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Enhanced surface activity of activated carbon by surfactants synergism

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Activated carbon (AC) modification has been intensively studied in order to design carbon electrodes with enhanced electrochemical performance. Hexadecyltrimethylammonium bromide (HDTMA) and Tween 80 were employed for enhancing the surface activity of AC *via* synergism. The synergistic effects of the mixed surfactants on AC surface activity in the light of interface behaviors were studied. Both field emission scanning electron micrographs and FTIR spectra indicated a successful adsorption of loaded surfactants. AC gained a good wettability originated from the surfactants, especially in the binary mixture (T80-HDTMA). The zeta potential results unveiled the positive charge density enhancement in the mixed surfactants system. Isoelectric point and point of zero charge implicate heterogeneous distribution of charges and the extent of surfactants treatment. Tween 80 displayed a significant size control dependence on AC particles. Electrochemical characterization revealed a higher specific capacitance and a decaying resistance of specific capacitance in AC-T80-HDTMA than AC-HDTMA at high concentration. In 5 g L⁻¹ of NaCl, AC-T80-HDTMA (0.01 : 0.01 mM) exhibits the specific capacitance of 209.79 F g⁻¹, at 0.8 V whereas AC-HDTMA (0.01 mM) and AC exhibited 186.5 F g⁻¹, 178.9 F g⁻¹, respectively. Moreover, the stability testing reveals a strong attachment of HDTMA in AC-T80-HDTMA than AC-HDTMA with the loss of 0.32% and 1.32%, respectively. The hypothetical synergistic mechanism of surfactants adsorption on the surface of AC was depicted as hydrophobic interaction and steric stabilization being the main keys for the synergy between cationic and nonionic surfactants. This study demonstrates the beneficial effects of mixed surfactants on AC electrode properties and discloses the impact on electrochemical performance.

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1. Introduction

Activated carbon (AC) has been recognized as a good candidate in adsorption process due to having a high specific surface.¹ Noteworthy, AC has been a workhorse adsorbent for the removal of a wide variety of pollutants from wastewater. However, it is basically an inert porous material which binds pollutants mostly *via* van der Waals or London dispersion forces, thus it is unable to bind certain chemicals including metals and most inorganic materials.² Capacitive deionization (CDI) has become a promising technology that relies on electrosorption, for the removal of cationic and anionic pollutants from brackish water and seawater by means of the capacitive effect. AC is widely used as a CDI electrode material and AC modification has been a research hotspot for the sake of enhanced surface chemistry since the charges are indispensable in the process. In order to improve the surface activity of AC for specific applications, imparting the cationic or anionic

charges on the surface is a prerequisite, especially in inverted CDI. This approach makes AC more effective, hydrophilic and acidic or basic due to the nature of charges.

Surfactants have been widely reported to induce different properties on the surface of AC, due to their aggregation behavior at the interface. Both cationic and anionic surfactants have been employed in the functionalization of AC. Choi and coworkers investigated cationic surfactant-modified AC for Cr(vi) removal from aqueous solution.³ AC modified with sodium dodecylsulphate and sodium diethyl dithiocarbamate were used for heavy metals removal from industrial phosphoric acid.⁴ Moreover, AC modified with sodium diethyl dithiocarbamate was studied for the removal of Zn, Cu, Cr whereas tetrabutyl ammonium iodide employed for the removal of CN⁻ from wastewater.⁵ Furthermore, AC-acetyltrimethylammonium chloride was applied for bromated removal⁶ and cetylpyridinium chloride, cetyltrimethylammonium bromide, cetyltrimethylammonium chloride were also employed in AC modification.⁷ In addition, Shu *et al.* loaded cationic surfactants on AC for perchlorate adsorption.⁸ However, the mixed surfactants systems have been reported for more advantages (synergism) than a single surfactant system.⁹ Indeed, ionic-nonionic systems have been

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considered to offer more benefits over ionic-ionic or nonionic-nonionic systems.¹⁰

To date, the aggregation behavior of mixed surfactants in bulk solution and at interface has been investigated to enhance the performance and maintaining the stability. Many studies have been conducted on the mixed surfactants systems concerning their properties, adsorption and synergism.¹¹ To the best of our knowledge, the studies about the synergistic effects of mixed surfactants on the surface activity of AC for electrochemical application have never been reported in the literature. Basically, a high accessibility of solution on the surface of adsorbents in adsorption process is very essential. However, AC is highly hydrophobic, and thus surfactants play the role to induce a high wettability for the sake of efficient performance in aqueous media.¹² Furthermore, the dispersion medium has to wet the whole surface of the particles, including external and internal surfaces.¹³ Therefore, surfactants are always good candidate to enhance wettability and reduce surface tension. Noteworthy, ionic surfactants have been reported for a high pH sensitivity and poor dispersion, whereas nonionic surfactants are less sensitive to electrolyte pH and better dispersion which is attributed to their steric stabilization.¹⁴

Fic *et al.*¹⁵ reported a profitable effects of nonionic surfactant (Triton X-100) on electrochemical properties of carbon electrode which is in accordance with the results reported by Ghasemi and Ahmadi.¹⁶ Moreover, Somasundaran and coworkers¹⁷ reported an increasing of cationic surfactant adsorption at the alumina–water interface in the presence of nonionic surfactant below saturation. Notably, due to the weakness of hydrophobic interaction, the detachment of surfactants from functionalized electrodes has been a challenge on electrochemical performance. Palko *et al.* reported adsorption capacity reduction of nitrate ions (NO_3^-) due to the loss of cetyltrimethylammonium ions from functionalized AC electrode surface.¹⁸ Dejan and coworkers¹⁹ reported the synergistic effects of nonionic surfactants (Tween 80, Tween 20, Tween 60 and Triton X-100) with anionic surfactant on micellization. In essence, coulombic repulsion among ionic surfactants prompts them to occupy more surfaces which limit the amount to be adsorbed at interface. Consequently, a continuous detaching of ionic surfactants in adsorbed state results to the fading of cyclic stability specifically in electrochemical applications that depend on the surface chemical charges. In other words, the loss of surfactants attenuates the surface charge density associated with the decay of AC electrode performance.

Herein, a systematic study of the synergism between Tween 80 (T80) and hexadecyltrimethylammonium bromide (HDTMA) on the surface activity of AC for electrochemical application (capacitive deionization) was traced. Aggregation behaviors of a binary mixture (T80-HDTMA) and HDTMA were explored in the light of interfacial properties characterization. The benefits of Tween 80 as a co-surfactant on the applications of AC functionalized with cationic surfactants were established. This research provides a novel electrode with potential application for inverted CDI. Furthermore, it sheds light on the beneficial impact of surfactants mixture on the surface activity of AC than a single surfactant. The synergistic effects of mixed surfactants

cannot only improve specific capacitance but also induce the stability of HDTMA in adsorbed state. Notably, nonionic surfactants are biodegradable and less toxic than cationic surfactants. The possible conformations illustrated in the last section of this work, indicate increased adsorption density and strong attachment of HDTMA in the presence of Tween 80 due to the fact that the steric stabilization, surfactant–surfactant lateral interaction and surfactant-AC hydrophobic interactions.

2. Experimental

2.1 Materials

Activated carbon (AC, YEC-8A) was obtained from Fuzhou Yihuan Carbon Ltd, China. Carbon black (VXC-72) was purchased from Cabot Corporation, U.S. cationic surfactant (HDTMA) nonionic surfactant (Tween 80) and *N*-methyl kelopyrrolidide (NMP) were purchased from Tianjin Yuanli Chemical Ltd, China. Polyvinylidene fluoride (PVDF, Kynar HSV 900) was obtained from Arkema, France. All analytical solutions were prepared with Milli-Q water.

2.2 Activated carbon modification

Stock solutions of cationic surfactant (HDTMA) and nonionic surfactant (Tween 80) were prepared at 10 mM and 0.01 mM respectively. 3 g of AC were added to 150 mL of HDTMA solutions (0.01, 0.7, 5, 10 mM) for adsorption. The binary mixture adsorption of HDTMA with Tween 80 was carried out sequentially and non-sequentially. For sequential adsorption 3 g of AC was added to 37.5 mL of Tween 80 solution (0.01 mM) under sonication for 2 h and dried in oven for 24 h at 70 °C. Then 150 mL of HDTMA solution was added and agitated at 170 rpm on shaker for 48 h. For non-sequential adsorption a molar fraction of 4 : 1 of HDTMA and Tween 80 for each concentration was added on 3 g of AC and then agitated on a shaker at 170 rpm for 48 h, similarly to the HDTMA system. The suspensions were filtrated, and the modified AC was dried in oven for 24 h at 70 °C. The amount of HDTMA loaded on AC was calculated from the difference between initial concentration and concentration in the filtrate. The virgin activated carbon was named AC, whereas modified activated carbon denoted AC-S. AC modified by HDTMA was named AC-HDTMA and AC modified by the binary mixture was named AC-T80-HDTMA.

2.3 Characterization

Both AC and AC-S were characterized by field emission scanning electron microscope (FE-SEM), Fourier transform infrared spectroscopy (FTIR). Wettability was evaluated by contact angle measurement. Zeta potential and isoelectric points were determined with Zetasizer. The point of zero charge was determined by drift method. The amount of cationic surfactant adsorbed and the stability on the adsorbent surface was estimated by two phase titration method. The particles size distribution was analyzed with Laser Particle Sizer. Specific capacitance and cyclic stability were determined by cyclic voltammetry (CV).

2.3.1 FE-SEM. Field emission scanning electron microscopy (S-4800, Hitachi, Japan) was used to analyze the surface



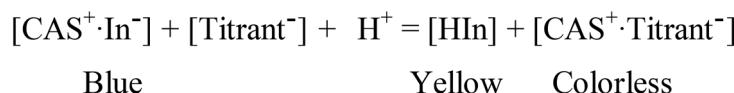
physical morphology and qualitative characteristics of both AC and AC-S. Before FE-SEM analysis, the specimens were sprayed with gold.

2.3.2 FTIR. Fourier transform infrared spectroscopy (FTIR-650, Guangdong, China) analysis was performed in the range of 400–4000 cm^{-1} . Transmission spectra of sample were recorded with applying KBr pellets technique (0.7% sample).

2.3.3 Contact angle. Wettability was evaluated by direct measurement of the contact angle with a conventional telescope-goniometer (CA-100C, Shanghai Zhenghong Instrument Co., Ltd, China). A slides-glass coated with both AC and AC-S samples were prepared. The contact angle formed by a drop of water resting on the surface to be tested was measured. A micrometer syringe was placed above the rotating specimen holder, and a drop of water expelled on the testing

2.3.6 Cationic surfactant titration and stability testing.

Quantitative analysis of HDTMA adsorption onto AC was performed with two phase titration method.²¹ A portion of filtrate was taken from each suspension after adsorption. The analyte for binary mixture was taken from the sample prepared sequentially in order to avoid interference of Tween 80. 10 mL of filtrate, 5 mL of phosphate buffer solution, 1 drop of tetrabromophenolphthalein ethyl ester indicator and 1.5 mL of 1,2-dichloroethane were mixed in a 150 mL flask and Milli-Q water was added to a total volume of 20 mL. The mixture was titrated with tetraphenylborate solution (5×10^{-2} mM) under intermittent shaking to ensure equilibrium between the aqueous and organic phases. The cationic surfactant loaded onto AC was calculated based on the difference between initial concentration and the concentration in filtrate.



surface. The measurements were repeated several times for both advancing and receding contact angle. First the advancing contact angle was measured by expelling the droplet of water through a microsyringe, and then the receding contact angle was measured by using the microsyringe to reduce the droplet volume for angle hysteresis assessment. For each measurement a new part of the surface was used.

2.3.4 Zeta potential (ζ) and isoelectric point (IEP). In order to investigate the surface charge density, zeta potential (ζ) was measured under different electrolytes (NaCl and Al(NO₃)₃) by a Zetasizer (Nano ZS, Malvern, United Kingdom). 50 mg of AC, AC-HDTMA (0.7 mM) and AC-T80-HDTMA (0.01/0.7 mM) were taken into 250 mL of electrolyte solutions with the same ionic strength (0.001 M). The mixtures were agitated on shaker at 170 rpm for 6 h, and then kept 15 min for sedimentation of big particles. Aliquots for measurements were taken under nitrogen at different pH. The reading of each sample placed in electrophoresis cell was taken three times and their average was determined. The pH at which ζ -potential is zero was considered as isoelectric point (IEP).

2.3.5 The point of zero charge (pH_{PZC}). The point of zero charge (pH_{PZC}) of AC, AC-HDTMA and AC-T80-HDTMA was determined following drift method.²⁰ A solution of 0.01 M NaCl was made and bubbled with nitrogen gas to expel dissolved carbon dioxide. 50 mL of the solution was added to a series of beakers (100 mL), and pH was adjusted with HCl and NaOH in the range of 2 to 12. 150 mg of adsorbents was added in each beaker. The suspensions were agitated for 48 h at 250 rpm. Then the samples were filtrated and the final pH was measured. The pH difference (Δ pH) between final pH (pH_f) and initial pH (pH_i) was plotted *versus* initial pH (pH_i), the point at which Δ pH equal to zero was considered to be the pH_{PZC}.

The stability of cationic surfactant (HDTMA) on the surface of adsorbent was tested after CV (1000 cycles). Electrolytes were titrated by two phase titration method as described above. The amount of HDTMA detached from electrodes was calculated and converted into the loss (%).

2.3.7 Particle size analysis. The particle size distribution of AC powder in different dispersant liquids was analyzed with a Laser Particle Size Analyzer (BT-9300ST, Dandong Bettersize, China). 0.05 g of AC was placed in a series of beakers and 100 mL of dispersants liquid were added. All samples were prepared under sonication and the measurement for Tween 80 and HDTMA were taken at different concentration.

2.3.8 Electrochemical measurement. Electrochemical characterization was conducted on a three-electrode system through cyclic voltammetry (CV) with a potentiostat (CHI660E, Shanghai Chenhua, China). Standard calomel electrode was employed as reference electrode. The working and counter electrodes were prepared by mixing AC or AC-S with carbon black and PVDF in the ratio of 8 : 1 : 1 respectively in NMP as solvent in order to get slurry of mixed solids. The slurry was coated on graphite-foil as current collectors and dried in oven at 70 °C for 24 h. CV curves were recorded in the potential window range between –0.4 to +0.4 V with a scan rate of 0.01 mV s^{–1}. All fabricated electrodes were tested in NaCl (5 g L^{–1}) solution as electrolyte. Capacitance was calculated from the CV curves according to the following expression:²²

$$C = \frac{S}{2v\Delta V} \quad (1)$$

where C is capacitance, S is the area of CV curve, v is the scan rate and ΔV is the voltage range.

3. Results and discussion

3.1 Morphology and interfacial characterization

The FE-SEM images in the Fig. 1 displays different morphologies between AC and AC-S (AC-HDTMA and AC-T80-HDTMA). The image of pristine AC in Fig. 1a shows roughness and macropores on the surface, whereas AC-S looks smooth on its surface with a layer of surfactants. Furthermore, the AC-T80-HDTMA sample in Fig. 1c shows a highly smooth surface and highly saturated with surfactants layer than AC-HDTMA sample in Fig. 1b. All these observations implicate effectiveness interaction between surfactants and AC surface *via* hydrophobic interaction.

The comparison of IR spectra of AC and AC-S in Fig. 2 shows the difference in both fingerprint and functional group regions. The wide band in the range of 3400–3500 cm^{-1} derive from the stretching mode of hydroxyl groups $-\text{OH}$ (3450 cm^{-1}).²³ The peaks in the range of 2700–3000 cm^{-1} can be attributed to the C–H bending vibration.²⁴ Two peaks at 2870 and 2930 cm^{-1} , associated with the anti-symmetric and symmetric stretching vibration of CH_2 from HDTMA chain.²⁵ The band in the region 1600–1750 cm^{-1} can be assigned to $\text{C}=\text{O}$ group.²⁶ The peaks in the range of 1250–1500 cm^{-1} can be assigned to C–H bending of CH_3R (1389 cm^{-1}) and CH_3N (1430 cm^{-1}) stretching.²⁵ The band at 1150 cm^{-1} is associated with ether $-\text{C}=\text{O}-$ symmetric and asymmetric stretching vibration of $-\text{C}=\text{O}-\text{C}-$ ring in Tween 80.^{27,28} The broad peaks in the range of 500–750 cm^{-1} correspond to CH_2 rocking (719 cm^{-1})²⁹ and C–O stretching.²⁴ The band at 488 cm^{-1} can be attributed to the anti-symmetric bending mode of the quaternary (alkyl) mode of the head of the methyl group $(\text{CH}_3)_3\text{N}^+$ in HDTMA.^{25,30}

The contact angle measurement revealed the wetting behavior, the change of hydrophobic and hydrophilic intensity of both AC and AC-S. Both advancing and receding contact angles have shown similar trend on the surface wettability. The values of contact angles revealed the order of wettability, AC-T80-HDTMA > AC-HDTMA > AC in Fig. 3. A high alteration of AC-T80-HDTMA wettability can be attributed to Tween 80 which has been reported for a high wetting power. Graca *et al.*³¹ reported the similar result for hydrophobic surface ($\theta > 110^\circ$) modification with Tween 80, the values decrease to 70° and 60° at 0.01 and 0.1 mM, respectively. Furthermore, Kumar with

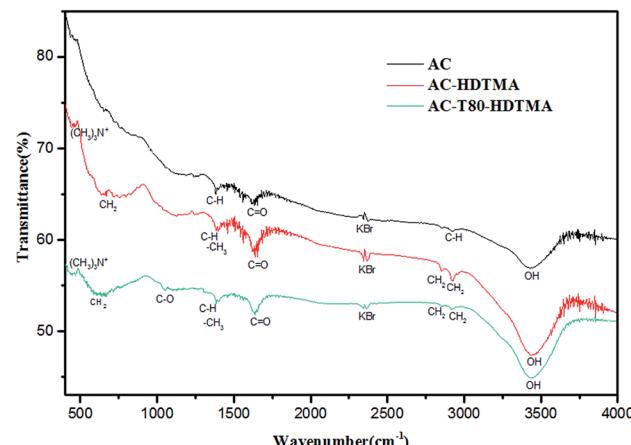


Fig. 2 FTIR transmission spectra of AC, AC-HDTMA and AC-T80-HDTMA.

coworkers³² reported a significant alteration of wettability on a carbonate surface modified with quaternary ammonium surfactants.

3.2 Zeta potential and point of zero charge

The ζ -potential of AC and AC-S at different pH is shown in Fig. 4. Based on the variation of ζ -potential, the surfactants rendered the surface of AC more positively charged. The shift of ζ -potential to more positive region can be attributed to the high adsorption of HDTMA due to the effect of co-surfactant (Tween 80). This result is in accordance with the previous works⁹ that adsorption of cationic surfactant increases due to the presence of nonionic surfactant which reduces repulsion between cationic head groups *via* shielding. A similar result was reported by Curbelo *et al.*³³ for enhanced adsorption of ionic surfactants in the presence of nonionic surfactants and *vice versa*. A significant increasing of ζ -potential in AC-S can be attributed to the dissociation of HDTMA. Xu *et al.*³⁴ reported a significant increasing of ζ -potential at pH > 4 for granular AC coated with cationic surfactant (CTAC), due to the CTA^+ dissociation from CTAC. Similarly, HDTMA as a strong acid cationic surfactant can be positively ionized at pH close to neutral range.³⁵

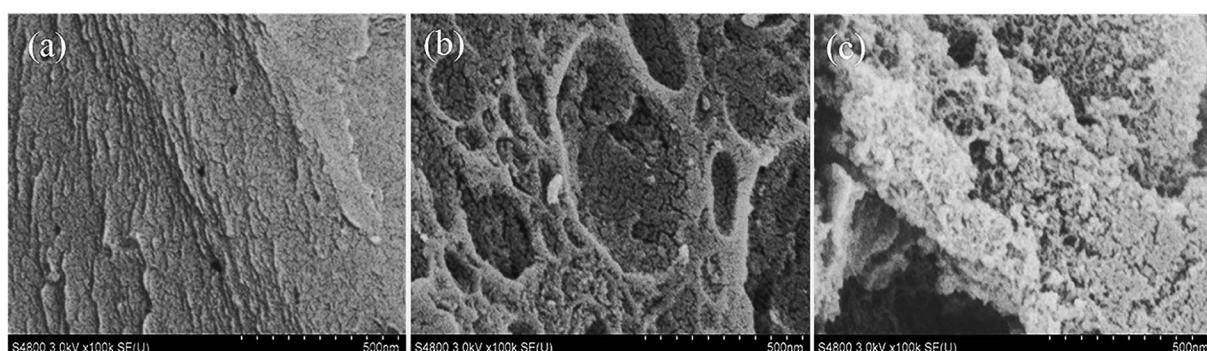


Fig. 1 Scanning electron microscopy images: (a) AC, (b) AC-HDTMA, (c) AC-T80-HDTMA.





Fig. 3 Contact angle formed by water droplets on (a) AC: $\theta = 124.63^\circ \pm 3.1$, (b) AC-HDTMA: $\theta = 87.47^\circ \pm 2.7$, (c) AC-T80-HDTMA: $\theta = 76.61^\circ \pm 2.9$.

The ζ -potential dependence on pH of AC-T80-HDTMA was less significant than AC-HDTMA and the reason might be the less pH sensitivity of Tween 80. Furthermore, the ζ -potential of AC shown in Fig. 4a displayed a very negative zeta potential than AC-S (AC-HDTMA and AC-T80-HDTMA). AC-S has shown the shifting of zeta potential from negative to positive direction, indicating the increasing of surface positive charges originated from HDTMA. The shifting of zeta potential from negative toward positive direction in AC-T80-HDTMA is relatively higher than AC-HDTMA, which implicates more surface charges (more HDTMA adsorbed) in AC-T80-HDTMA than AC-HDTMA. Nevertheless, the net surface charge has remained in negative region, and this can be attributed to the usage of low concentration. At low HDTMA concentration, ζ -potential of AC-S stays negative and becomes progressively positive with increasing of concentration.³⁵ The relation between ζ -potential, surface charge density and the valence of electrolyte ion could be stated in the following equations.³⁶

$$\sigma = \pm \left[\frac{kT\epsilon}{2\pi} \right]^{1/2} \left\{ \sum_i n_i \left[\exp\left(-\frac{Z_i e \zeta}{kT}\right) - 1 \right] \right\}^{1/2} \quad (2)$$

where σ is surface charge density, ϵ is dielectric constant, e is electron charge, k is Boltzmann constant and T is the temperature. n_i and Z_i are the ion number per unit liquid and the valence of ions, respectively.

$$\frac{1}{k} = \frac{3}{ZC^{1/2}} \quad (3)$$

where $1/k$ is the diffuse layer thickness in Angstrom (\AA), Z , C denote the valence and concentration, respectively.

The ζ -potential can be indicator of the surface charge density. Low ζ -potential indicates less surface charges, whereas

high ζ -potential indicates more charges on the surface of particles, which is in agreement with eqn (2). The increase of ζ -potential after modification indicates augmentation of positive charges on the surface. HDTMA imparts the positive charge on AC surface, thus resulting in increased charges density. Fig. 4b shows the trend of ζ -potential in $\text{Al}(\text{NO}_3)_3$ electrolyte where it became highly positive. The high positive ζ -potential can be attributed to the effect of Al^{3+} ions on electrical double layer (EDL). The type of cations in electrolyte holds influence on the variation ζ -potential. Monovalent cations yield more negative ζ -potential than divalent cations whereas trivalent cations yield more positive ζ -potential than divalent.³⁷ According to eqn (3) multivalence cation (Al^{3+}) exerts a significant influence on ζ -potential. Indeed, a solution with the same molarity and constant surface charge, a change of cation valence affects not only the ζ -potential but also the thickness of the EDL.³⁸ The ζ -potential becomes positive due to the specific adsorption of Al^{3+} counter ions in the Inner Helmholtz Plane (IHP) of the stern layer.³⁹ At low pH range of AC suspensions, Al^{3+} ions are in the non-hydroxyl form, while they can form hydroxyl complexes such as $\text{Al}(\text{OH})^+$, $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_3$ at low concentration or with increasing pH.⁴⁰ As a consequence, hydroxylated aluminum cations lead to a decreasing of ζ -potential at low and high pH range, while the highest ζ -potential observed in the range close to neutral pH.

Isoelectric point (IEP) and point of zero charge (pH_{PZC}) are important parameters in studies of chemical and electrochemical surface properties of adsorbents. According to electrochemical characterization of AC, IEP value has been suggested as the only representative of the external surface charges of carbon particles in the solution, whereas the pH_{PZC} varies to the net total of internal and external surface charges of

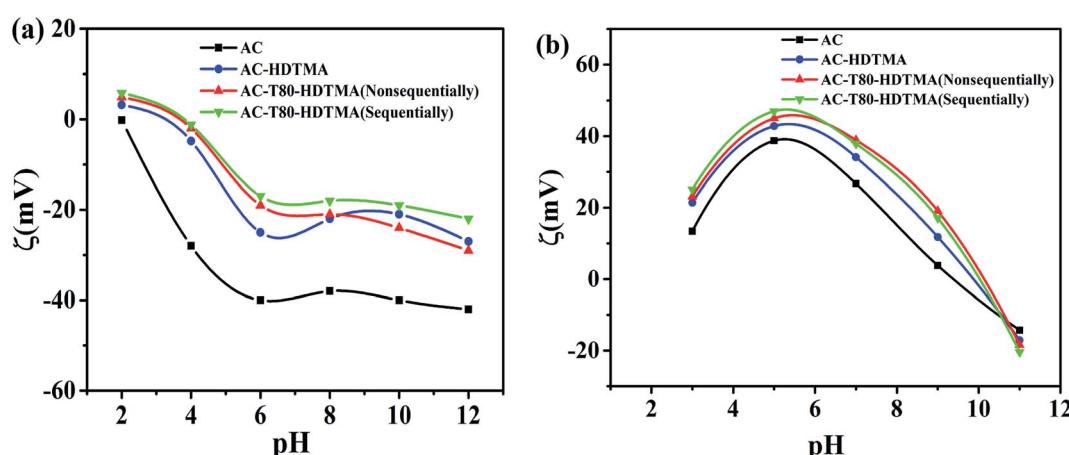


Fig. 4 The variation of ζ -potential (a) in 0.001 M NaCl , (b) in 0.001 M $\text{Al}(\text{NO}_3)_3$.



the particles.^{41–43} The difference ($\text{pH}_{\text{PZC}}\text{--IEP}$) could be interpreted as a measure of the charge distribution on the surface.⁴¹ The values greater than zero indicates that the particle is more negatively charged on external than internal, whereas the values close to zero indicate homogeneity distribution of the surface charges.⁴¹ IEP and pH_{PZC} values of AC and AC-S in the Fig. 4a and 5 are shown in the Table 1. pH_{PZC} increasing after modification indicates augmentation of positive charges density imparted by cationic surfactants. The differences of $\text{pH}_{\text{PZC}}\text{--IEP}$ values of AC-S indicate that the treatment of original AC with surfactants has affected the surface at different extents. Moreover, the mixed surfactants render AC to the higher pH_{PZC} than single surfactant, which make AC-T80-HDTMA relatively a better adsorbent than AC-HDTMA. Song *et al.*⁴³ reported a similar interpretation for surface modification of coconut-based AC, where modified AC with a high pH_{PZC} exhibited the highest positive ζ -potential. In addition, the increase of pH_{PZC} for modified AC induces acidic behavior. The protons release becomes beneficial for cationic adsorption near neutral pH. Contrarily a low pH_{PZC} of virgin AC induces basic behavior near neutral pH thereby readily adsorb protons which compete with cations during adsorption.

3.3 Cationic surfactant titration and stability test

Cationic surfactant titration and stability testing data are summarized in Table 2. 2 wt% of AC, HDTMA (0.7 mM) and T80-HDTMA prepared sequentially with Tween 80 (0.01 mM). Cationic titration shows a very high adsorption of HDTMA in both AC-HDTMA (91%) and T80-HDTMA (98%). Although the levels of adsorption are close to each other, further adsorption of HDTMA in the AC-T80-HDTMA formulation was observed beyond Critical Micelle Concentration (CMC, HDTMA-CMC = 0.9 mM and Tween 80-CMC = 0.015 mM). This additional adsorption in the mixed system can be attributed to the effect of Tween 80, where steric stabilization bestows a free space prompted for adsorbing more HDTMA. Somasundaran *et al.* disclosed a continuous adsorption of surfactants mixture at the interface even above the CMC.⁹

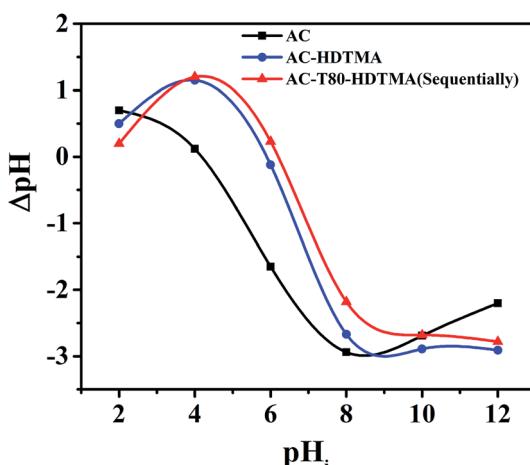


Fig. 5 pH_{PZC} of AC and AC-S in 0.01 M of NaCl.

Table 1 pH_{PZC} and IEP of AC and AC-S

Type of adsorbent	pH_{pzc}	IEP	$\text{pH}_{\text{pzc}}\text{--IEP}$
AC	4.2	1.98	2.22
AC-HDTMA	5.9	3.3	2.6
AC-T80-HDTMA	6.3	3.9	2.4

The loss of cationic surfactant during cyclic voltammetry reveals the level of HDTMA stability on the solid surface. The low loss (0.32%) in mixed surfactants indicates a high attachment of HDTMA on the surface of functionalized AC in the presence of Tween 80. Contrarily, a relatively high loss (1.32%) of HDTMA indicates a low stability on the surface of adsorbent. A better packing of ionic with nonionic surfactants mixture at interface, brings more advantages apart from steric stabilization and adsorption density. Both HDTMA and Tween 80 have a very long hydrophobic chain tail (very low inductive effect) with 16C and 18C, respectively. Therefore chain-chain lateral interaction and chain tail-activated carbon interaction induce a strong hydrophobic interaction.

The lateral chain-chain interaction between surfactants on interface, results into surfactants clusters formation at the interface.⁴⁴ Qun *et al.*⁴⁵ suggested the chain-chain interaction between surfactants in adsorbed state as the main cause for synergism. Electrochemical characterization, specifically the cycling stability has been reported in many literatures for nonionic surfactants.^{15,16,45} A high stability in AC-T80-HDTMA formulation can be also attributed to the favorable packing of surfactants in adsorbed films, due to the dissimilarity and large difference in size, between the head groups of HDTMA and Tween 80.⁴⁷ Furthermore, the presence of two sp^2 hybridized C-atoms in the chain tail of Tween 80 can involve in the synergism. This weak dipole can polarize hydrocarbon chains of co-surfactants, generating a weak induced dipole.¹⁹ This electrostatic attractive interaction between induced dipole and dipole contribute to the high stability and synergy in general.

3.4 Particle size distribution

The comparative effects of dispersant liquids (Tween 80, HDTMA and Water) on AC particles size are shown in Fig. 6. Tween 80 solution provides a highly dispersed suspension with a remarkable size decrease of the particles. In Fig. 6a, the modes of the particle size distribution were found in the regions 6.7–11 μm , 11.2–18.25 μm and 12.8–21.48 μm for 0.1, 0.01 and 1 mM Tween 80, respectively. Insufficient or too much concentration might impede solid dispersion or increase particles size *via* agglomeration; hence the proper concentration is critical. Guo *et al.*⁴⁸ reported the particle size of ultra-fine powders in aqueous media decreases with the increase of SDS concentration, then increases with further concentration increasing. The size increasing was attributed to the binding of surfactant molecules on the fully occupied particle surface through hydrophobic interaction beyond equilibrium adsorption capacity, which causes agglomeration of the particles. In Fig. 6b, the mode was found in the regions 33.8–42.15, 42.15–

Table 2 Analytical data for HDTMA titration after AC modification and after CV

	AC-T80-HDTMA	AC-HDTMA
Initial concentration (C_i)	0.7 mM	0.7 mM
Number of moles in solutions	0.105 mmol	105 mmol
Concentration of filtrate after adsorption	1.95×10^{-3} mM	3.07×10^{-3} mM
Number of moles adsorbed	0.103 mmol	0.095 mmol
Adsorption (%)	98%	91%
Number of moles in electrode before CV	1.55×10^{-3} mmol	1.06×10^{-3} mmol
Concentration in electrolyte after CV	2.5×10^{-5} mM	7×10^{-5} mM
Number of moles in electrolyte after CV	5×10^{-6} mmol	1.4×10^{-5} mmol
Loss (%)	0.32%	1.32%

67.4 and 47.3–75 μm at 10, 1 and 0.1 mM HDTMA, respectively, which are larger than the ones from Fig. 6a. The comparative effects of dispersant liquids (Tween 80, HDTMA and water) are shown in Fig. 6c, where water and HDTMA displayed the mode with big particle (34–78.5 μm) while Tween 80 displayed small particles (11–21 μm). The size distribution under sonication with time was also investigated in Fig. 6d. 90–120 min was found as the optimal time for dispersion process. Small particles are highly required for effective adsorption. However, AC powder particles and clumps always tend to stuck together to

form agglomerates and aggregates. A well dispersed suspension is critical in order to get individual particles in stable state. One of the goals of using Tween 80 is to keep particles apart and this barrier to agglomeration makes adsorption of HDTMA more effective. Obviously, Tween 80 does not only disperse particles but also downsizes agglomerates by inducing steric barrier which expands the surface for adsorption.

Tween 80 is well known for a high Hydrophilic–Lipophilic Balance (HLB) and has been widely used as dispersant and stabilizing agent. Suchomel *et al.*⁴⁹ applied Tween 80 for simple

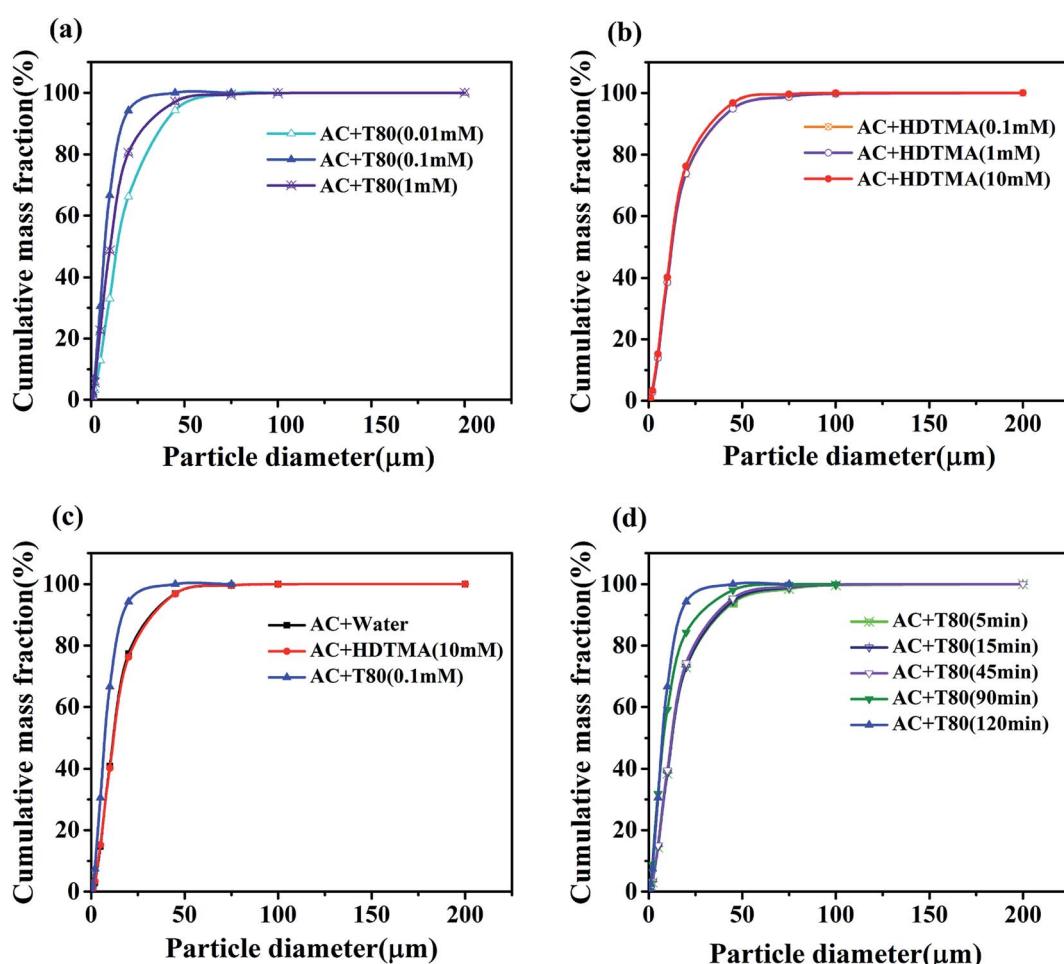


Fig. 6 Particle size distribution of AC (a) as function of Tween 80 concentration, (b) as function of HDTMA concentration, (c) as function of Water, HDTMA and Tween 80, (d) as function of sonication time (0.1 mM of Tween 80).

size-controlled synthesis of nanoparticles. This class of surface acting agents acts as stabilizing agents by inducing steric stabilization. Steric stabilization is the presence of physical barriers on particles that prevent them from coming close enough to allow the van der Waals attractive forces among particles to dominate.⁵⁰ The conformation of surfactants at the moment when adsorbed on the surface is controlled by both solution-surfactants and particles-surfactants interaction. The increasing of closeness between particles in order to minimize van der Waals attraction forces is the key for steric stabilization.^{51,52} The presence of stabilizing agents reduces attraction at the closest distance among particles and hence the prevention of agglomeration makes the manipulation of particles easily under steric stabilization dominance. Dispersion of solids in the liquid can be stabilized by steric barriers in the presence or absence of electrical barriers. Tadros⁵¹ reported two effect of steric stabilization: (1) mixing effect and (2) entropic effect. These forces supply the repulsive barrier that prevents particle agglomeration in such sterically stabilized systems. Although ionic surfactants act as stabilizing agents *via* electrostatic stabilization, steric stabilization has more advantages over electrostatic stabilization. Steric stabilization has low sensitivity on high concentration of electrolytes, low viscosities for high solids dispersions and is equally effective in aqueous and non-aqueous media.⁵³

3.5 Electrochemical characterization

Fig. 7 shows the specific capacitance (F g^{-1}) of AC and AC-S at different concentrations of surfactants. At low concentration (less than CMC), electrodes display improved specific capacitance. This enhancement can be attributed to the stable porosity and good wettability that can induce a high usable surface area and lower internal resistance of carbon electrodes, which is in accord with the work of Fang *et al.*⁵⁴ Similarly, Tamborini *et al.*⁵⁵ assigned surfactants as porosity stabilizer in porous carbons. Furthermore, Zhang *et al.*⁴⁶ disclosed the impact of optimal concentration of CTAB on the surface and pore size of carbon electrode, associated with the high capacitance, cyclic stability and low resistance. Fig. 7a shows the

variation in specific capacitance of AC modified with various concentrations at a voltage of 0.8 V. The specific capacitance of AC was 178.9 F g^{-1} , while AC-HDTMA, AC-T80-HDTMA displayed 186.5 and 209.79 F g^{-1} respectively (at 0.01 mM).

Noteworthy, T80-HDTMA displays more wetting power than HDTMA. The decreasing of the surface tension on interface allows a better penetration of electrolyte into the pores. Furthermore, the effect of Tween 80 on size distribution of AC particles contribute to the specific capacitance improvement. Basically, nonionic surfactants hold a remarkable detachment ability on powdered particles from parent agglomerates. Consequently, the formation of individual particles or smaller agglomerates generate a high surface with more adsorption sites. In Fig. 7b, AC-T80-HDTMA displayed better cycling stability than AC-HDTMA. The mixed surfactants can be accredited to maintain porosity of AC than a single cationic surfactant. Ghasemi and Ahmadi¹⁶ investigated the effect of nonionic and ionic surfactant on capacitive behavior on nanocomposites. Notably, nonionic surfactant induced the highest capacitance improvement and excellent cycling stability. Also, nonionic surfactant have been reported for their beneficial effects not only on charge propagation but also on electrode voltage window. In addition, Akinori *et al.* delineated improvement of capacitance with addition of surfactants to an aqueous electrolyte.⁵⁶

In a sense, a radical improvement of EDL specific capacitance was ascribed to the effective access of electrolyte the inner surface of electrode micropores. However a progressive decreasing of specific capacitance at high concentration ($>\text{CMC}$) was observed. The capacitance decaying can be attributed to the reduced specific surface area and pore volume covered by micelles, where the micelles formation makes the access of electrolyte to the pore more difficult. Moreover, the excess surfactants molecules in the pores causes retardation of ions transport and decreasing of usable surface. Despite of the decreasing of specific capacitance at high concentration, the T80-HDTMA has shown a resistance on diminishing of capacitance compared with HDTMA due to the reasons mentioned previously.

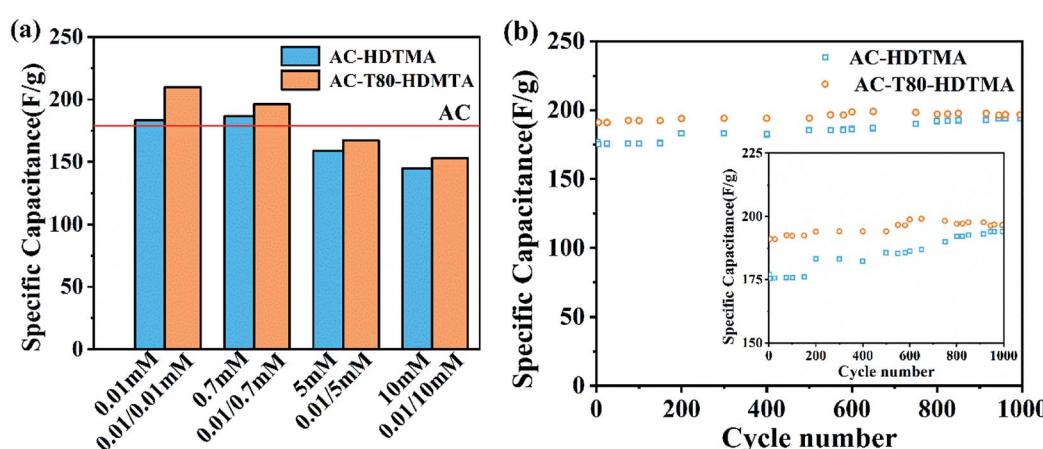


Fig. 7 The influence of surfactants on (a) specific capacitance, (b) cyclic stability testing.

4. Mechanism of Tween 80 and HDTMA synergism

The synergism between ionic and nonionic surfactants can be explained in the light of their thermodynamic alternative arrangement in solution or at interface.⁵⁷ Unlike nonionic surfactants, ionic surfactants solvation in water is always limited by coulombic repulsion force that rises from head groups with similar charges. A similar situation occurs during adsorption on interface, where coulombic repulsion dominates the surfactants arrangement mechanism which causes molecules to stay away from each other. Nonionic surfactants mixed with ionic surfactants have been widely reported to avert coulombic repulsion *via* steric hindrance, which brings ionic surfactant molecules close to each other. Adsorption density of cationic surfactant increases, due to the presence of nonionic surfactant which reduces the repulsion between cationic head groups *via* shielding was reported as the main cause. A high surface activity of nonionic surfactants and hydrophobic interaction with ionic surfactants are considered to be the main factors for entropic effect in the mixture.⁴⁴

Basically, the synergism between ionic and nonionic surfactants can lead to increased adsorption of ionic surfactants.³³ Indeed, adsorption tests have proved reinforcement between ionic and nonionic surfactants in the mixed system. Moreover, they may also force each other to adsorb at interface, even when an individual adsorption could not occur.³³ Steric effect of nonionic surfactant can be regarded as one of the main keys for the stability and enhanced adsorption density of ionic surfactants at interface. Naturally, surfactants are amphiphilic molecules with both polar region (hydrophilic head) and nonpolar region (hydrophobic tail). Hence, their aggregation behaviors in solution result to the different conformations. Hydrophilic group is favorable to associate with water molecules whereas hydrophobic tail is thermodynamically unfavorable to associate with water molecules. Rulison⁵⁷ reported a thermodynamic conflict which perpetually rises in the water with regard to surfactants, where he described the interaction of water molecules with hydrophilic group, as the most favorable solution for that conflict.

The orientation of surfactants at interface originates from heterogeneity of their molecules. Since AC is highly hydrophobic, the hydrophobic parts of surfactant molecules, under the control of entropic and enthalpic favorability are forced to associate with AC surface. Knowing that, the mechanisms of HDTMA and Tween 80 arrangement on the surface of AC particles in suspension have been proposed in Fig. 8 that portrays adsorption of surfactants on AC particles. Graca *et al.*³¹ disclosed the mechanism of aggregational behavior of Tween surfactants at interface, wherein alkyl chains adsorb at the hydrophobic surface whereas the ethylene oxide head groups oriented into the water solution. Fig. 8a shows the hypothetical arrangement of HDTMA under coulombic repulsion control. HDTMA molecules tend to occupy the sites far from each other on the surface of AC particles in order to minimize coulombic repulsion force among their head groups with the same

charges. Fig. 8b displays a distinct arrangement of HDTMA with Tween 80 in a binary system. Tween 80 induces a steric hindrance that quenches coulombic repulsion among head groups of cationic surfactant molecules. HDTMA molecules come close to each other thus a free space is prompted to adsorb additional HDTMA molecules.

The aggregation of surfactants on the solids surface has the similar analogy to aggregation in the bulk solution. Gangula *et al.* reported admicelles and hemimicelles as new investigated phenomena of surfactants adsorption on the solid surface.⁵⁸ The formation of the bilayer, which is analogue to the micelles in bulk solution, on the solid surface during adsorption was coined admicelle and a monolayer formation was, coined hemimicelle. It is well known that micelles formation occurs at CMC. On the contrary, admicelle occurs when surfactant concentration is less than CMC.⁵⁸ The formation of admicelles and hemimicelles on the surface, depends on different parameters, including surfactants concentration, electrolyte type and concentration, adsorbents pH and surface chemistry.^{13,59,60}

The proposed mode of adsorption in Fig. 8c, depicts the interactions of AC sites with a mixed solution of Tween 80 and HDTMA at concentration close to CMC. In Fig. 8c hydrophobic chains of both cationic and nonionic surfactants interact with AC *via* hydrophobic interaction, and chain-chain lateral interaction among surfactants in adsorbed state. At high concentration, the surface becomes saturated and hence the occurrence of admicelles formation takes place. The excess cationic surfactants start to penetrate the monolayer of surfactants in adsorbed state. In fact, AC has dual nature for adsorbing both non polar and polar compounds, thus the mechanism of adsorption leads to different orientation of surfactants on the surface. Both hydrophobic tail and hydrophilic head might interact with AC, either by hydrophobic interaction (dominant), or dispersion forces. In the Fig. 8d, both HDTMA and Tween 80 molecules may take different orientations depending on the AC sites they interact with. The formation of the second layer might be originated from hydrophobic interaction between surfactants with opposite orientation, or the penetration into the monolayer to form a mixed conformation.

AC modified with surfactants hold potential application in electrosorption process, where surface charges and wettability play a significant role. AC electrodes functionalized with ionic surfactants have recently attracted considerable attention in capacitive deionization technology (CDI), specifically inverted capacitive deionization system. Fig. 9 shows adsorption of anions on AC modified with a binary mixture of Tween 80 and HDTMA. The presence of Tween 80 shows enhanced adsorption density of HDTMA, in the perfect packing (high stability) which are both worthy in electrosorption process. Indeed, enhanced adsorption density of HDTMA induces a high adsorption capacity of anion pollutants. Moreover, improved packing imparts the stability of surfactants on the surface. These peculiar effects are among the ultimate goals of mixed surfactants system application for the sake of enhanced surface activity of AC, which could never, occurs for a single surfactant system.



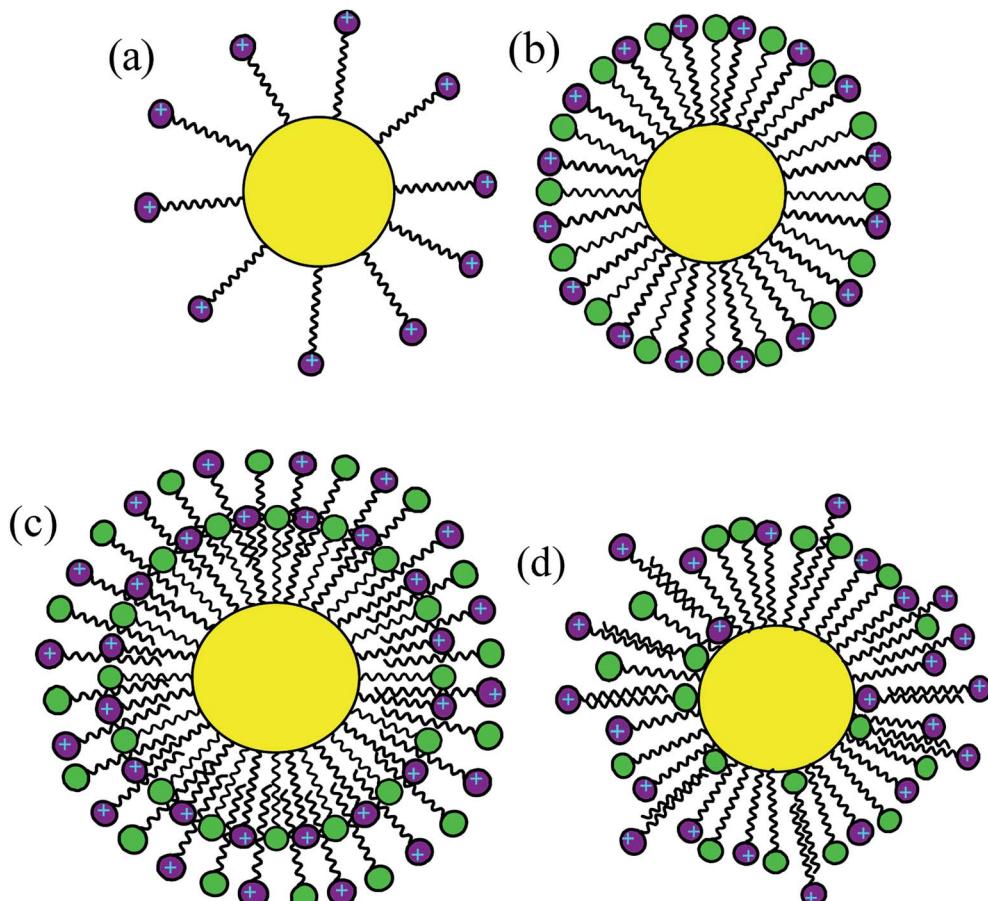


Fig. 8 The arrangement of (a) HDTMA, (b) T80-HDTMA on the surface of AC particle in the form of monolayer (hemimicelle) at low concentration, (c) penetrated, (d) mixed bilayer (admicelle) at high concentration.

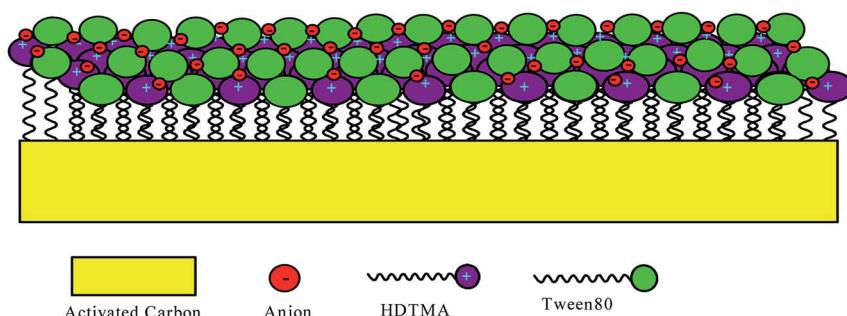


Fig. 9 Adsorption of anions on functionalized AC electrode.

5. Conclusion

A well-designed surfactants mixture can enhance physical/chemical and electrochemical properties of AC electrode to the level a single surfactant cannot reach individually. The Tween 80 and HDTMA mixed system revealed tremendous benefits over HDTMA system in this study. AC gained a good wettability due to the effect of Tween 80 which is very crucial in adsorption process. Cationic titration in the AC-T80-HDTMA formulation treated sequentially, revealed enhanced adsorption density of HDTMA. Furthermore, zeta potential values

unveiled more positive charge density for AC treated with mixed surfactants than single surfactant. Isoelectric point (IEP) and the point of zero charge (pH_{PZC}) revealed the extent of modification and charge distribution. A significant size dependence activity of Tween 80 on powdered activated carbon was observed. Electrochemical characterization revealed a better enhancement of specific capacitance in AC-T80-HDTMA than AC-HDTMA even at the concentration higher than CMC. The stability testing revealed a high attachment of HDTMA on the surface of functionalized AC particles in the presence of Tween 80, with a stable cycling. Moreover, the hypothetical mechanism

of surfactants on the surface of AC particles was depicted. The formulation of nonionic surfactant mixed with ionic surfactants induces better interfacial behaviors than individual ionic surfactant. In a sense, a mixture of HDTMA with Tween 80 holds peculiar effects on enhancement of AC surface activity. However, inadequate amount of Tween 80 could impede the synergism; hence the optimal molar fraction with ionic surfactants is highly recommended. For further investigation, we would like to shed the light on the effects of these surfactants on Electrical Double Layer (EDL) thickness and adsorption capacity of AC-S. The impact of dissimilarity and difference in size between the head groups of HDTMA and Tween 80 on ions selectivity is worthy to be further explored.

Conflicts of interest

There are no conflicts to declare.

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