosity and the percentage of the mixture HCPC /SDBS at different temperatures and concentration (0.1M) for phenol.

However equations[10,11] (eq:1-3) were used to calculate the thermodynamic parameters for the process of supramolecular gel formation type HCPC in the presence of SDBS using different concentrations of phenol and different temperatures. The results in table (2) showed that the values of the free energy ΔG^{0} for the process of supramolcular gel, for combination of HCPC /SDBS in the presence of different concentrations of phenol were positive when the viscosity decreases and the temperature increase[17]. Hence when phenol was added to the combination of surfactants acts on clusters formation [18] known as supramolcular gel and thus give us the so-called micelles.

The enthalpy value for the process of micelles formation for HCPC / SDBS mixture in the presence of phenol was calculated, fig: 4. The negative sign for ΔH^{o} means that the process was exothermic [11]. The pronounce increase in the viscosity was predominantly belongs to the hydrogen bonding which in turn diminished surfactants role in the formation supramolecular gel due to the presence of phenol. The values of entropy for the process of micelles formation for mixture of HCPC/SDBS showed that the spontaneous formation of supramolcular gel mainly due to increases in random (ΔS^{o}). The values of activated energy of viscosity (Ev) Table 2 also reflected the rheology change of solution due to the formation of supramolcular gel . In other words, the magnitude at Ev depends on the number of intermolecular physical bonds that broken due to the mobility. Thus, it is clear that there is a significant increase in Ev at the ratio that parallel to supramolcular gel formation through the radio (12/3). This indeed supports the suggested relations for evaluation the thermodynamic properties.

The presence of phenol in the mixture of HCPC/ SDBS will interfere with the process of supramolcular gel (micelles) formation through forming hydrogen bonding[19] with polar groups of surfactants reducing the charge on the surface micelles.

The conductivity measurements of these mixtures have been carried out as illustrated in Table (3); and Fig.:**6** they show the conductivity relation in consistence with that of the viscosity, such that as the conductivity decreases with increasing viscosity, This also could reflect the accuracy of our measurements.

Table 1: Viscosity (η) values for the *HCPC/ SDBS* mixed system at different temperatures

HCPC	SDBS	$\eta\times10^2$ (pas . s)			
		20C^o	25C^o	30C^o	35C^o
0	15	0.1722	0.1380	0.1093	0.0861
13.5	1.5	0.1813	0.1555	0.1323	0.1192
12	3	2.9128	2.0035	1.2449	0.6647
10.5	4.5	1.3592	1.0083	0.6320	0.3546
9	6	0.6293	0.4654	0.2580	0.1986
7.5	7.5	0.3187	0.2449	0.1984	0.1436
6	9	0.2118	0.1359	0.11171	0.1067
4.5	10.5	0.1897	0.1556	0.1325	0.1036
3	12	0.1771	0.1458	0.1187	0.1006
1.5	13.5	0.1676	0.1232	0.1154	0.0895
15	0	0.1368	0.1222	0.1092	0.08211

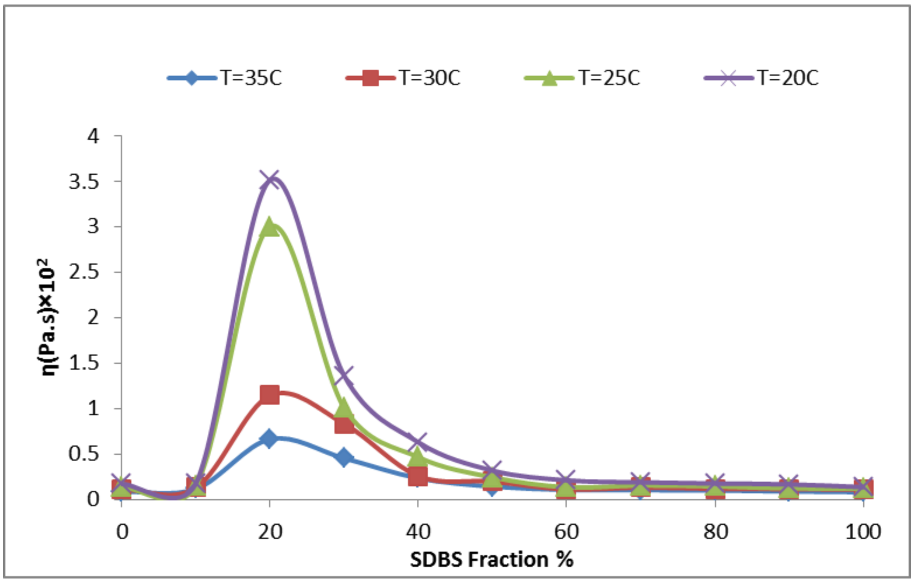


Fig 1: Dynamic viscosity of *SDBS/ HCPC* mixed system as a function of *HCPC* weight fraction in the mixture at different temperatures

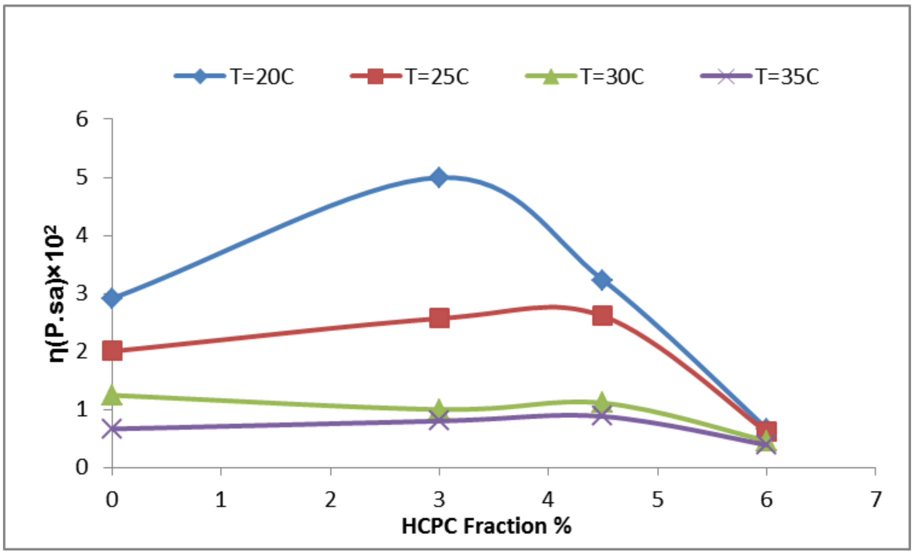


Figure 2: shows the relationship between viscosity and the percentage of the mixture HCPC/ SDBS at different temperatures in Phenol(0.1M)

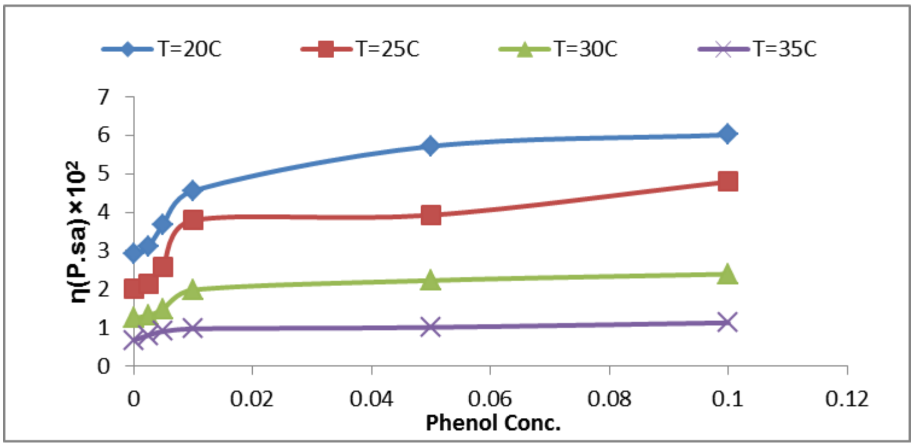


Figure 3: shows the relationship of phenol concentration and viscosity of (HCPC/SDBS) at different temperatures (ratio 12/3)

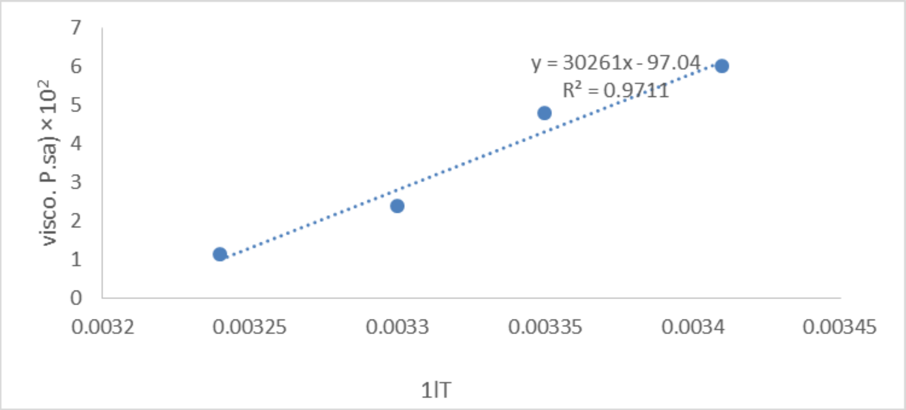


Fig.4. the Relationship between Ln η and 1/T for calculate ΔH to SDBS/HCPC mixture at different temperature at concentration (1 ×10^{-5})

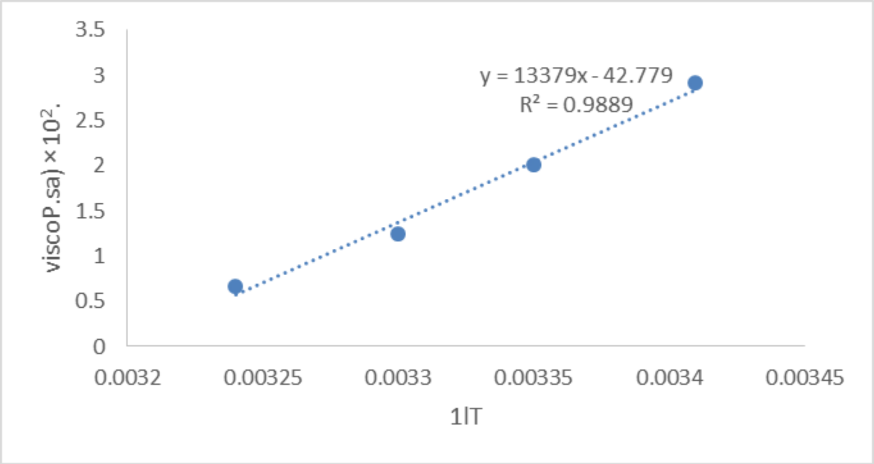


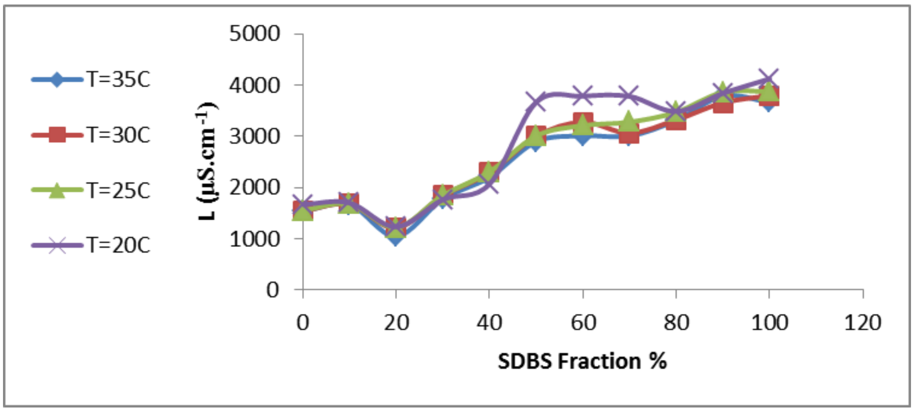
Fig. 5: the relationship between η and 1/T for calculate E_a to HCPC/SDBS mixture at concentration (0)

Table 2: Viscosity (*η*) values and other related thermodynamic functions for the *HCPC/ SDBS* mixed system in phenol at different temperatures.

Phenol Conc.	η (Pa.s) x 10^2(ΔG° kJ.mol^{-1}){ΔS° J.mol^{-1}.K^{-1} }				ΔH° kJ.mol^{-1}	Ea J.mol^{-1}
	20C°	25C°	30C°	35C°		
	Ratio 12/3					
0	2.9128 (-6.5283) (-248.458)	2.0035 (-5.7120) (-244.292)	1.2449 (-4.6085) (-240.264)	0.6647 (-3.076) (-236.369)	- 72804.86	111233.00
0.0025	3.1113 (-6.6889) (-230.348)	2.1291 (-5.8627) (-226.486)	1.3162 (-4.7488) (-222.752)	0.8002 (-3.5522) (-219.140)	-67498.87	114791.39
0.005	3.6671 (-7.0895) (-241.257)	2.5782 (-6.3371) (-237.212)	1.4783 (-5.0416) (-233.302)	0.8982 (-3..8482) (-229.518)	-70695.60	139192.98
0.01	4.5540 (-7.6174) (-267.165)	3.7853 (-7.2891) (-262.684)	1.9786 (-5.776) (-258.354)	0.9678 (-4.0394) (-254.166)	-78287.18	185344.00
0.05	5.7123 (-8.1698) (-292.551)	3.9221 (-7.3771) (-287.645)	2.2228 (-6.0696) (-282.342)	1.0051 (-4.1363) (-278.316)	-85725.65	234379.97
0.1	6.0096 (-8.2934) (-288.663)	4.7893 (-7.8722) (-283.821)	2.3898 (-6.252) (-279.143)	1.1259 (-4.4271) (-274.617)	-84586.63	251589.95
Phenol Conc.	Ratio 10.5/4.5					
0	1.3592 (-4.6705) (-227.302)	1.0083 (-4.0099) (-223.490)	0.6320 (-2.8998) (-219.806)	0.3546 (-1.4671) (-216.242)	-66604.28	50200.76
0.0025	1.8096 (-5.3681) (-257.414)	1.1201 (-4.2706) (-253.099)	0.6996 (-3.1560) (-248.926)	0.3887 (-1.7023) (-244.890)	-75427.93	69524.99
0.005	2.8999 (-6.5174) (-324.195)	1.2318 (-4.5062) (--318.762)	0.8002 (-3.4946) (-313.505)	0.3991 (-1.7700) (-308.422)	-94995.76	118283.27
0.01	3.5570 (-7.0152) (-304.160)	1.8787 (-5.5525) (-299.062)	0.8888 (-3.7592) (-294.133)	0.6119 (-2.8649) (-289.361)	-89126.08	145669.59
0.05	4.5328 (-7.6061) (-327.284)	2.0123 (-5.7228) (-321.796)	0.9227 (-3.8536) (-316.495)	0.6768 (-3.1231) (-311.359)	-95901.99	187987.85
0.1	4.9978 (-7.8440) (-323.850)	2.5671 (-6.3264) (-318.421)	1.0003 (-4.0571) (-313.174)	0.8013 (-3.5557) (-308.092)	-94895.99	209637.51
Phenol Conc.	Ratio 9/6					
0	0.6293 (-2.7937) (-203.402)	0.4654 (-2.0935) (-199.992)	0.2580 (-0.6417) (-196.696)	0.1986 (+0.0179) (-193.505)	-59599.74	22132.69
0.0025	0.9929 (-3.9052) (-256.372)	0.4982 (-2.2623) (-252.076)	0.3011 (-1.0311) (-247.921)	0.217 (-0.209) (-243.899)	-75121.14	37534.38
0.005	1.2333 (-4.4336) (-144.370)	0.6707 (-2.9993) (-141.955)	0.4670 (-2.1373) (-139.615)	0.3969 (-1.7558) (-137.356)	-42305.78	40344.51
0.01	1.9858 (-5.5946) (-166.136)	1.9897 (-5.6948) (-168.348)	0.7999 (-3.4936) (-160.659)	0.7440 (-3.3657) (-158.052)	-48683.45	71638.41
0.05	2.6720 (-6.3179) (-200.757)	1.5324 (-5.0475) (-197.393)	0.9874 (-1.5967) (-194.147)	0.8231 (-3.6245) (-190.988)	-58828.20	90439.69
0.1	3.2296 (-6.7799) (-299.258)	2.6078 (-6.3654) (-225.413)	1.1113 (-4.0244) (-221.701)	0.880 (-3.7958) (-218.103)	-67179.61	125574.65

Table 3: The conductivity values of (HCPC/ SDBS) mixture at different temperatures

HCPC	SDBS	L(µS.cm-1)			
		20 C°	25 C°	30 C°	35C°
0	15	1671	1554	1543	1538
13.5	1.5	1703	1680	1674	1666
12	3	1235	1223	1209	1050
10.5	4.5	1765	1847	1841	1777
9	6	2067	2307	2288	2202
7.5	7.5	3661	3009	3002	2896
6	9	3783	3211	3277	3011
4.5	10.5	3781	3280	3065	3008
3	12	3487	3472	3322	3313
1.5	13.5	3841	3862	3655	3788
15	0	4123	3872	3796	3667



Figure(6): The relationship between conductivity and SDBS% fraction to SDBS/HCPC mixture at different temperature

Conclusion

The results indicated that the cationic HCPC and anionic SDBS surfactants revealed a big tendency towards formation of supramolcular gel in the presence of phenol. The reason for this is the viscosity of the surfactants HCPC/ SDBS increases due to the intermolecular interactions and ability to form hydrogen bonding.

This has proven that the rheological properties for the supramolecular dynamic were differ from that for high molecular weight polymers which composed of carbon based backbones covalently bonded. The phenols was interacted with process of micelles formation and formed hydrogen bonding with the polar groups of the surfactants and by result reduced the charge on the supramolcular gel surfaces. Moreover, the phenol has no role in the mechanism of supramolcular gel because there was no effect on the ratio that gave the highest viscosity.

Through the study supramolcular gel to mix the solution aim of this study using connectivity measurements to find a relationship between conductivity and viscosity of the solution is a mixture of different temperatures. This is what has been reached in this research but not a linear relationship .

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دراسة تاثير الفينول على تكوين الجزيئات الكبيرة الهلامية

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الملخص

يتضمن البحث دراسة لبعض محاليل المواد الفعالة سطحيا بوجود الفينول. اذ تم استخدام المضافات على النظام الثنائي للمواد الفعالة سطحياً من خلال إضافة الفينول بتراكيز مختلفة (*0.0025 - 0.1M*)) على مزيج من الـ صوديوم دودايسيل بنزين سلفونيت SDBS والسالب الـ هيكساسيتايل بريدينيوم كلورايد الموجب HCPC وتأثيره على اللزوجة وبدرجات حرارية مختلفة بمدى (20-35 C^{o})، اذ وجد ان التفاعل ما بينSDBS / HCPC وبنسب تتراوح (9/6 and 10.5/4.5, 12/3) بزيادة تركيز الفينول تقود الى زيادة في تكوين التجميع الذاتي للمذيلات. كما تم قياس التوصيلة للمحاليل المحضرة والتي تعتبر من القياسات الرئيسية والمدعمة في اعطاء قيم تثبت تكوين التجميع الذاتي اذ وجد ان التوصيلية تزداد كلما قلت اللزوجة. وتم حساب الدوال الثرموديناميكية للمذيلات المتكونة، بالاضافة الى حساب طاقة تنشيط التمذيل والتجمع لذاتي والتي تدل على التفاعلات الفيزيائية هي تفاعلات ذات قوة بين الجزيئات.

الكلمات المفتاحية: التصادم، الجزيئات الكبيرة الهلامية، القوة بين الجزيئات.