Desalination and Water Treatment
www.deswater.com

1944-3994/1944-3986 © 2012 Desalination Publications. All rights reserved
doi: 10/5004/dwt.2012.3066

44 (2012) 190–196
June

A method of making an aqueous dispersion of polyaniline and inhibiting corrosion in cooling water

Hassene Brinis*, Mohamed El Hadi Samar

Department of Process engineering, Faculty of Engineering Sciences, Badji Mokhtar University,
P.O. Box: 12 Annaba, 23000, Algeria
Tel. +213 661 884 401; Fax: +213 37327931; email: hassenebrinis@gmail.com

Received 24 June 2011; Accepted 22 November 2011

ABSTRACT

The present study provides a process for the dispersion of polyaniline after its synthesis, to improve the solubility of the polyaniline in an aqueous medium in the presence of nonionic surfactant (fatty alcohol ethoxylate). The surfactant selected based on their chemical composition and their Hydrophile-Lipophile-Balance and the induced steric hindrance effect. The dispersion process was developed, and the polyaniline dispersion was characterized by the electrical conductivity and in the macroscopic phase boundary. The polyaniline dispersions have been studied for their possible use in such fields as a corrosion inhibitor. In our case, the corrosion inhibitor was employed in industrial cooling water, which contains hardness and operating at temperature of 41°C and pH of 8.7. The weight-loss and corrosion polarization resistance (corrater system) methods were carried out to study the corrosion of carbon steel. Inhibition efficiencies of nearly 80% have been observed even at as low concentration of 50 mg l^{-1}.

Keywords: Polyaniline; Dispersion; Nonionic surfactant; Cooling water; Corrosion inhibition; Corrosion test; Carbon steel

1. Introduction

The polyaniline was first prepared in 1834 and rediscovered by MacDiarmid in 1984. Until the date, the polymers have been investigated extensively for over 100 y and attracted interest as a conducting material for several important reasons: the monomer is inexpensive, the polymerization reaction is straightforward and proceeds with high yield, and polyaniline has excellent stability as shown by Allan MacDiarmid and leading researchers working on conducting polymers [1,23].

In the present study, the polyaniline was obtained by chemical methods found in the literature [2,20,21]. The obtained polymer (emeraldine salt) was characterised by infrared and UV-Vis absorption techniques. The polyaniline besides their application in advanced technologies [3,4] can have a tremendous impact on control of corrosion either by way of using them as an inhibitor. The use of polyaniline as a corrosion inhibitor was limited because it has been considered as extremely poor solubility in aqueous systems; this is making an obstacle to use as a corrosion inhibitor.

Many works have been done on improving the solubility of polyaniline, because of its low solubility in most common solvents and very tough to disperse due to high surface tension; the industrial application of polyaniline is limited. To improving its solubility in water and to prevent dopant migration [5], polyaniline has been modified in the selfdoped form by introducing protonic acids into the side chains [6–10]. A different approach to obtain polyaniline soluble in some solvent is to produce colloidal polyaniline [11,12], and emulsion-polymerization [13].

---

*Corresponding author.

Another method attempting to produce water-soluble polyaniline is to polymerize protonic-acid or to copolymerize aniline with similar monomers, such as *N*-(4-sulfophenyl)aniline and *o*-anthranilic acid to yield poly(aniline-*co*-*N*-(4-sulfophenyl) aniline) and poly(aniline *co*-*o*-anthranilic acid) respectively. However, the two copolymers are only partially soluble in water. In addition to the above methods, there is a new water soluble self-doped polyaniline has been proposed by grafting polyaniline [9].

An objective of the present study is to disperse polyaniline in an aqueous system in the presence of nonionic surfactants, to improve the dispersion (solubility) property and to make polyaniline soluble without deterioration or degradation of polymer [14–17]. Large range of surfactants was selected based on their chemical composition and their hydrophilic–lipophilic balance (HLB). The HLB value gives a quantitative measure of the amphiphilicity of the surfactants. For the case of nonionic surfactants, it is generally defined as shown in Eq. (1) below [14]:

$$HLB = 20\left(\frac{M_H}{M_H + M_L}\right) \tag{1}$$

where M_H is the molecular weight of the hydrophilic portion of the surfactant molecule; M_L is the molecular weight of the hydrophobic or lipophilic portion.

To appreciate the role of a surfactant, we must understand the physicochemical properties of surfactant solutions. Several physical properties of the solution as osmotic, pressure, conductivity, relative viscosity, and surface tension change when a surfactant is dissolved in water. Beyond a particular level of concentration (CMC), there is a sudden change in the slope of these physicochemical properties. The critical micelle concentration (CMC) value is defined, in terms of the pseudo-phase model, as the concentration of maximum solubility of the polymer in that special solvent [14,18].

When a nonionic surfactant is added to water with a sparingly polyaniline dissolved in the Camphor Sulphonic Acid (CSA) under stirring, the solubility of the polyaniline is found to increase. The apparently higher solubility is attributed to the presence of micelles, which really become a kind of reservoir for the excess polyaniline, as shown in Fig. 1.

One type of nonionic surfactants was chosen: ethoxylated fatty alcohol (alcohol (C18) poly (18) ethoxylate) which has an effect in reducing the interfacial tension between the water and the polyaniline [16]. The dispersed polyaniline was performed and stable aqueous dispersions of the polyaniline up to 80°C and the pH range from 1 to 9 was obtained.

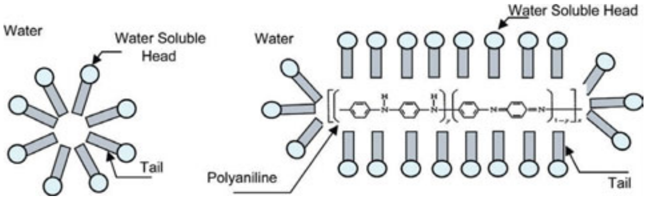

Fig. 1. Schematic representation of micelle formation in polyaniline dispersion.

The polyaniline is interesting as a corrosion inhibitor due to having π bonds in their structures (π electrons are delocalized over the whole molecule) [1,19]. This is making easy their adsorption the metal. Furthermore, the adsorption of polyaniline is influenced by the presence of functional groups such as (=NH) and (*R* = *R*) in the molecule. It has also noted that the molecular area and molecular weight of the inhibitor play important roles [20].

In this paper, we synthesized polyaniline by chemical oxidative polymerization of aniline in acidic aqueous condition. The characterization was carried out by using UV-Visible and Infrared spectroscopy (FTIR) and then the polyaniline dispersion process was performed. Some early work on polyaniline dispersion has been discussed in a number of publications [21,22,24] to enhance the solubility of polyaniline in water and organic solvent, while the stability of polyaniline is limited by the time with low conductivity of dispersion. The polyaniline dispersion obtained is completely soluble in an aqueous system with an increase in conductivity, and the dispersion stability of the polyaniline has been explored over the pH and temperature range. Another important result, the potential use of polyaniline dispersion in protecting metals from corrosion as an inhibitor in cooling water was confirmed.

2. Experimental

2.1. Materials and equipments

Materials need for the aniline polymerization, and the polyaniline dispersion are the following: Aniline ($C_6H_5NH_2$), hydrochloric acid (HCl), ammonium persulfate ($(NH_4)_2S_2O_8$), potassium dichromate, ammonium hydroxide (NH_4OH), DMSO solvents, CSA as dopant, phenolic solvents (m-cresol) and nonionic surfactants (Alcohol (C18) poly (18) ethoxylate) with the molecular weight (Mw 1062 g mol^{-1}).

The equipments required for the polymerization of aniline include the following: 2-l jacketed reaction vessel with an anchor stirrer paddle, ice bath, Vacuum Filter Apparatus with filter funnel and flask. Water bath, whatman #42 filter paper and test tubes.

The characterization of polyaniline and polyaniline dispersion were carried out with the following equipments: UV-vis spectroscopy (Hitachi model U-3010 spectrophotometer), pH meter HI8417, Gel Permeation

Chromatograph (GPC) and FT-IR measurements (Perkin-Elmer model 1000 FTIR Spectrophotometer with samples in KBr pellet form). The electric conductivity measurements were made using cascade microtech four-probe standard method and (Corrater RCS 900 HS) to measure the corrosion rate.

To perform water analysis, we will combine three methods: titration method, Hach method (Model DR/2010) and colorimetric method. The following reagents were used:(0.02 N) sulphuric acid solution (H_2SO_4), phenolphthalein and methyl orange indicators; 0.0282 N silver nitrate solution, 0.01 M EDTA solution; ammonium thiocyanate solution, sulfa ver four powder pillow, molybdate three and citric acid powder pillow and amino acid F powder pillow. The equipments used for the water analysis are: spectrometer PYE unicam Pu 8600, hydrometer (range of 1.000–1.220 Sg), thermometer (range of −10–100°C).

2.2. Polyaniline synthesis

Polyaniline was synthesized by chemical oxidative polymerization of aniline ($C_6H_5NH_2$) in acidic aqueous environments, using a method similar to that reported by MacDiarmid et al. [2,23,24], 0.15 mol ammonium persulfate ($(NH_4)_2S_2O_8$) aqueous solution or potassium dichromate was added dropwise to 0.22 mol aniline dissolved in 1 M HCl solution (the reaction is very exothermic), both solutions being pre-cooled to 0°C and the dopant/monomer together with the oxidant/monomer ratio was fixed at (1:1 M) to avoid degradation of polyaniline [2,25,26]. The chemical oxidation of aniline represented by the equation (Fig. 2).

The reaction was allowed to proceed for about 2 h under constant stirring in an ice bath and nitrogen atmosphere. The polymerization reactions were carried out in a 2 l jacketed reaction vessel with an anchor stirrer paddle. The syntheses were stopped when the solution takes the characteristic green color. The precipitate which had formed was removed by filtration, washed repeatedly with 1 M HCl aqueous solution then dionized water and dried under vacuum for about 24 h. The material thus obtained is in its salt form (ES): polyemeraldine hydrochloride (PANI-HCl), and is green colored. The above obtained PANI-HCl salt form was converted into the polyemeraldine base (EB) form by treating it with a 0.1 M ammonium hydroxide (NH_4OH) solution for about 2 h while stirring and the insoluble polyaniline was separated by filtration and washed with acetone and deionized water to remove unreacted monomer. The obtained powder was then dried in a vacuum oven at 60°C for 24 h, when low-molecular weight fractions can be removed from the polyaniline base by extraction with solvents DMSO, The resulting weight average molecular weight (M_w) is about 7 10^4 g mol^{-1} in about 92% yield as determined by GPC.

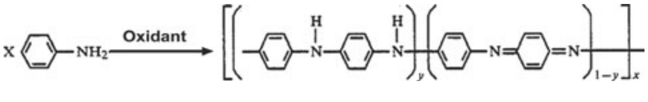

Fig. 2. Synthesis of polyaniline by chemical polymerization of aniline.

A portion of the polymer was ground to a fine powder and dissolved in CSA as dopant and phenolic solvents (m-cresol). The polyaniline can be classified by its oxidation states [27,28], as follows:

- Leucoemeraldine base (LEB), the polymer is in the fully reduced oxidation state.
- Emeraldine base or polyaniline base (PANiEB), the polymer is in the half oxidation state.
- Pernigraniline base (PNB), the polymer is in the fully oxidized form.

Several studies have been performed to investigate the structural parameters of the polyaniline pernigraniline base (PANI-PNB) and electronic properties of the polyaniline LEB (PANI-LB) [29,30].

2.3. Polyaniline dispersion

To make polyaniline dispersion, many methods have been developed, such as emulsion and dispersion polymerizations and many surfactants and templates have been tested to improve the process ability of this polymer [21,23,31,32].

A soluble polymer was formed when a dispersed polyaniline have been made with a nonionic surfactants and polyaniline. A wide range of nonionic surfactants can be used as below:

- Fatty Alcohol Ethoxylates.
- Fatty Acid Ethoxylates.
- Alkylphenol Ethoxylates.
- Ethoxylates Fatty Amines.

The ethoxylated fatty alcohol is a particularly preferred to disperse polyaniline using steric mechanism effect [25]. The chemical structure of a surfactant as used here having the following formula: $R\text{-}(CH_2CH_2O)_nOH$, wherein R is $C_{18}H_{37}$ and $n = 18$.

The dispersed polyaniline was prepared by dissolving 50 mg of polyaniline in 25 ml of CSA and kept under constant stirring to obtain polyaniline dispersion in room temperature. Measure 10 ml from the previous solution, place sample into breaker or flask and dilute to 100 ml with deionized water. At room temperature and under constant mixing with a stirring rod we start add nonionic surfactants dropwise, while there is recoding of temperature and conductivity with fraction volume of nonionic surfactants.

Alcohol (C18) poly (18) ethoxylate ($C_{54}H_{110}O_{19}$) for the molecular weight (Mw 1062 g mol^{-1}) and HLB number calculated by the Eq. (1) is 15.26, will be used for this study, after dissolving 500 mg of surfactant in 100 ml deionized water, carefully dropwise the surfactant, measure the conductivity with fraction volume. A series of a dispersion process was performed by increasing the surfactant concentration to 10 and 20 g ml^{-1}, while the conductivity was plotted versus the volume fraction of surfactant at 22°C to determine the CMC point.

3. Results and discussion

3.1. Characterization of polyaniline

3.1.1. Polyaniline UV-visible spectra

The Fig. 3 shows the UV-Visible spectrum of polyaniline; we can observe two absorption bands characteristic of polyaniline in its emeraldine base form, at wavelengths between 328–346 and 610–643 nm [33,34].

The absorption band in the UV region is attributed to the chain of the aromatic nuclei and corresponds to the π–π^* transitions of the polymeric skeleton [34,35]. On the other hand, the absorption band appearing in the visible region indicates an interaction between the benzenic nuclei and the quinone diimine structure.

3.1.2. Infrared spectroscopy

The IR spectrum of the polymer was recorded in the spectral range of 400–4000 cm^{-1}. Fig. 4 shows the FTIR spectrum of polyaniline dissolved in CSA. The most important vibrationally bands which allow the identification of polyaniline are: 830 cm^{-1}, out-of-plane C-H bond [34,36], 1160 cm^{-1} aromatic C-N-C bond [34]; 1500 cm^{-1} aromatic C=C double bond [34], peak at 1302 cm^{-1} is associated with an angular deformation of the C-N stretching, and 1590 cm^{-1} nitrogen bond between benzenoid and quinoid rings [37]. The doping of polyaniline can be observed at 1122 cm^{-1} in the formation of the pola-rons $H^+N = Q = NH^+$[35]. Peak at 1034 cm^{-1} shows S = O groups associated with the sulfonic acid (CSA) [35].

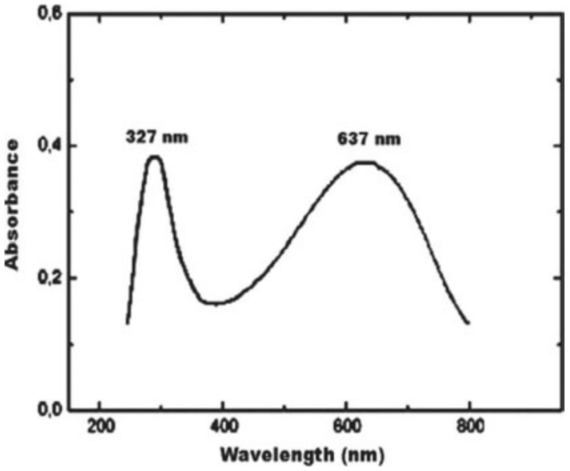

Fig. 3. UV-visible spectrum of polyaniline.

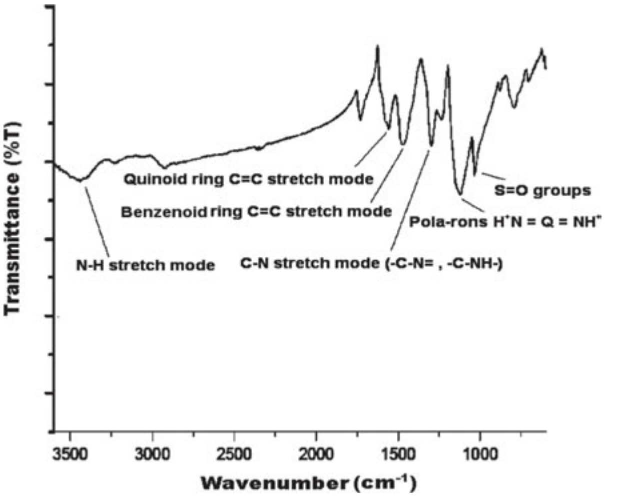

Fig. 4. FTIR spectrum of polyaniline/CSA.

3.2. Characterization of polyaniline dispersion

3.2.1. Electric conductivity

The electric conductivity measurements were made using cascade microtech four-probe standard method. Fig. 5 shows the conductivity evolution until the CMC was reached; the conductivity will suddenly increase, and will show an abrupt change in slope in a narrow volume fraction or concentration range. The increase of electric conductivity in the dispersed systems, compared to dionized water, results from the very low dispersion of conducting polymer into a dispersion system.

The formation of polyaniline dispersion in a micellar system was observed when 5 mg ml^{-1} of dissolved surfactant in dionized water used for dispersion process of 200 mg l^{-1} of polyaniline. The CMC value was obtained at 1.03 10^{-3} mol l^{-1} concentration of (Alcohol (C18) poly (18) ethoxylate) for the conductivity of aqueous solution at 22.9 μS cm^{-1}, measured at room temperature. At very low surfactant concentration (below 10^{-3} mol l^{-1} of $C_{54}H_{110}O_{19}$), the surface tension of polyaniline/surfactant solutions remain invariant. Above (10^{-3} mol l^{-1} of $C_{54}H_{110}O_{19}$), surface tension slowly decreases and reaches a constant value, when the concentration of surfactant is about 2 10^{-3}mol l^{-1}, at the volume fraction $\Phi = 0.75\%$.

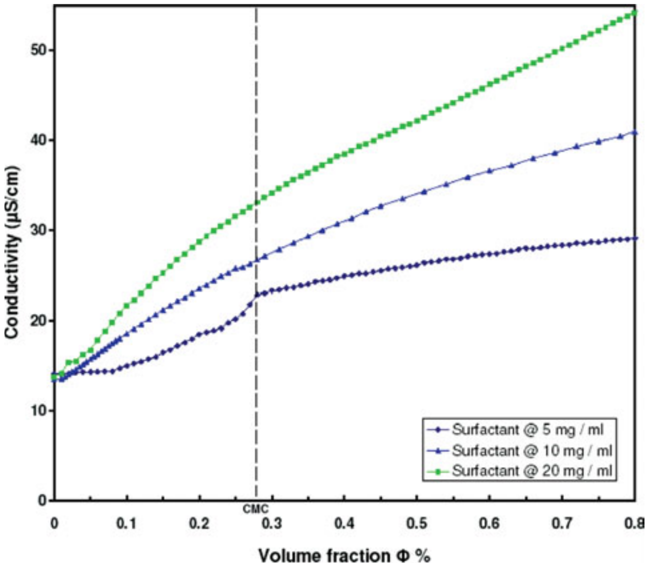

Fig. 5. Changes in the conductivity of dispersed polyaniline in water as a function of the volume fraction of the surfactant.

3.2.2. Dispersion stability

The dispersion stability of the polyaniline was evaluated by the observation of the settling in the macroscopic phase boundary for the concentration suspension. Therefore, the ratio of sedimentation is simply defined as shown in Eq. (2) below: [38].

$$\text{Ratio of sedimentation} = 1 - \frac{\text{Volume of the superna tantliquid}}{\text{Volume of the entire suspension}} \quad (2)$$

Several samples were prepared and placed in test tubes in different conditions such as temperature by standing in a heat water bath and pH .The observation shows the stability of the polyaniline dispersion for 2 d test times, no sedimentation, no float to the top and just one aqueous phase observed (slightly white waxy to green slightly). The stability tests were performed over the pH range of 1–10 and temperature up to 80°C.

3.3. Corrosion inhibitor essays

The polyaniline dispersion prepared in the present study was evaluated for controlling corrosion of industrial cooling equipment. Most cooling water systems are in continuous use, so it is rare to have access to inspect the actual system to observe or measure corrosion and corrosion inhibition. Several tools have been developed to measure corrosion by indirect means. Some of the more common of those employed today are the pilot plant [39]. The tests were conducted on evaporate pilot cooling tower, as show in the schematic drawing in Fig. 6. The metals were used for the tests are a carbon steel, the chemical composition average with mass ration is given as follow: C = 0.08%, Mn= 0.52%, Si = 0.21%, P = 0.005%, S = 0.007%, and iron.

The system design allows decreases cycles of concentration by continuous addition of make-up water and blowdown.

The water leaving the basin passes through a heat exchange rod, which includes two heat exchange rods running at approximately 1000 watts. The water then passes through a corrosion coupon rack, in accordance with this technique, dried, precleaned and pre-weighted coupons (three specimens) of carbon steel with dimensions of (13 mm^3 × 102 mm^3 × 2 mm^3) are suspended. The flow and therefore, velocity through the rack is selected and controlled. There are positions for both meter probes and corrosion coupons so that short-term and long-term corrosion rates can be effectively measured. The corrosion meter Corrater RCS 900 HS (Corrosion Polarization Resistance Method) will be use for a range of 0–10,960 mg dm^{-2} d^{-1} (0–2000 mpy). The unit duplicates heat transfer surfaces, Since temperature or heat flux can have a significant effect on the scaling, fouling, or corrosion rates being experienced in a system, monitoring this variable is important [40,41]. The basin water temperature, pH, cycle of concentration, dosage of corrosion inhibitor and water chemistries are controlled. Analytical tests were performed for the cooling water and make up water samples as shown in Table 1.

Microscopic and chemical analysis of deposit samples from accumulated residue in the tower basin of a system with deposition potential indicators expressed as a scaling or saturation index as shown in Table 2. One such index is the Larson-Skold which provides an indication of corrosion of carbon steel. The Larson-Skold value is 1.62, an indication the tendency towards high corrosion rates of a local type should be expected.

The data in Table 3, illustrate the effectiveness of the methods of the present study in inhibiting corrosion of carbon steel metal; tests were evaluated by Corrosion

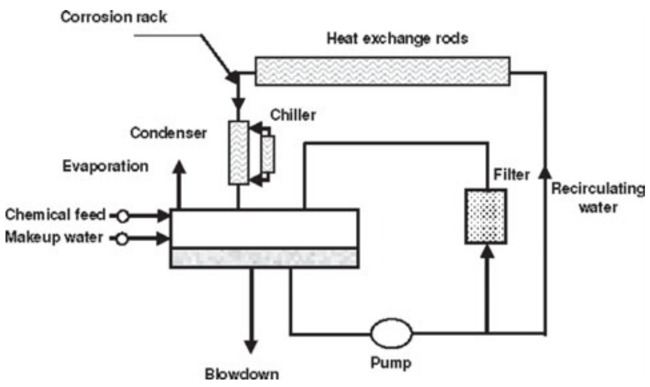

Fig. 6. Flow diagram of dynamic test.

Table 1
Cooling tower, makeup water samples analysis with residual ratios (COC)

Parameter	Makeup	Tower	COC
Temperature, °C	26	41	NA
pH	7.75	8.70	NA
Conductivity, µS cm^{-1}	475	1171.3	2.47
Total alkalinity, mg l^{-1} as $CaCO_3$	124.79	287.5	2.3
Calcium, mg l^{-1} as $CaCO_3$	139.46	363.50	2.61
Magnesium, mg l^{-1} as $CaCO_3$	83.54	208.80	2.50
Sodium, mg l^{-1}	18.00	183.89	NA
Chloride, mg l^{-1}	48.79	185.80	3.81
Sulfate, mg l^{-1}	65.77	210.00	3.19
Total iron, mg l^{-1} as Fe	ND	0.15	NA
TDS, mg l^{-1}	304.00	749.6	2.47
Silica, mg l^{-1} as SiO_2	1.88	4.5	2.39

ND: Not detectable.
NA: Not applicable.
COC: Cycle of concentration.

Table 2
Deposition potential indicators

Simple indices		Saturation level (mg l^{-1})	
Langelier	2.01	Calcite ($CaCO_3$)	53.50
Ryznar	4.68	Aragonite ($CaCO_3$)	45.16
Puckorius (Practical)	5.22	Magnesite ($MgCO_3$)	17.93
Larson–Skold	1.62	Anhydrite ($CaSO_4$)	0.0436
Stiff Davis	1.82	Gypsum ($CaSO_4 \times 2H_2O$)	0.0607
Oddo–Tomson	2.02	Brucite ($Mg(OH)_2$)	0.0340

Table 3
Corrosion inhibiting efficacy of dispersed polyaniline in cooling water

Concentration of corrosion inhibitor (mg l^{-1})	Corrosion rate (mg dm^{-2} d^{-1})	Inhibitor efficiency (%)
Blank	36.77	None
20	8.33	77.35
30	8.11	77.94
50	7.01	80.92
100	6.47	82.71
150	6.36	82.41

Polarization Resistance Method and coupon weight-loss method in the system. Coupons are removed, cleaned, dried and weighted, and also inspected, no pitting was observed on coupon surfaces, after 28 d exposures, showed a corrosion rate of only 1.48 mpy (8.09 mg dm^{-2} d^{-1}). Equipments inspections and exchanger tube surface testing have confirmed excellent corrosion protection. The efficiency of the inhibitor was expressed in Eq. (3) below:

$$\text{Inhibitor Efficiency (\%)} = 100\left(\frac{\text{CR}_{\text{uninhibited}} - \text{CR}_{\text{inhibited}}}{\text{CR}_{\text{uninhibited}}}\right) \quad (3)$$

where $\text{CR}_{\text{uninhibited}}$ is the corrosion rate of the uninhibited system; $\text{CR}_{\text{inhibited}}$ is the corrosion rate of the inhibited system.

The blank solution when no polyaniline dispersion or corrosion inhibitor was employed, defines the corrosion rate of the carbon steel in uninhibited cooling water. The test data in Table 3 show the polyaniline dispersion is effective to reduce the corrosion rate to less than 2 mpy (10.96 mg dm^{-2} d^{-1}) at 20 mg l^{-1} of polyaniline dispersion. Since a corrosion rate of 2–4 mpy (10.96–21.92 mg dm^{-2} d^{-1}) is generally considered to be an acceptable rate in open cooling systems [41,42], the excellent corrosion protection afforded by the compositions of this research can be readily appreciated.

The corrosion inhibiting composition of the present study is particularly advantageous in that the composition is capable of inhibiting corrosion in a wide variety of conditions encountered in a processing subject to corrosion, including high pH, high temperature and water quality.

4. Conclusions

We have presented an efficient process for the preparation of conductive polyaniline dispersion. The polyaniline has been synthesized with the method of chemical oxidative polymerization based on an aqueous solution polymerization system, and then the polymers have been characterized by FTIR and UV-Visible spectroscopy. A next step after polymerization, it is the dispersion (solution) of polyaniline was performed in water as an external phase. The Fatty Alcohol Ethoxylate (Alcohol (C18) poly (18) ethoxylate) as nonionic surfactant is used to change the physicochemical of the dispersed and the continuous phase properties. The CMC 1.03 10^{-3} mol l^{-1} was found with 22.9 µS cm^{-1} the conductivity of aqueous solutions. The stable aqueous dispersions of the polyaniline were obtained, and tests in a wide range of temperature and pH. Another objective of this study to show that the polyaniline dispersion can also find applications as a corrosion inhibitor for carbon steel metal, which used for the cooling water systems, that contains a concentration of inorganic salts or ions, which are much higher than ordinary water and operated at a temperature, usually reach 41°C. A quantity of 50 mg l^{-1} of polyaniline dispersion was maintained the corrosion rate below 2 mpy (10.96 mg dm^{-2} d^{-1}) where the inhibitor efficiencies reach 80%.

References

[1] A.J. Heeger, Nobel lecture: Semi-conducting and metallic polymers: The fourth generation of polymeric materials, Rev. Mod. Phys., 73(3) (2001) 681–700.

[2] A.G. MacDiarmid and A.J. Epstein, Polyaniline synthesis, chemistry and processing, the Fifth Intern Kyoto Conf on New Aspects of Organic Chemistry, 34 (1992) 271–298.

[3] N. Berezina, I. Falina, A. Sytcheva, S. Shkirskaya and S. Timofeyev, New generation of nanocomposite materials based on perfluorinated membranes and polyaniline. Intercalation phenomena, morphology and transport properties, Desalination, 14 (2010) 246–251.

[4] A.Yu. Pulyalina, G.A. Polotskaya, I.G. Suschenko, T.K. Meleshko, L.M. Kalyuzhnaya and A.M. Toikka, Pervaporation membranes based on composites of polyimide with polyaniline or its copolymer, Desalination, 14 (2010) 158–164.

[5] A.G. MacDiarmid, Synthetic metals: A novel role for organic polymers, Angew. Chem. Int. Ed., 40 (2001) 2581–2590.

[6] J. Yue and A.J. Epstein, Synthesis of self-doped conducting polyaniline, J. Am. Chem. Soc., 112(7) (1990) 2800–2801.

[7] S.A. Chen and G.W. Hwang, Synthesis of water soluble self acid doped polyaniline, J. Am. Chem. Soc., 116 (1994) 7939–7940.

[8] B.A. Deore, I. Yu and M.S. Freund, A switchable self-doped polyaniline: Interconversion between self-doped and non-self-doped forms, J. Am. Chem. Soc., 126 (2004) 52–53.

[9] H.K. Lin and S.A. Chen, Synthesis of new water-soluble self-doped polyaniline, Macromolecules, 33 (2000) 8117–8118.

[10] A.J. Epstein, J.M. Ginder, F. Zuo, H.S. Woo, D.B. Tanner, A.F. Richter, M. Angelopoulos, W.S. Huang and A.G. MacDiarmid, Insulator to metal transition in polyaniline: Effect of protonation in emeraldine, Synth. Met., 21 (1987) 63–70.

[11] J. Stejskal, M. Spirkova, A. Riede, M. Helmstedt, P. Mokreva and J. Prokes, Polyaniline dispersions: The control of particle morphology, Polymer, 40 (1999) 2487–2492.

[12] P. Petrov, P. Mokreva, C.B. Tsvetanov and L. Terlemezyan, Colloidal aqueous dispersion of polyaniline nanotubes grafted non-covalently with poly(ethylene oxide)-blockpoly(acrylic acid) copolymer, Colloid Polym. Sci., 286 (2008) 691–697.

[13] P.J. Kinlen, Emulsion-polymerization process and electrically-conductive polyaniline salts, US Patent No. 5863465, 1999.

[14] A.M. Fernandez and L. Jebbanema, The effect of surfactant selection on emulsion polymer properties, Paint & Coatings Industry., 23(8) (2007) 62–69.

[15] J. Stejskal and I. Sapurina, Polyaniline: Thin films and colloidal dispersions, Pure Appl. Chem., 77(5) (2005) 815–826.

[16] S. Talwar, L.F. Scanu and S.A. Khana, Hydrophobic interactions in associative polymer/nonionic surfactant systems: Effects of surfactant architecture and system parameters, J. Rheol., 50(6) (2006) 831–847.

[17] D. Chattopadhyay, M. Chakravorty and B.M. Mandal, Hydroxypropylcellulose stabilized polyaniline dispersions: Role of polymerization medium, Polym. Int., 50 (2001) 538–544.

[18] R.E. Goldstein, Model for phase equilibria in micellar solutions of non ionic surfactants, J. Chem. Phys., 84(6) (1986) 3367–3378.

[19] F. Chen and P. Liu, Conducting polyaniline nanoparticles and their dispersion for waterborne corrosion protection coatings, ACS Appl. Mater. Interfaces, 3(7) (2011) 2694–2702.

[20] S. Sathiyanarayanan, K. Balakishnan, S.K. Dhawan and D.C. Trivedi, Prevention of corrosion of iron in acidic media using poly (o-methoxy-aniline), Electrochim. Acta, 39(6) (1994) 831–837.

[21] S. Palaniappan and C.A. Amarnath, Process for preparing of conductive polymer dispersion, US Patent No. 7468149 B2, 2008.

[22] T. Maruyana and Y. Sekine, Method for producing conductive polyaniline and organic polymer composition, US Patent No. 0218381 A1, 2005.

[23] A.G. MacDiarmid, D. Hill, Y.N. Xia and J.M. Wiesinger, Methods for preparing conductive, US Patent No.5403913, 1995.

[24] J. Stejskal and R.G. Gilbert, Polyaniline preparation of a conducting polymer, Pure Appl. Chem., 74(5) (2002) 857–867.

[25] S.A. Noding, S.J. Babinec and C.L. Scortichini, Process for preparing polyaniline, US Patent No. 5792830, 1998.

[26] M. Chakraborty, B.M. Mandal and D.C. Mukherjee, Oxidative degradation of polyaniline during the chemical oxidative polymerization of aniline in aqueous methanol medium, Polym. Int., 54 (2005) 1158–1162.

[27] W.J. Feast, J. Tsibouklis, K.L. Pouwer, L. Groenendaal and E.W. Meijer, Synthesis, processing and material properties of conjugated polymers, Polymer, 37(22) (1996) 5017–5047.

[28] G.G. Wallace, G.M. Spinks, L.A.P. Kane-Maguire and P.R. Teasdale, Properties of polyanilines, In: Conductive electroactive polymers : Intelligent polymer systems, 3rd edn., Taylor & Francis Group, New York, 2009.

[29] A.K. Mishra and P. Tandon, DFT study and heat capacity of polyaniline pernigraniline base, J. Chem. Phys., 113(29) (2009) 9702–9707.

[30] A.K. Mishra and P. Tandon, A comparative ab initio and DFT study of polyaniline leucoemeraldine base and its oligomers, J. Chem. Phys., 113(44) (2009) 14629–14639.

[31] R. Gangopadhyay, Exploring properties of Polyaniline—SDS dispersion: A rheological approach, J. Colloid Interface Sci., 338(2) (2009) 435–443.

[32] M. Chakraborty, D.C. Mukherjee and B.M. Mandal, Dispersion polymerization of aniline in different media: A UV-visible spectroscopic and kinetic study, Langmuir, 16(6) (2000) 2482–2488.

[33] A.A.M. Farag, A. Ashery and M. Abdel Rafea, Optical dispersion and electronic transition characterizations of spin coated polyaniline thin films, Synth. Met., 160(1,2) (2010) 156–161.

[34] R.A. Vera, B.H. Romero and Y.E. Ahumada, Synthesis and characterization of polyaniline and poly-ortho-methoxyaniline: Behaviour against carbon steel corrosion, J. Chil. Chem. Soc., 48(1) (2003) 35–40.

[35] D. Kim, J. Choi, J.Y. Kim, Y.K Han and D. Sohn, Size control of polyaniline nanoparticle by polymer surfactant, Macromolecules, 35 (2002) 5314–5316.

[36] A.K. Mishra, P. Tandon and V.D. Gupta, Vibrational dynamics of polyaniline pernigraniline base form: A conducting polymer, Macromol. Symp., 265 (2008) 111–123.

[37] H.J. Lee, B.D. Chin, S.M. Yang and O.O. Park, Surfactant effect on the stability and electrorheological properties of polyaniline particle suspension, J Colloid Interface Sci., 206 (1998) 424–438.

[38] B.D. Chin and O.O. Park, Dispersion stability and electrorheological properties of polyaniline particle suspensions stabilized by poly(vinyl methyl ether), J. Colloid Interface Sci., 234 (2001) 344–350.

[39] M. Schweinsberg, B. Mayer and W. Hater, Evaluation of Corrosion Inhibitors for Cooling Water by Physico-Chemical Methods, the European Corrosion Congress, Germany, 1999.

[40] N.K. Frank, Corrosion Control, In: The Nalco Water Handbook, 2nd ed., McGraw-Hill, New York, 1988.

[41] C. Frayne, Cooling Water Treatment Principles and Practice, Chemical Publishing Co., New York, 1999.

[42] D.A. Duke and J.L. Kubis, Cooling water scale and corrosion inhibitor, US Patent No. 6998092, 2006.