The Effects of Fe²⁺ on the Aggregation Behavior of Residual Hydrophobic Modified Polyacryamide

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Abstract

The influences of Fe^{2+} on the aggregation behavior of residual hydrophobic modified polyacryamide (HMPAM) in treated oily wastewater were studied by fluorescence spectrum and DLS. The result of I_1/I_3 showed that the polarity of hydrophobic domain increased and the size of hydrophobic domain may be decreased with the increasing of Fe^{2+} in produced water. Fe^{2+} was helpful for the increase of hydrophobic domain, therefore due to the aggregation degree for HMPAM.

Keywords

Aggregation Behavior, Fluorescence Spectrum, Residual
Hydrophobic Modified Polyacryamide

1. Introduction

Polymer flooding plays a major role in global crude oil recovery [1], especially in China [2] [3]. Usually, there was residual polymer in treated oily wastewater produced from polymer flooding (TOWPF). TOWPF can be used for reinjection or polymer flooding [4] [5]. In addition, there were many other substances in the TOWPF, such as emulsified oil, suspended solid, Fe^{3+}, Fe^{2+}, cationic water clarifier and SRB bacteria so on. These substances have great influence on thestability of residual polymer, especially for Fe^{2+}. If the polymer is not stable, then it might aggregate and sedimentate in the buffer vessel, thereby affecting the reinjection process. Therefore, it's necessary to investigate the aggregation behavior of residual polymer in water. Currently, lots of literatures have reported on the influences of temperature and concentration of salt on the aggregation behavior of the polymer used in polymer flooding in water [6] [7] [8] [9]. However, there is no reports found to discuss on the effect of Fe^{2+} on the aggregation behavior of

the polymer produced in polymer flooding in water. Generally, Dynamic Scattering Light (DSL) and fluorescent microscopy method [8] [9] are most frequently used to study the aggregation behavior of polymer in water. In this paper, DSL and fluorescent microscopy were used to investigate the effects of Fe^{2+} on the aggregation behavior of residual polymer systematically, and the results are expected to be applied in the analysis for the stability of residual HMPAM in TOWPF.

2. Experiments

2.1. Materials and Instruments

TOWPF was taken from an offshore oilfield in china. In this offshore oilfield, oily wastewater treatment process is shown in **Figure 1**.

The oil displacement agent was hydrophobic modified polyacryamide (HMPAM). Therefore, there was residual HMPAM in the produced wastewater. The produced wastewater containing HMPAM was treated by skimmer, air floatation and walnut shell filter in turn and TOWPF was obtained [10] and came to buffer vessel. Its quality is listed in **Table 1**. In general, the TOWPF would be stay in buffer vessel for about 2 - 48 h. However, during this period, precipitates containing HMPAM would appear at the bottom of buffer vessel [11] [12]. This phenomenon represented that the stability of residual HMPAM in TOWPF was destroyed by some reason.

Pyrene was received from Aladdin-Reagent Corporation (Shanghai, China).

Fluorescence spectrum was measured by LS55 fluorescence spectrophotometer (PerkinElmer Corporation, England).

Dynamic light scattering (DLS) experiments were performed using Brookhaven Instruments 90 Plus/BI-MAS (Brookhaven Instruments, NY, USA). Hydrodynamic radius (R_h) was investigated by the DLS and calculated according to the CONTIN algorithm.

Size exclusion chromatography (SEC) analysis was conducted using a Water 515 liquid chromatograph instrument connected with a Waters 2410 refractive index detector at 30°C. The gel permeation column was linear ultrahydrogel (7.8×300 mm^2), and the

Table 1. The composition of simulation formation (mg/L).

NaCl	KCl	CaCl$_2$	MgCl$_2$·6H$_2$O	Na$_2$SO$_4$	Na$_2$CO$_3$	NaHCO$_3$
7341.9	66	764.7	1327	126.1	25.1	428.9
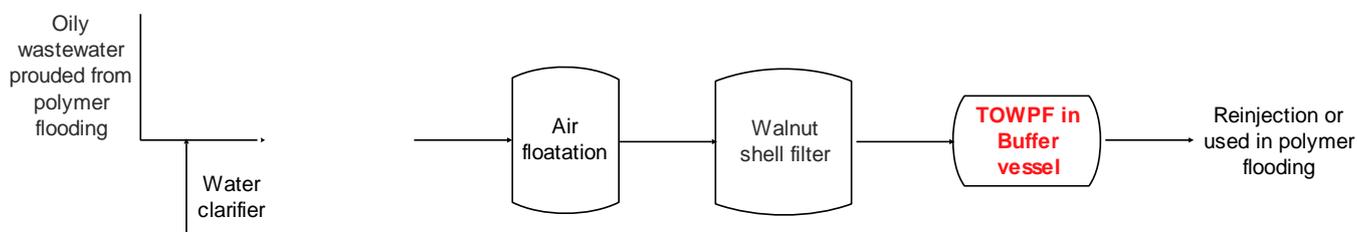
Figure 1. The oily wastewater treatment process in one offshore oilfield in China.

solvent used was distilled water. Polymer standards of Dextran were used from NICPBP (National Institute for the Control of Pharmaceutical and Biological Products). The samples were dissolved in 0.1 M NaCl solution and analyzed at a flow rate of 0.8 mL·min^{-1}. Number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) were measured by SEC.

Intrinsic viscosities ($[\eta]$) of polymers were measured with the "five-spot"dilution method using an Ubbelohde viscometer at 30˚C, where the solvent was 1 M NaCl solution. Viscosity-average molecular weight (M_w) was calculated as follows [13]:

$$[\eta] = 4.75 \times 10^{-3} M$$

2.2. Extraction of Residual HMPAM in TOWPF

Firstly, 2 L TOWPF was concentrated to 200 mL. Then, the concentrated TOWPF was purified by osmotic membrane with molecular weight cut off 10,000 for three days. At last, after vacuum drying for 8 h under the condition of 60˚C, the HMPAM in TOWPF was obtained. The structure of HMPAM is shown in **Figure 2**.

2.3. Aggregation Behavior Study of Residual HMPAM

2.3.1. Preparation of Residual HMPAM Solution Containing Pyrene

Firstly, 1 L HMPAM aqueous solution (60 mg/L) was prepared by using simulation formation water as solvent (the composition of simulation formation is listed in **Table 2**). Then, 5 mL solution of pyrene in ethanol (concentration of pyrene was 500 mg/L) was added into the HMPAM aqueous solution. At last, the mixture was allowed to heat at 65˚C for 2 h to remove the ethanol and HMPAM solution containing pyrene was obtained.

2.3.2. Fe^{2+} Mixed with Residual HMPAM Solution Containing Pyrene

Firstly, the substance which was listed in **Table 2**, such as oil, suspended solid, Fe^{3+}, and so on, was added respectively to 800 mL HMPAM solution containing pyrene (the dosage of substance was referred to **Table 1**).
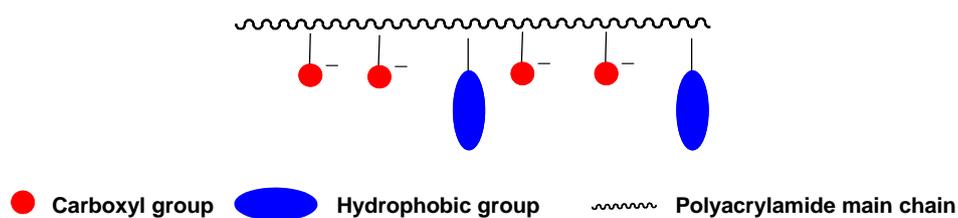
Figure 2. The structure of HMPAM.

Table 2. The characterizations of residual HMPAM.

M_n (g/mol)	M_w (g/mol)	M_η (g/mol)	PDI
3.61×10^5	1.41×10^6	1.00×10^6	3.91

Then, the mixture was stirred by an emulsifying machine at 7000 r/min for 15 min. At last, the mixture was distributed into four tubualted bottles (see **Figure 3**) for the next experiment.

2.3.3. Fluorescence Spectrum and DLS

Firstly, four tubualted bottles were kept at 65°C for 0 h, 8 h, 24 h and 48 h, respectively. Then, different samples were obtained successively from the bottom of tubualted bottle. The first 50 mL was the bottom solution, the intermediate 100 mL was the middle solution and the last 50 mL was the top solution.

The solutions at different layers were filtered by 0.8 μm microporous membrane and then the aggregation behavior of residual HMPAM was investigated by the fluorescence spectrum and DLS.

Because hydrophobic groups in HMPAM were not water-soluble, they would aggregate and hydrophobic domain can be formed by hydrophobic groups from one HMPAM molecular or several HMPAM moleculars [14] [15]. Pyrene would be soluble in the hydrophobic domain. The vibronic structure of the fluorescence spectrum of the monomeric pyrene is known to be sensitive to the local polarity. In particular, the raito I_1/I_3 of the intensities of the first and third vibronic peaks increases on going from aliphatic to polar solvents [16] [17] [18], and can be used as an index of the effective local polarity of the pyrenesolutilization site in the hydrophobic domain. The raito I_1/I_3 was calculated as the ratio of the intensity of peak I_1 (374.0 nm) to that of peak I_3 (385.0 nm) of the vibration fine structure of pyrene monomer emission. In addition, usually, the I_1 or I_3 would increase with number of hydrophobic domain because more pyrene can be soluble in the solution when there were more hydrophobic domains. Therefore, the value of I_1 can reflect the number of hydrophobic domain at the same experimental condition. For DLS, the R_h obtained by DLS can reflect the size of HMPAM aggregates.

3. Results and Discussion

3.1. Characterization of Residual HMPAM

The characterization of residual HMPAM is listed in **Table 2**. It can be found that its molecular weight was not high, but its polydispersity was high. Because its molecular weight was not high, its mobility may be similar with the small molecule surfactant. There were intermolecular aggregation for residual HMPAM.
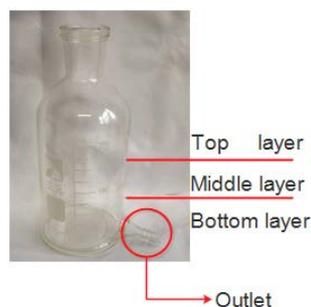
Figure 3. The picture of tubualted bottle.

3.2. Fluorescence Spectrums

Figure 4 shows the fluorescence spectrums of blank residual HMPAM solution at different layers and different times. The fluorescence spectrums of blank residual HMPAM solution at different layers were very close at the same time. As time increasing, the fluorescence intensity increased. **Table 3** lists the I_1/I_3 of blank residual HMPAM solution at different layers and $I_{1,t}/I_{1.0h}$ at different times. The results showed that the I_1/I_3 of blank residual HMPAM solution at different layers were closed and were about 0.85. Interestingly, the I_1/I_3 was not influenced by time. This phenomenon presented that the polarities of hydrophobic domain formed by residual HMPAM at different layers of blank residual HMPAM solution were the same. Therefore, the blank residual HMPAM solution was homogeneous and the polarity of hydrophobic domain was not changed during 48 h. Meanwhile, the increasing $I_{1,t}/I_{1.0h}$ represented that the number of hydrophobic domain could increase with time because the formation of hydrophobic domain was a slow process for blank residual HMPAM solution.
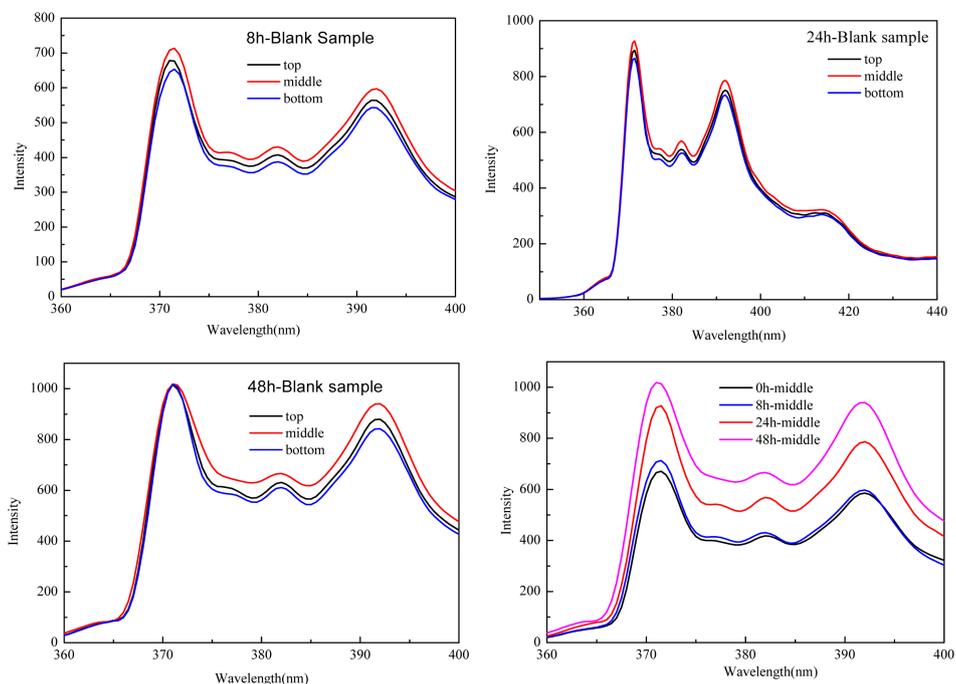
Figure 4. Fluorescence spectrums of blank residual HMPAM solution at different layers and different time.

Table 3. The I_1/I_3 of blank residual HMPAM solution at different layers and $I_{1,t}/I_{1,0h}$ at different times.

Layer	I_1/I_3			Time	$I_{1,t}/I_{1,0h}$
	8h	24h	48h		
Top layer	0.84	0.83	0.84	8h	1.06
Middle layer	0.85	0.84	0.88	24h	1.38
Bottom layer	0.85	0.83	0.83	48h	1.52

Table 4 shows the influence of Fe^{2+} on the fluorescence spectrums of residual HMPAM solution at different layers and different times. After the addition of Fe^{2+} into residual HMPAM solution, the I_1/I_3 was much larger than that of blank and not influenced by time too. It showed that the polarity of hydrophobic domain was increased. The reason of Fe^{2+} for increasing I_1/I_3 may be the chelation between these substances and carboxyl group in HMPAM. After the chelation, the moving ability and rotation ability of HMPAM decreased and the hydrophobic group used to formation of hydrophobic domain was decreased (see Figure 5). Therefore, the polarity of hydrophobic domain increased.

In addition, as shown in **Table 4**, after the addition of Fe^{2+}, the $I_{1,t}/I_{1,0h}$ increased with time,. Compared to the $I_{1,48h}/I_{1,0h}$ of blank HMPAM solution. It can be found that the addition of Fe^{2+}, the HAPAM solution had much larger $I_{1,48h}/I_{1,0h}$ than that of blank. It represented that the Fe^{2+} was helpful for the increase of hydrophobic domain. Usually, the increasing hydrophobic domain means the increasing aggregation degree. In summary, when there was Fe^{2+}, HMPAM solution had the largest aggregation degree ($I_{1,48h}/I_{1,0h} = 1.89$); After the addition of Fe^{2+}, the chelation between Fe^{2+} and carboxy group in HMPAM would increase with time during 48 h. Therefore, the number of hydrophobic domains increased with time obviously.

3.3. DLS Results

Usually, the increasing hydrophobic domain may be caused by increasing number of HMPAM aggregates or increasing size of HMPAM aggregates. The results of DLS can reflect that whether the size of HMPAM aggregate increased or not. **Figure 6** and **Table 5** showed the effects of Fe^{2+} on the relationship between R_h of HMPAM at different
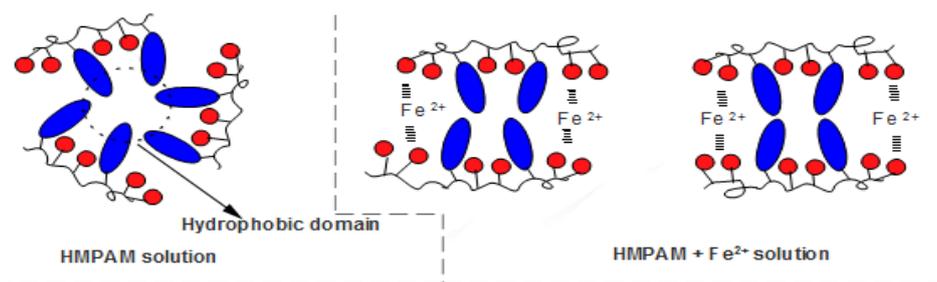
Figure 5. The change of aggregation behavior of residual HMPAM after the addition of Fe^{2+}.

Table 4. The influence of Fe^{2+} on the I_1/I_3 of residual HMPAM solution at different layers and different times.

Layer	I_1/I_3			Time	$I_{1,t}/I_{1,0h}$
	8h	24h	48h		
Top layer	1.17	1.18	1.20	8h	1
Middle layer	1.17	1.19	1.18	24h	1.40
Bottom layer	1.17	1.19	1.17	48h	1.89
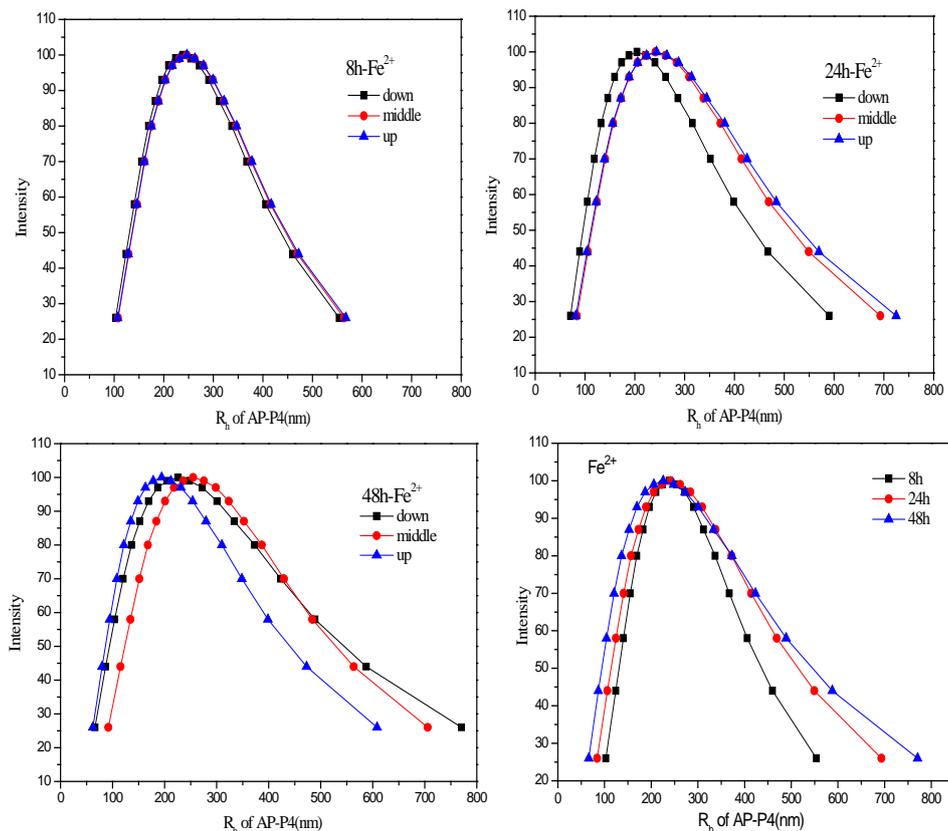
Figure 6. The effects of Fe^{2+} on the relationship between Rh of HMPAM and time.

Table 5. The influence of Fe^{2+} on the R_h value of residual HMPAM solution at different layers and different times (nm).

	8 h	24 h	48 h
Top layer	240.7	243.4	194.3
Middle layer	246.5	241.4	254.9
Bottom layer	238.7	204.4	225.6

time. For blank residual HMPAM solution, the R_h had no great change with time. When there was Fe^{2+} in solution, the R_h had no great change with time, too. The results showed that the increasing of $I_{1,t}/I_{1,0h}$ was caused by the increasing number of HMPAM aggregate.

4. Conclusion

The influences of Fe^{2+} on the aggregation behavior of residual HMPAM in TOWPF were studied by fluorescence spectrum and DLS. The results showed that Fe^{2+} can cause the aggregation of HMPAM molecular chains and increase the number of polymer aggregates largely due to the chelation between carboxyl groups and Fe^{2+}, which may result in precipitating in water and producing lots of oily sludge. Therefore, some chelat-

ing agent should be added into produced water contain residual HMPAM during the treatment process for the sake of shielding the influences of Fe^{2+}.

Supported

References

[1] Wever, D.A.Z., Picchioni, F. and Broekhuis, A.A. (2011) Polymers of Enhanced Oil Recovery: A Paradigm for Structure-Property Relationship in Aqueous Solution. *Progress in Polymer Science*, **36**, 1558-1628. http://dx.doi.org/10.1016/j.progpolymsci.2011.05.006

[2] Zhang, L.J. and Yue, X.A. (2008) Displacement of Polymer Solution on Residual Oil Trapped in Dead Ends. *Journal of Central South University of Technology*, **5**, 84-87. http://dx.doi.org/10.1007/s11771-008-0320-4

[3] Zhang, L.J., Yue, X.A. and Guo, F. (2008) Micro-Mechanisms of Residual Oil Mobilization by Viscoelastic Fluids. *Petroleum Science*, **5**, 56-61. http://dx.doi.org/10.1007/s12182-008-0009-1

[4] Qu, G.H., Gong, X.G. and Liu, Y.K. (2014) New Research Progress of the Demulsification of Produced Liquid by Polymer Flooding. *Journal of Chemical and Pharmaceutical Research*, **6**, 634-640

[5] Liu, Y.G., Tang, H.M., Chen, H.X., Li, Y.G., Shan, W. and Gao, J.C. (2010) Study on Produced Water Quality Variation Rule from Polymer Flooding and Mechanism of Formation Damage. *Offshore Oil,* **12**, 86-91.

[6] Han, T., Xu, G.Y., Chen, Y.J., Zhou, T., Tan, Y.B., Lv, X. and Zhang, J. (2012) Improving Performances of Hydrophobically Modified Polyacrylamide in Mineralized Water by Block Polyether with Branched Structure. *Journal of Dispersion Science and Technology*, **33**, 697-703. http://dx.doi.org/10.1080/01932691.2011.579852

[7] Zhao, Y.Z., Zhou, J.Z., Xu, X.H., Liu, W.B., Zhang, J.Y., Fan, M.H. and Wang, J.B. (2009) Synthesis and Characterization of a Series of Modified Polyacrylamide. *Colloid and Polymer Science*, **287**, 237-241. http://dx.doi.org/10.1007/s00396-008-1975-y

[8] Liu, J.X., Peng, T.J., Meng, K.Q., Wang, H., Zhao, Z.C. and Wang, L.Q. (2016) Kinetic Behavior in Self-Assembly Process of Associative Polymer Solutions. *Journal of Macromolecular Science, Part A*, **53**, 215-221. http://dx.doi.org/10.1080/10601325.2016.1143316

[9] Zhong, C.R., Luo, P.Y. and Meng, X.H. (2010) Aggregation Behavior of a Water-Soluble Terpolymer with Vinyl Biphenyl Characterized by a Fluorescent Probe. *Journal of Applied Polymer Science*, **116**, 404-412

[10] Zhang, J., Jing, B., Fang, S.W., Duan, M. and Ma, Y.Z. (2015) Synthesis and Performances for Treating Oily Wastewater Produced from Polymer Flooding of New Demulsifiers Based on Polyoxyalkylated N,N-Dimethylethanolamine. *Polymers for Advanced Technologies*, **26**, 190-197. http://dx.doi.org/10.1002/pat.3433

[11] Hu, G.J., Li, J.B. and Zeng, G.M. (2013) Recent Development in the Treatment of Oily Sludge from Petroleum Industry: A Review. *Journal of Hazardous Materials*, 261, 470-490. http://dx.doi.org/10.1016/j.jhazmat.2013.07.069

[12] Tuncal, T. and Uslu, O. (2014) A Review of Dehydration of Various Industrial Sludges. *Drying Technology*, **32**, 1642-1654. http://dx.doi.org/10.1080/07373937.2014.909846

[13] Feng, Y.J. (1999) Study of Aqueous Solution Structure and of Hydrophobically Associating Water-Soluble Polymer and Its Effect on the Solution Rheology, South West Petroleum University, Chengdu, 87 (in Chinese).

[14] Zhang, J., Jing, B., Tan, G.R., Fang, S.W. and Wang, H. (2015) Effect of Structure of Graft on the Properties of Graft Copolymers of Acrylamide and Surfactant Macromonomers Dilute Aqueous Solutions. *J.Macromol. Sci., Phys,* **54**, 253-261.

[15] Fang, S.W., Duan, M., Long, W.H., Xia, Y.N., Li, L.Y., Wang, H. and Zhang, L.H. (2014) Synthesis of Copolymer of Acrylamide and a Cationic-Nonionic Bifunctional Polymerizable Surfactant and Its Micellar Behavior in Water. *Journal of Dispersion Science and Technology*, **35**, 301-306 http://dx.doi.org/10.1080/01932691.2013.771364

[16] Aguiar, J., Carpena, P., Molina-Bolivar, J.A. and Ruiz, C.C. (2003) On the Determination of the Critical Micelle Concentration by the Pyrene 1:3 Ratio Method. *Journal of Colloid and Interface Science*, **258**, 116-122. http://dx.doi.org/10.1016/S0021-9797(02)00082-6

[17] Kim, J.H., Domach, M.M. and Tilton, R.D. (2000) Effect of Electrolytes on the Pyrenesolubilization Capacity of Dodecyl Sulfate Micelles. *Langmuir*, **16**, 10037-10043. http://dx.doi.org/10.1021/la0005560

[18] Ismail, D.D.K. (2008) Aggregation and Adsorption Properties of Sodium Dodecyl Sulfate in Water-Acetamide Mixtures. *Journal of Colloid and Interface Science*, **327**, 198-203. http://dx.doi.org/10.1016/j.jcis.2008.07.045