Binding of cationic surfactants to humic substances

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Abstract

Commercial surfactants are introduced into the environment either through waste products or site-specific contamination. The amphiphilic nature of both surfactants and humic substances (HS) leads to their mutual attraction especially when surfactant and HS are oppositely charged. Binding of the cationic surfactants dodecyl-pyridinium chloride (DPC) and cetyl- or hexadecyl-pyridinium chloride (CPC) to purified Aldrich humic acid (PAHA), Dando humic acid (DHA), Inogashira humic acid (IHA), Laurentian fulvic acid (LFA) and Strichen Bs fulvic acid (SFA) is studied at pH 4.5 to 5 at 0.005 M NaCl. For PAHA CPC binding is also studied at pH 5 and 0.1 M NaCl. Measurements with the Mütek Particle Charge Detector (PCD) and polyDADMAC, a strong cationic polyelectrolyte, are used to determine the charge of the HS samples. PCD measurements with the surfactants reveal that the surfactant-HS complexes reach their iso-electric-point (IEP) before the critical micelle concentration (CMC) is reached. At the IEP the adsorption values (mol/g) of CP^+ and DP^+ to PAHA are the same, i.e. at the IEP the charge associated with the HS is neutralized by bound surfactant ions. For the other humic acids (HAs) CPC binding at the CMC corresponds with the charge obtained with polyDADMAC, but for the fulvic acid (FA) samples CP(C) adsorption at the IEP is larger than the FA charge. The surfactant-HS complexes flocculate around the IEP. Binding isotherms are obtained using surfactant electrodes. The results for CPC and DPC to the HA samples show a pseudo-plateau near the IEP, which is missing in the isotherms to the FA samples. The CP^+-PAHA isotherms at 0.005 M and 0.1 M intersect at the IEP. The affinity of CP^+ binding to PAHA is larger than that of DP^+ due to the longer aliphatic tail of CPC. The bound amount of DP(C) decreases in the order PAHA >> IHA ≈ DHA >> LFA ≈ SFA. The results demonstrate that cationic surfactant binding to HS is due both to electrostatic and hydrophobic attraction and that the fate of HS in aqueous environmental systems can be strongly affected by cationic surfactants.

***Keywords*:** surfactant binding isotherms; cationic surfactants; humic acid, fulvic acid; isoelectric-point; surfactant electrodes; particle charge detector; polyDADMAC

1. Introduction

Natural organic particles can be divided in fulvic acids (FA), humic acids (HA) and humins. The solubility discriminates HA and FA from humins (insoluble). FA and HA are soluble in aqueous solution in a wide pH range and both contain acid functional groups that can dissociate and give the particle a negative charge [1]. Together FA and HA are denoted as humic substances (HS) in this paper. The molar mass of FA particles is much smaller than that of HA particles and at a given pH the charge/g of FA is generally higher than that of HA. HA particles are often considered to be polydisperse and of amphiphilic nature [2, 3]. Recent insights [4] also point to a micellar type of particle structure composed of sub-units.

Due to their solubility, HSs can easily be transported in the aqueous phase through soil and other natural waters and they play an important role in the distribution of contaminants in the environment [5]. Contaminant binding to HS may significantly impact the total and free contaminant concentrations present in surface and ground waters as well as in soils. Contaminant mobility in natural waters can be reduced by binding to precipitated HS or it can be increased by binding to dissolved HS. However, under certain conditions contaminants may also flocculate/precipitate dissolved HS and this will reduce the mobility of the complex. The extent of flocculation/precipitation depends on the conditions, the type of HS and the nature of the contaminant. The interaction of contaminants with dissolved HS may also affect the binding of both to soil mineral particles [6-11].

Surfactants can be considered as a special class of organic contaminants that may affect the fate of HS [12]. Surfactants can be introduced into the environment by wastewater discharge, point-charge pollution [13], deliberate action, e.g. to remediate

contaminants from soil or from ground water [14, 15] and natural secretion from aquatic plants [16]. Wastewater treatment may remove some of the surfactants, yet detectable levels persist [17-19]. Previous studies performed on surfactant-HA interactions can be found in refs. [12, 20-25]. Koopal et al.[12] and Adou et al. [24] mention that humic acid is removed from the aqueous phase by forming neutral hydrophobic complexes with cationic surfactants. Only two studies describe binding isotherms of cationic surfactants to HSs [12, 25]. In general, it is well known that interactions between ionic surfactants and oppositely charged polyelectrolytes are quite strong [26, 27] and that phase separation may occur [28].

The objective of this study is to investigate the binding of the cationic surfactants dodecyl-pyridinium chloride (DPC) and cetyl- or hexadecyl-pyridinium chloride (CPC) to a range of HSs at a given pH and salt concentration. The work is an extension of the studies of Koopal et al. [12] and Yee et al. [25] with the aim to assess the importance of cationic surfactant - HS interactions for a range of humic substances at relatively low pH. In order to investigate the binding two complementary titration methods are used. With the particle charge detector method [29, 30] the amount of surfactant that is needed to neutralize the charge of a HS is measured. With the second method a surfactant selective membrane electrode [12, 25, 31-36] is used to detect the free monomer surfactant concentration after each surfactant addition and this allows the calculation of the complete binding isotherm. This method was also applied in the previous study [12] but here we use more sensitive surfactant electrodes.

2. Materials

Aldrich Humic acid (Aldrich H1,675-2) is purified by using the method described by Vermeer et al. [10], except for the treatment with the Dowex resin. The final freeze-dried product is denoted as PAHA (purified Aldrich HA). Aldrich humic acid is chosen because it is easily available and studies [37-38] of various humic acids including Aldrich have shown that ion binding of PAHA is similar to that of other humic acids. Potentiometric proton titration results of PAHA can be found in [10, 39]. Table 1 contains some relevant data.

Dando humic acid (DHA) and Inogashira humic acid (IHA) are supplied by the Japanese Humic Substance Society (JHSS) and they are isolated according to the method recommended by the International Humic Substance Society (IHSS) [40]. DHA was extracted from brown forest soil in Dando, Aichi Prefecture, and has an ash content of 0.67%. IHA was extracted from the ando soil in Inogashira, Shizuoka Prefecture, and has an ash content of 0.49%. Both samples were obtained from A-horizons, some data are presented in table 1, more details can be found in [41].

Laurentian fulvic acid (LFA) was obtained from C.H. Langford and is obtained from a sample of podzol (Laurentian Forest Preserve) near Quebec, Canada. The preparation and a first characterization of the sample have been reported by Wang et al. [42]; Vermeer et al. [11] have provided a further characterization. The weight average molar mass of LFA is about 10 kD, which is high for a FA. Potentiometric proton titrations of LFA have been carried out by Avena et al. [39], however, these results deviate seriously from those reported by Vermeer et al. [11]. The data are summarized in table 1.

Strichen Bs fulvic acid (SFA) is extracted from a Bs horizon from a peaty podzol (Strichen Soil Association, Scotland) using the methods recommended by the IHSS [40]. The preparation and characterization (including potentiometric proton titrations) of SFA

has been reported by Filius et al. [43]. Weng et al. [44] report a molar mass of 683 D. The relevant data are summarized in Table 1.

The Stock solutions of the HAs are made in measuring flasks by dissolving the HAs at pH 10.5, shaking for at least 6 hours and then bringing the pH to neutral and the volume to the appropriate level. Stock solutions of the FAs are made by dissolving the FAs in pure water, shaking for at least 2 hours and then fixing the volume. NaCl is added just before each experiment.

The n-dodecylpyridinium chloride (DPC; >98% purity) and n-hexadecyl- or cetyl-pyridinium chloride (CPC; >98% purity) are supplied by Sigma-Aldrich and used as received. The two surfactants display a linear aliphatic tail. From the absence of a minimum in the plots of the surface tension of the air-water interface against the log surfactant concentration it is concluded that the samples contain no or very little surface-active impurities.

A solution (20%wt, density 1.04g/cm^3) of the strong cationic polymer poly-diallyldimethylammonium chloride (poly-DADMAC), molar mass 162 kD, was obtained from Sigma-Aldrich.

Water used for the experiments was twice de-ionized and filtered through an activated carbon column and a micro filter (EASYpure UV), that resulted in a resistance greater than 18.3 MΩ·cm. The inorganic chemicals used were of analytical grade quality (obtained from Merck or Sigma-Aldrich).

3. Methods

3.1. Particle charge detector / iso-electric-point measurements

Iso-electric-points (IEP) of HS complexes with large organic cations can be measured using a "Mütek Particle Charge Detector" (PCD03). This apparatus acts by moving a piston inside a cylindrical sample cell up and down and this produces an electrokinetic signal depending on the charge of the particles present in the cell. Most investigators assume that the signal is a streaming potential of particles that are bound to the walls of cell and the piston [29, 30], but it is also possible that the particles and the mobile counterions in the solution move with different velocities [45]. The method has been discussed in relation to other electrokinetic measurements by Barron et al. [46]. Dentel and Kingery [29] and Walker et al. [30] provide quantitative models of the technique based on the assumption that the particles completely cover the walls of piston and cell. In any case the method is well suited to measure the charge sign of colloidal particles or complexes and in the case of titrations with a complexing agent of opposite charge the charge reversal point or IEP can be precisely detected. The method is, for instance, popular in water purification practice to measure the amount of polymeric cationic flocculants needed to neutralize the charge of dissolved natural organic matter [47]. Here the PDC03 is used to determine the charge of the HS samples at the given conditions with poly-DADMAC [47] and to determine the IEP of the HS-cationic surfactant complexes. With the PDC03 equipment a titrant solution is added with an automatic titrator (Mütek PCD-Two) in steps of 0.02 mL into 25 mL of HS solution that is placed in the reaction vessel and the potential (mV) of the titrant-HS complexes is recorded together with the solution pH. The rate of addition is 30s per step, but in some titrations the first 15 steps are added at 5 s/step. The titrations for DHA and IHA were carried out with small amounts of HA, because the amounts available were small.

3.2. Surfactant electrode

The equilibrium concentration of surfactant monomers in solution is determined with a membrane electrode that is selective for cationic surfactants. This use of surfactant electrodes has become routine for the study of polymer-surfactant interactions [31, 33, 34] and is also deemed the most suitable for our experimental system. The electrode membrane is prepared according to the procedure described in [25]. This type of membrane has been used before in several surfactant studies [e.g. 25, 32, 35, 36]. The electrode is made by mounting the membrane (polyvinylchloride (PVC) with Elvarroy 742 (Du Pont) plasticizer) on the top of a PVC tube with a cross section of 11 mm by using tetrahydrofuran. The tube is filled with the reference solution that contains the surfactant and NaCl. The surfactant concentration in the reference solution, C_{0S}, is $2.5x10^{-4}$ M for DPC and $2.5x10^{-5}$ M for CPC. The values of C_{0S} for the two surfactants are lower than their critical micelle concentrations (CMCs). This facilitates the measurement of low surfactant concentrations and minimizes leakage through the membrane. The reference solution is in contact with an Ag/AgCl electrode to be able to measure the potential. The Ag/AgCl electrode is reversible, not sensitive to polarization effects and it gives a stable reading if the internal solution contains a fixed concentration of NaCl (C_{0N}; 0.005 M or 0.1 M). The concentration C_{0N} is made the same as that in the samples to minimize the liquid junction potential over the membrane. The surfactant electrode assembly has a resistance >10 MΩ.

3.3. Electrochemical cell

The surfactant electrode potential (EMF in mV) is measured relative to a commercial Ag/AgCl (3.3 mol/L KCl) reference electrode equipped with a ceramic plug (Schott, Type B2920). Schematically the set-up is as follows:

{Internal Ag/AgCl electrode | reference solution (C_{0S},C_{0N}) | selective membrane}

| *test solution* (C_S, C_N) | Ag/AgCl (3.3 M KCl) reference electrode |

where C_S and C_N are respectively the surfactant and NaCl concentration in the test solution. The blank or the sample solution is contained in a double walled glass cell of 100 mL (Schott) covered with a lid that holds the electrodes and, in the case of titrations, the burette tips. Because of the high resistance of the surfactant electrode all cables are screened ("co-ax"), the internal Ag/AgCl electrode is connected to earth, the entire cell is covered with aluminum foil that is also connected to earth (Faraday cage) and a high impedance input voltmeter is used for the EMF readings.

3.4. Cell calibration

The calibration of the electrochemical cell is done in two steps. At relatively high surfactant concentrations the electrochemical cell is calibrated by titrating a concentrated surfactant solution into the reaction cell containing 50 mL of solution with a given NaCl concentration and pH≈5. Surfactant additions were made using a motorized piston burette (Schott T100; 5 mL burette, minimum dosage of 2 μL) and an automated titration device (Schott TR250). The solution was mixed with a magnetic stirrer. A mixing time of one to three minutes was allowed after each aliquot addition. The stirring was then stopped and the electrode potential was recorded. The reaction cell was kept at a constant temperature of 25 ± 0.5°C, and maintained in an argon atmosphere. In the low concentration range (10^{-7}-10^{-5} M for DPC and $2.5\cdot10^{-8}$-10^{-6} M for CPC) the titration method is unsatisfactory

and the calibration of the cell is done by refreshing a given solution repeatedly until the cell and electrode walls are equilibrated at the given concentration and the EMF value of the cell becomes constant. This requires multiple times rinsing at each surfactant concentration for a good result. Also with this procedure the cell is kept at a constant temperature of 25 ± 0.5°C and argon atmosphere is applied.

An electrochemical cell that functions properly yields according to the Nernst equation a straight calibration line (EMF in mV versus the logarithm of the surfactant concentration) below the critical micelle concentration (CMC) of the surfactant. Blanks measured should have a correlation coefficient of at least 0.990. The data presented in this study adhere to these criteria.

3.5. Binding isotherms

Binding isotherms are generated by employing the surfactant titration protocol in the presence of HS. However, in this case, after each aliquot addition, the electrode potentials are recorded at time intervals of 20 seconds until the electrode potential is stable with respect to time (equilibration criterion ≤ 5 mV/min). A maximum equilibration time of 10 minutes is allowed if this equilibration criterion is not met. The quantity of free surfactant is calculated from the equilibrium monomer concentration and the known total solution volume. Binding to HS is determined by subtracting the free amount from the quantity initially added to the solution. Accordingly, the binding isotherm is obtained. The pH was also recorded. In order to get accurate EMF readings at low surfactant concentrations, the surfactant electrode and cell must be well washed with blank solution before the titration starts (EMF << EMF of lowest surfactant concentration in blank experiment).

4. Results

4.1. HS titration with poly-DADMAC

The amount of polyDADMAC to reach the IEP of the HS-polyDADMAC complex at an initial pH of 5 and 0.005 M NaCl is measured for the different HS samples using the PCD03. PolyDADMAC is a strong cationic polyelectrolyte with a calibrated charge of 5.9 mmol/g [48] and this value is used for the calculation of the HS charge (mmol/g) per g bound polyDADMAC. Kam and Gregory [47] have shown that for cationic polymers with a charge density of around 3 mmol/g or greater a stoichiometric relation is observed between the charge of humic substances and that of cationic polyelectrolytes. During the titrations the pH is slighly lowered to around 4.7 at the IEP. This is due to proton release from the HS (some charge adaptation). The titrations are carried out with different initial amounts of HS. In general clear IEPs are found, but the titration curves of the HAs are much steeper around the IEP than those of the FAs. The final results for the different HS samples are depicted in Fig. 1; within experimental error regression lines pass through the origin. This indicates that at the IEP of the complex the solution concentration of polyDADMAC is very low which means there is a high affinity between HS and poly-DADMAC. The calculated charges in mmol/g HS are collected in Table 1. In general these values compare well with the quoted literature values derived from proton titrations. The value obtained for LFA is about the average of the cited results. These results are in agreement with the findings of Kam and Gregory [47]. By measuring simultaneously potential and the pH with the PCD03, the charge adjustment of the humic substance due to its interaction with poly-DADMAC can also be estimated. By comparing proton titration results with poly-DADMAC results it should be kept in mind that the relative

proton charge obtained with a proton titration should be transformed in an absolute proton charge and for this the HS charge density at a given pH and the same salt concentration is requiered. This latter value is not always accurately known. The present results and those obtained by Kim and Gregory [47] indicate that the polyDADMAC results at low electrolyte concentration and a given pH could be used to obtain such a reference value.

4.2. HS charge neutralization with surfactant

The electrokinetic potential as a function of the added amount of CPC as measured with the PCD03 and the course of the pH during the titration are depicted in Fig. 2a and 2b respectively for three different PAHA concentrations indicated in the figure. Similar results are obtained for the DPC-PAHA system, see Fig. 3. Both for CPC and DPC the electrokinetic potential reverses charge in the course of the titration which indicates that both surfactants can bind super-equivalently to the PAHA. The IEP can be accurately determined. The pH plots show that as a result of surfactant binding some protons are released; the release is most significant around the IEP. Clearly the dissociation of the acid groups of PAHA is promoted due to increased screening of the charge of the PAHA by the surfactant. Similar measurements were made for the other HS samples. For CPC the results resemble those of PAHA: charge reversal occurs in a steep part of the titration curve and the change in pH is largest around the IEP. For DPC the charge reversal and pH change around the IEP are more gradual for the other HS than for PAHA. The gradual slopes make the measured IEP´s less accurate.

The amounts of CPC and DPC needed to reach the IEP of the humics are plotted in Fig. 4 as a function of the HS concentration. For CPC the dependence is linear and the lines pass within experimental error through the origin. Therefore, at the IEP the amount

of CPC in the solution is negligible (≤ 0.002 mmol, corresponding to a solution concentration ≤ 0.08 mmol/L) as compared to the bound amount. This is indicative for the high affinity between HS samples and CPC. The slopes of the lines represent the amounts of bound surfactant at the IEP in mmol/g of HS. Assuming a 1:1 stoichiometry these values can be interpreted as the charge in mmol/g HS at the given pH and they are included in table 1. For the HA samples these charge values are slightly higher than those observed with poly-DADMAC (see table 1). Most likely the reason for this is that upon surfactant binding the charge adaptation is a bit larger (better screening). However, for the two FA samples charge values measured with CPC are significantly larger than those measured with poly-DADMAC. The reason for this difference with HA is most likely the relatively low affinity between FA and CP^+, so that FA-CP(C) complexes at the IEP contain some neutral CPC as well.

The results for DPC can also be approximated as straight lines, but the scatter is larger than for CPC and the lines have intercepts above the origin. For PAHA the slope of the DPC line is very similar to that found for CPC and the intercept is 0.035 mmol. The latter value corresponds to 1.4 mmol/L DPC in solution. Most likely also DP^+ binds with a 1:1 stoichiometry to the charged groups of PAHA. For SFA the DPC slope (4.49 mmol/g) is also close to that of CPC, but for DHA, IHA and LFA the slopes for DPC (4.6; 3.5; and 7.4 mmol/g, respectively) are substantially larger than with CPC and for all these HSs the intercept is around 0.12 mmol, which corresponds with 4.8 mmol/L DPC in solution. This value is 3-4 times higher than that for DPC-PAHA. Two conclusions can be drawn: (1) the DP^+-PAHA affinity is relatively high and (2) the affinity of CP^+ for the HS samples is much higher than that of DP^+. The latter can be explained by hydrophobic attraction: the aliphatic tails of the surfactants are removed from an aqueous environment

to the much more hydrophobic environment of the surfactant-HS complex at the IEP and the longer the aliphatic tail is the stronger is this hydrophobic attraction. The first conclusion explains that the slope for DPC-PAHA agrees well with that of CPC-PAHA, whereas for the other HSs DPC leads to a steeper slope. The impression that with DPC a higher HS charge is found at the IEP than with CPC must be an artifact. There is no reason to believe that the screening of the HS charge by DP^+ is better than that by CP^+ when the DP^+-HS affinity is weaker. Therefore, we have to conclude that, except for PAHA, at the IEP some chloride ions must be included in the DP(C)-HS complexes. Chloride inclusion is most likely caused by the fact that around and above the IEP the DPC concentration is relatively high and that some DPC is bound in its neutral form (the behavior of alkylpyridinium surfactants often shows some dependence on the type of counterion, indicating incomplete dissociation). With CPC the affinity for HAs is so high that there is hardly CP^+ left in solution and even less neutral CPC. Therefore the effect is insignificant for CPC.

When the surfactant titrations are stopped at the IEP and the sample is left at rest precipitation/flocculation of the complexes is observed. This is in agreement with the observations by Adou et al. [24] and Koopal et al. [12]. For the DP(C)-LFA complexes flocculation already occurred during the surfactant titration.

4.3. Calibration lines for CPC

The measured calibration lines of CPC at 0.005 M NaCl are depicted in Fig. 5. The calibrations are performed from very low CPC concentrations (10^{-8}M) to relatively high concentrations (10^{-3}M) beyond the CMC. Upon the gradual increase of the monomer surfactant concentration, the CMC is reached. At this concentration, the chemical potential of the surfactant monomers becomes practically constant due to micelle

formation, and therefore, the EMF response of the electrode remains constant. This corresponds to the small plateau at the end of the calibration lines. The basic property of the calibration curves is their linear response as a function of the logarithm of the concentration (up to the CMC). Calibration 1 and 4 cover a surfactant concentration range from 10^{-8}M to 10^{-3}M. Calibration 1 is carried out before contact of the cell and electrodes with PAHA and calibration 4 after a titration with PAHA and subsequent thorough cleaning of the cell and electrodes by excessive rinsing with pure water. The linear regions of both calibrations coincide within experimental error and the slopes are in the range of 54 to 56 mV. These values are close to the theoretical Nernstian slope of 59.2 mV and indicate that the electrodes work well over a large concentration range. The position of the kink represents the CMC of CPC at 0.005 M NaCl ($2.8x10^{-4}\pm5\ x10^{-6}$ M). The CMC value is in line with the trend of the CMC values at different ionic strength reported by Van Os et al. [48].

Calibration curves 2 and 3 are obtained by titration after contact with PAHA and only a few rinsing steps. They are systematically shifted somewhat (up to 10 mV at 10^{-4} M CPC) with respect to calibrations 1 and 4. The slopes of these calibration curves are slightly lower (54-55 mV/decade) than those of the well cleaned electrode but the regression coefficients are above 0.995. This is most likely due to some adsorption of PAHA at the surfactant electrode. The effect of PAHA adsorption on the electrode is also visible in the potential at which the CMC is reached; this potential gradually decreases after repeated contact with PAHA. However, the CMC itself is not affected. The systematic difference between the two sets of calibrations indicates that the calibration line measured after contact with PAHA should be used for the calculation of the CPC adsorption. Because of the small uncertainty range of the calibration curves measured

after contact with PAHA a small parallel shift (<3mV) of the calibration curve is allowed for the calculation of the binding curves. As additional calibration point for this calculation the IEP (ads; conc. range) measured with the PCD03 can be used.

The CPC calibration curves at 0.1 M NaCl after contact with PAHA and a few times rinsing with pure water have slopes of only 38.3 to 41.9 mV which is considerably lower than the Nernst value of 59 mV. Nevertheless, the regression coefficients are still within the limits and also the value of the CMC of 3.5×10^{-5} M, is in good agreement with the value quoted in [48], 3.8×10^{-5} M. The small value of the slope indicates a much stronger effect of PAHA on the membrane electrode than at 0.005 M NaCl. The reason for this is not clear. For the calculation of the CPC binding isotherm at 0.1 M NaCl we have used the calibration line that is measured directly after contact with PAHA.

4.4. Calibration lines for DPC

The calibration lines of DPC in 0.005 M NaCl are collected in Fig.6. The behavior is very similar as for CPC. A difference with the CPC calibration lines is that the same EMF is reached at higher surfactant concentrations (about a decade); this means that the electrode is more sensitive for CPC than for DPC. Also for DPC the slope of the lines and the EMF at the CMC are somewhat decreased after contact with PAHA, but the value of the CMC is not affected. The slopes of the calibration lines range from 57.9 for the "pure electrode" to 54.8 mV for the electrode after contact with several HSs; all values are close to the theoretical slope of 59.2 mV. The long calibration gives a good regression line from 1×10^{-7} M to the CMC at $1.52 \times 10^{-2} \pm 5 \times 10^{-4}$ M DPC. This CMC value is in line with the trend of the CMC values of DPC at different ionic strength reported in [49]. For the calculation of the binding curves the same procedure is followed as described for CPC. As additional calibration point we have used the solution concentration of DPC at

the IEP (Fig. 4) together with the charges of the HS as measured with polyDADMAC and CPC.

4.5. Binding of CPC and DPC

Two typical examples of a titration of PAHA with CPC at 0.005 M salt and pH≈5 are depicted in Fig. 7. The difference between the two curves is caused by using different amounts of PAHA. For sake of comparison also the blank measured directly after the binding experiments is plotted. The difference between the blank and the PAHA titration is caused by the adsorption. The curves in the presence of PAHA start at cell EMF values that are negative and that correspond with free monomer concentrations that are around 10^{-8} M or lower. However, at these very low concentrations the electrode signal is not selective any more. Clearly adsorption takes place (total added monomer concentration >> free monomer concentration), but the equilibrium concentration at which this happens cannot be measured accurately. Once the cell EMF values start to increase, the free monomer concentration can be established and the bound amount can be calculated as a function of the monomer concentration. The situation is similar for CPC at 0.1 M salt. Also in the case of DPC a similar behavior is found, see Fig 8 that depicts the raw results for the HA samples. Note that blank and DPC-HA titration curves are much closer than for CPC. The consequence is that the calculated binding isotherms for DPC are less accurate than those of CPC.

The CP^+-PAHA binding isotherms at 0.005 M and 0.1 M NaCl and pH 4.5 to 5 are depicted in Fig. 9 as single and double logarithmic plot. The various symbols at 0.005 M salt in panel (a) indicate repeated experiments and show that there is a good reproducibility except at concentrations very close to the CMC. Here the curves measured at 0.1 g/L PAHA differ from that at 0.25 g/L. The steep part of the curve at 0.25g/L

nicely matches with the CMC of CPC, but the curves at 0.1g/L rise steeply before the CMC. We believe that this is an artifact that is due to PAHA interaction with the electrode. This will occur at all PAHA concentrations, but with more PAHA present the error in the calculated ´bound amount´ is much less. The adsorbed amount in the IEP (2.03 mmol/g; ≤0.08mmol/L) at pH 4.5 and 0.005 M and 0.1 M NaCl measured with the PCD03 is indicated with a dotted line. In the double logarithmic plot the duplicate experiments were left out for sake of clarity, only the more accurate curve measured at the high PAHA concentration is shown. For both salt concentrations the bound amount rises gradually till a pseudo-plateau around the adsorption value of the IEP and somewhat before the CMC. For 0.1 M salt the pseudo-plateau is very weak, but it can be clearly seen in the double logarithmic plot. This indicates that around the IEP the electrostatic attraction vanishes and becomes an electrostatic repulsion. The fact that the binding still progresses is due to the hydrophobic attraction. The steep increase of the isotherm very near the CMC is an artifact and indicates that the CMC of the surfactant is reached: added monomers are bound in micelles formed in solution. The start of the isotherm at 0.1 M NaCl occurs at a higher surfactant concentration than that at 0.005 M because the electrostatic attraction between PAHA and CP^+ is screened better. After charge reversal of the CP^+-PAHA complex the electrostatic repulsion between the surfactant molecules in the complex is screened better and this leads to a stronger adsorption at 0.1 M. This explains that the two isotherms intersect and that the intersection point corresponds with the IEP of the complex. A close agreement between intersection point of the isotherms and the IEP will only occur when there is no specific binding of salt ions to the complex. For PAHA-CP^+ this is indeed the case because the IEP´s measured at 0.005 M and 0.1 M salt coincided. In the double logarithmic plot it can be observed that the initial slope of

the binding curve at 0.005 M is close to unity (Henry slope), whereas that at 0.1 M is larger than unity. This indicates that at low salt concentration the binding is fairly ideal. At high salt concentration even at the lowest measured concentration cooperativity in the binding is already important. At high salt concentration not only the electrostatic attraction between PAHA and CP^+ is screened, but also the lateral electrostatic repulsion between the surfactant molecules and this makes the hydrophobic attraction more pronounced. The ideality of the curve at 0.005 M extends up to about 0.2 mol/kg. This is a pseudo-ideality that results from the compensation of the heterogeneity of the binding by some kind of structurally induced lateral attraction at very low concentrations. At higher concentrations the decrease in electrostatic attraction is overcompensated by the increase in hydrophobic attraction and this leads to a slope of the isotherm slightly larger than unity (positive cooperativity).

During the titration to obtain the binding isotherm also the pH is registered. Similarly as with the PCD03 measurements, a relatively strong change in pH from about 5.5 to 4.5 is observed close to the IEP, i.e. around the pseudo-plateau of the isotherm. From this change in pH the change in the charge (mmol charged sites/g) of the humic acid can be calculated. This has been done and the result is also incorporated in Fig. 9 (open symbols). At 0.005 M NaCl it is clear that the charge adjustment becomes significant when the binding of CPC is close to the plateau value and that the adjustment is about 10% of the charge at the IEP. At 0.1 M salt charge adjustment is similar.

The DP^+-HA and DP(C)-FA binding isotherms at 0.005 M NaCl and pH 4.5 to 5 are depicted in Fig. 10, both as single and double logarithmic plot. The binding isotherms are calculated by slightly adjusting (>3mV) the position of the calibration curves obtained directly after the HS titration. The effect of the adjustment is significant for equilibrium

concentrations larger than 10^{-4}M DPC. The binding of DP^+ to the HS is in the order of PAHA>>IHA≈DHA>>SFA≈LFA. The binding behavior of DP^+ to the HA samples is distinctly different from that to the FA samples. The shape of the isotherms for the HA samples is similar to that of the CP^+ isotherm with a sigmoidal shape and a steep rise close to the CMC. The pseudo-plateau at high concentrations is also present and best observed in the double logarirthmic plot. The pseudo-plateau for DP^+-PAHA corresponds reasonably well with the IEP measured with the PCD03, but it is not as pronounced as with CPC. The pseudo-plateaus for DHA and IHA occur at surfactant binding levels that are lower than the bound amounts at the PCD03-IEP. As the psuedo-plateau levels must be related to a lowering of the electrostatic affinity, this shows that the PCD03-IEPs represent a complex in which also neutral DPC is incorporated. Somewhat before the pure CMC the curves rise vertically. This must mean that the CMC in solution (in the presence of HS) is reached. A CMC just before the ´pure´ CMC was also observed in our previous study [12] and explained by the fact that the complex precipitates but that some HA remaining in solution affects the CMC.

The binding curves of DP(C) to the FA samples first show a hesitation to bind and then steeply rise before the CMC. The rise becomes vertical at the CMC in the presence of FA. Here the difference between DP(C)-FA binding and FA screened micellization has vanished; there is no pseudo-plateau observable, also not in the double logarthmic plot. In general, this shape occurs when the affinity for the sites is lower than the lateral affinity: only with some bound surfactant the binding increases strongly with concentration. The double logarithmic plot shows that the DP(C)-FA binding isotherms are nearly linear with a slope that is somewhat smaller than unity even at very low concentrations. This is due to the heterogeneity of the binding sites. For PAHA-DP^+ the initial slope is about

unity, followed by a slope lower than unity. This indicates that the binding is non-cooperative (the initial slope of unity might be a combination of heterogeneity and some lateral attraction). The log-log plots of DHA-DP^+ and IHA-DP^+ are slightly steeper than the plot of PAHA-DP^+ and seem to have an initial slope larger than unity. Possibly there is some restructuring of these HAs at very low surfactant binding but a firm conclusion is not possible, it may also be a measurement artifact.

The pH changes during DP^+-HS binding experiments also range from 5.5 to 4. The relatively low pH at the end of the experiment is caused by an acid impurity of our DPC; the pH of the blank titration also changes from 5.5 to 4. Nevertheless from the difference we have calculated the charge adjustment for the DP^+-HS systems and found 0.9 to 2% increase in charge around the IEP, see the plusses in Fig. 10.

4.6. Comparison of CPC and DPC binding

In Fig.11 the results of CP^+ and DP^+ binding to PAHA at 0.005 M are compared. The main difference is that the CP^+ isotherm occurs at lower concentrations than the DP^+ isotherm. This has been remarked already with the discussion of the IEPs and it is due to the stronger hydrophobic character of CP^+. In general, the shift corresponds well with the shift of the CMC (see the indicated values). The fact that this is also the case at very low bound amounts indicates that even the first molecules that bind to the humic acid are already embedded in a fairly apolar environment. Apparently the core of the PAHA molecules is fairly hydrophobic and the hydrophobicity of the complex may increase with increased surfactant binding. In both plots we see that at intermediate adsorption values the CP^+ isotherm is slightly steeper than the DP^+ isotherm. As mentioned before, the double logarithmic plot indicates that at about 0.2 mol/kg the CP^+ binding progresses by positive cooperativity (slope >1) and this does not occur for the less hydrophobic DP^+. At

higher concentrations the positive cooperativity with CP^+ leads to a relatively ´early saturation´ and therefore a more pronounced pseudo-plateau for CP^+ than for DP^+.

5. Discussion and Conclusions

The charge of the complexes of cationic surfactant and HS changes from negative to positive as the bound amount increases. In agreement with the results reported by Koopal et al. [12], this observation indicates that the surfactant ions bind super-equivalently to HSs. In the present paper this has been worked out in more detail and for different HSs.

The bound amount (mmol/g) of CP^+ at the IEP of the CP^+-HS complex is a measure of the amount of dissociated groups of the HS. The long chain surfactant CPC is well suited to determine the charge because the amount of surfactant required to reach the equilibrium concentration in solution is very small compared to that for the binding. DPC is less suited because here the affinity is less, the amount in solution is not negligible compared to the bound amount and some DPC may become included in the complex. The binding of CP^+ causes an increase of the dissociation of the acid groups of the PAHA by about 10%. The main increase occurs around the IEP of the surfactant-HS complex.

At 0.005 M the surfactant electrodes used in this study are slightly affected by contact with HS. For measurements of CPC the resulting uncertainty in the binding isotherms is very small. For DPC this uncertainty affects the top part of the isotherm. Reliable binding isotherms of DP(C) have been obtained by using the independently measured DPC concentration at the IEP and the HS charge as reference point. With CPC at 0.1 M NaCl the surfactant electrode is strongly affected by contact with PAHA, but the electrode behaved reproducible and the CMC of CPC at 0.1 M NaCl is found at the correct concentration.

At 0.005 M NaCl only a weak cooperativity is detected for the CP^+, but at 0.1 M the CP^+-PAHA isotherm shows even at very low concentrations positive cooperativity. Koopal et al. [12] also found cooperative binding for CPC at 0.025M. This cooperativity is directly related to the long aliphatic tail of CP^+. The increase in cooperativity with increasing salt concentration occurs because the electrostatic repulsion between the bound surfactant molecules decreases. Although the CP^+-PAHA isotherm at 0.1 M is steeper than that at 0.005 M it starts later and both isotherms intersect at the IEP. This behavior is also caused by the increased screening of the electrostatic interactions: before the IEP is reached the electrostatic attraction with the surface is weaker and after the IEP the lateral electrostatic repulsion is weaker. Although super-equivalent adsorption occurs due to hydrophobic attraction, the binding progresses only little after the charge compensation (pseudo-plateau for the HA samples). The electrostatic repulsion sets in and the increase in the free surfactant concentration is limited because the IEP occurs close to the CMC whereafter normal micellization is favored. Pseudo-plateaus after charge compensation were also found in the previous study [12]. We may conclude that hydrophobic attraction is an important contribution to the affinity but that the level of adsorption just before the CMC is largely determined by the charge of the HS at the given pH.

At 0.005 M NaCl the CP^+-PAHA binding occurs at lower concentrations than that of DP^+-PAHA, and the shift of the curves is similar to the shift of the CMCs, even at very low surfactant concentration. This reveals the importance of the hydrophobic attraction for the binding and, moreover, that the core of the PAHA molecules must be of similar hydrophobicity than the core of the micelles. Also this result is in agreement with that by Koopal et al. [12] for PAHA at 0.025M and different pH values. Yee et al. [28] observed

for n-alkylpyridinium bromide binding to HAs at high pH and 0.03 M ionic strength also parallel shifts of the isotherms with increasing chain length, but did not reveal the behavior at very low concentrations.

At 0.005 M NaCl the binding of DP(C) to HSs decreases in the order of PAHA >> IHA ≈ DHA >> SFA ≈ LFA. This indicates that the hydrophobicity of these HS samples decreases in the same order. At very low concentrations "Henry-behavior" is observed for DP^+ binding to the HA samples, at higher concentration the hydrophobic attraction increases, but this is counter-balanced by the decrease in electrostatic attraction. The shape of the DP(C) isotherms to the FAs is distinctly different from that of the HAs and indicative for a relatively weak interaction. DP(C) binding to the FA samples reflects at low concentrations the heterogeneity of the FA. Close to the CMC the isotherm rises steeply due to cooperative binding. Yee et al. [28] observed for DPC very similar differences between HA and FA at pH 9.2 and 0.03M salt.

Similarly as in [12] the CMC of DPC in the presence of HS is somewhat lower than the ´pure´ CMC. This may be caused by the presence of some HS left in solution after the IEP is reached and phase separation (observed as flocculation of the complex) occurs. However, this result has to be considered with some reservation because the accuracy of this part of the binding curve is limited.

Our overall conclusion is that cationic surfactants bind to humic substances even at very low concentrations. This binding drastically changes the physicochemical characteristics, such as, charge density, hydrophobicity and internal structure of humic substances. Therefore, even small amounts of cationic surfactants in the aquatic environment will affect the nature and fate of the humics. Considering the limited attention paid in literature to cationic surfactant binding to humic substances, it seems

that the role of cationic surfactants in natural systems is underestimeted. A reason for this might be that most of the synthetic surfactants used in domestic life and industries are anionic and these surfactants do not (strongly) bind to the humics [12].

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Figure Captions

Fig. 1. Result of the HS titrations with polyDADMAC. The charge in mmol is obtained from the amount of polyDADMAC needed to reach the IEP of the complex.

Fig. 2. PCD-potential of the CPC-PAHA complex (a) and the solution pH (b) as a function of the added amount of CPC at 0.005 M and 0.1 M salt.

Fig. 3. PCD-potential of the DPC-PAHA complex (a) and the solution pH (b) as a function of the added amount of CPC at 0.005 M salt

Fig. 4. Amount of surfactant needed to reach the IEP of the HS-surfactant complex. The samples and surfactants are indicated in the figure.

Fig. 5. CPC calibration curves for CPC-PAHA system at 0.005 M NaCl.

Fig. 6. DPC calibration curves for DPC-HA systems at 0.005 M NaCl. (a) entire concentration range; (b) detail at relatively high DPC concentration.

Fig. 7. Blank and titration curves for the CPC-PAHA system at 0.005 M NaCl. The titration curves are measured 0.25 and 0.1 gPAHA/L. The calibration curve after contact with PAHA is depicted.

Fig. 8. Blank and titration curves for the DPC-HA (0.1g/L) systems at 0.005 M NaCl. The calibration curve after contact with PAHA is depicted.

Fig. 9. Binding isotherms of CPC to PAHA at 0.005 M and 0.1 M NaCl (closed symbols) and the adjoining proton release (open symbols). Panel (a) single logarithmic scale, panel (b) double log scale. In panel (a) the reproducibility of the isotherm in 0.005 M is also shown.

Fig.10. DPC-HA and DPC-FA binding isotherms at 0.005 M salt and pH 4.5 to 5.

Fig.11. Comparison of the CPC-PAHA and DPC-PAHA isotherms at 0.005 M salt and pH4.5 to 5.

Table 1. *Characterization of the HSs used in this study*.

name	C %	O %	H %	N %	particle mass Dalton	charged groups pH ≈ 5; I ≈ 0.005 M mmol/g			references
						H-titr[1]	pDADMAC[2]	CPC[2]	
PAHA	55.8	38.9	4.6	0.6	20 000	1.8	1.93	2.05	10, 39
DHA	53.0	36.9	5.3	4.5	-	1.9*	2.06	2.04	41
IHA	54.8	36.6	4.3	4.0	-	2.2*	2.40	2.50	41
LFA	45.1	49.7	4.1	-	9 000	1.6-4.3*	2.34	3.12	11, 39, 42
SFA	43	-	-	-	680	3.5	3.13	4.41	44, 45

[1] approximate value derived from proton titrations reported in the literature (* estimated as 0.5 times the COOH-groups).
[2] Measured in this study, see text.

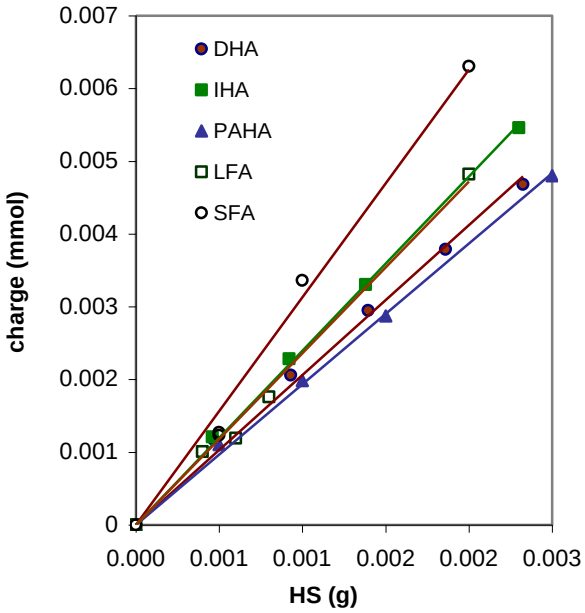

0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
charge (mmol)
DHA
IHA
PAHA
LFA
SFA
0.000
0.001
0.001
0.002
0.002
0.003
HS (g)

Fig. 1

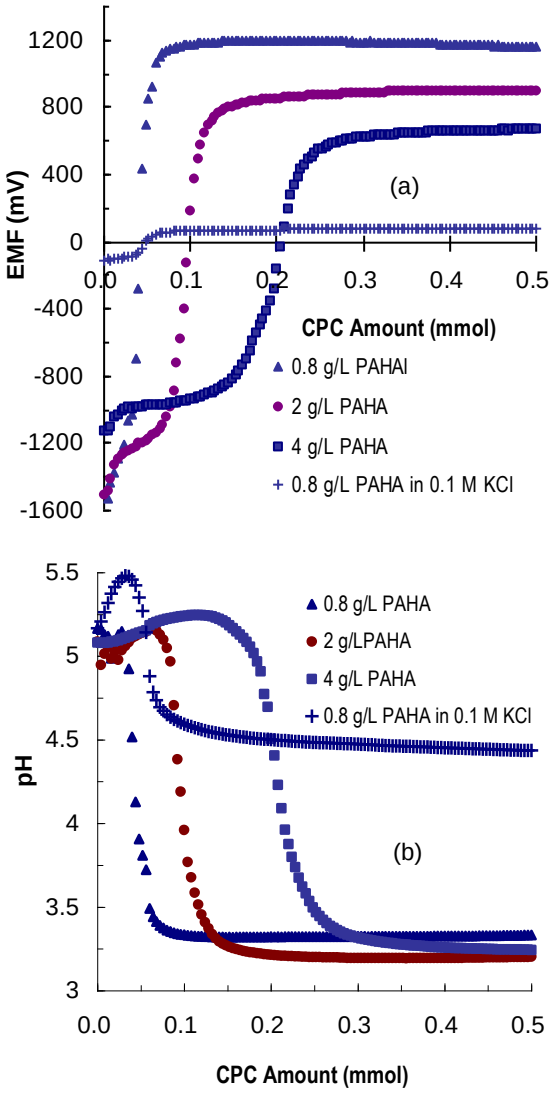

1200
800
400
0
-400
-800
-1200
-1600
EMF (mV)
(a)
0.0
0.1
0.2
0.3
0.4
0.5
CPC Amount (mmol)
0.8 g/L PAHAl
2 g/L PAHA
4 g/L PAHA
0.8 g/L PAHA in 0.1 M KCl
5.5
5
4.5
4
3.5
3
pH
(b)
0.8 g/L PAHA
2 g/LPAHA
4 g/L PAHA
0.8 g/L PAHA in 0.1 M KCl
CPC Amount (mmol)

Fig. 2

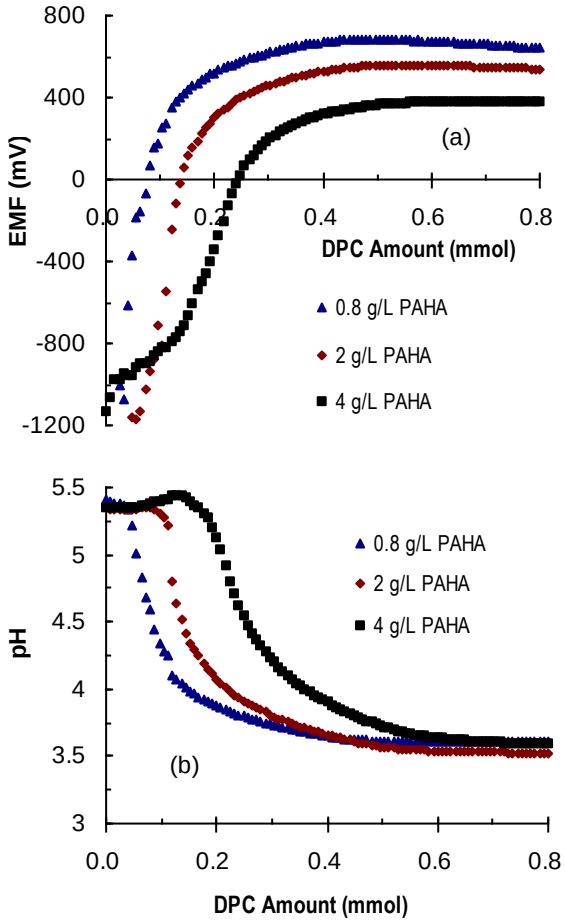

800
400
0
-400
-800
-1200
EMF (mV)
(a)
0.0
0.2
0.4
0.6
0.8
DPC Amount (mmol)
0.8 g/L PAHA
2 g/L PAHA
4 g/L PAHA
5.5
5
4.5
4
3.5
3
pH
(b)
0.0
0.2
0.4
0.6
0.8
DPC Amount (mmol)
0.8 g/L PAHA
2 g/L PAHA
4 g/L PAHA

Fig. 3

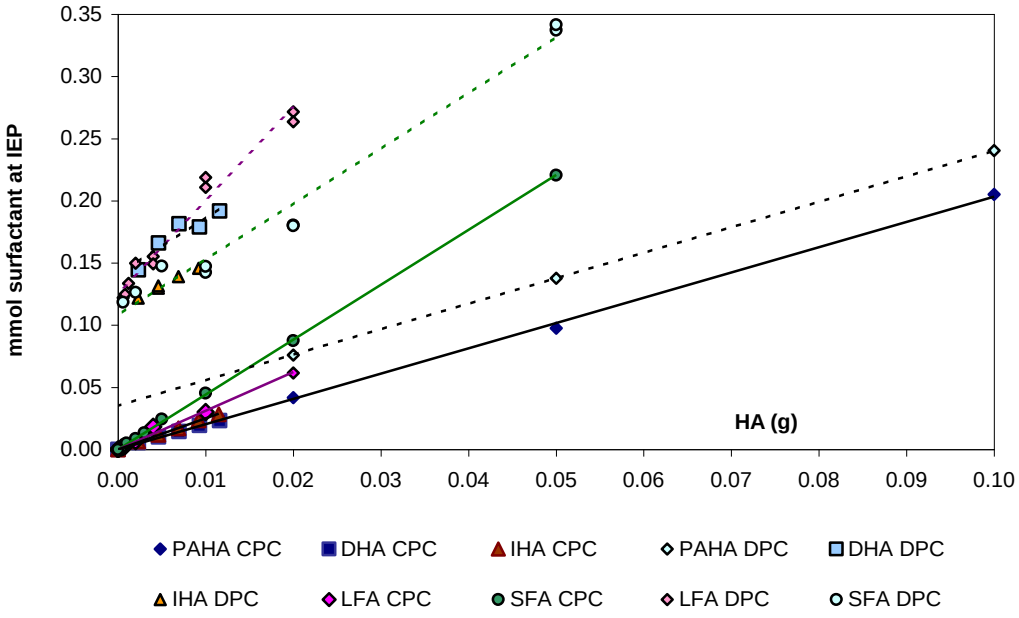

mmol surfactant at IEP
HA (g)
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.10
PAHA CPC
DHA CPC
IHA CPC
PAHA DPC
DHA DPC
IHA DPC
LFA CPC
SFA CPC
LFA DPC
SFA DPC

Fig. 4

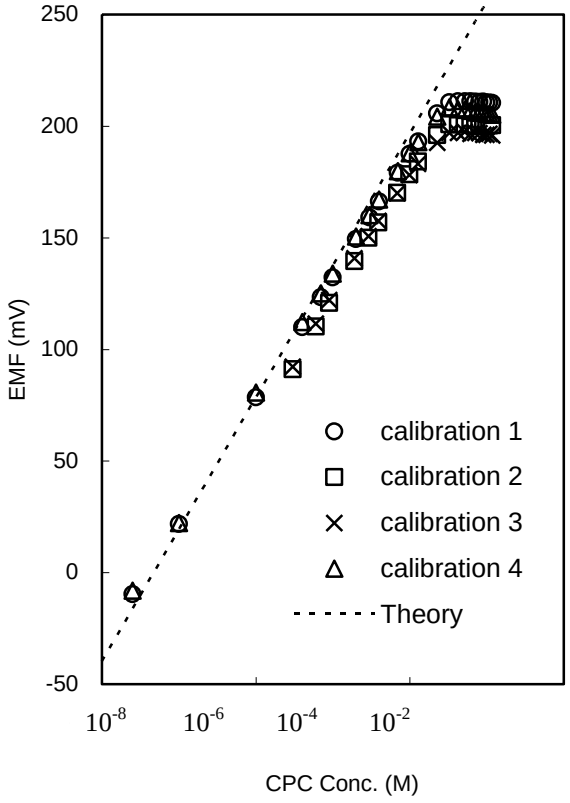

EMF (mV)
CPC Conc. (M)
250
200
150
100
50
0
-50
10-8
10-6
10-4
10-2
calibration 1
calibration 2
calibration 3
calibration 4
Theory

Fig. 5

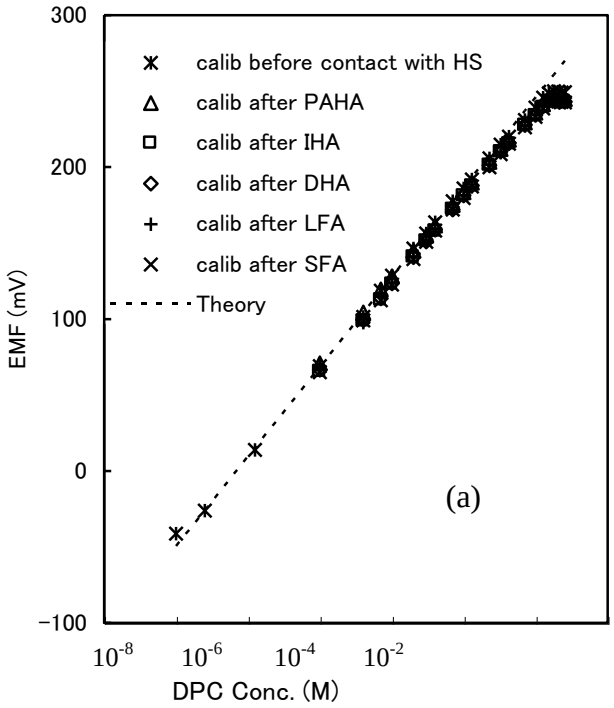

300
200
100
0
−100
EMF (mV)
calib before contact with HS
calib after PAHA
calib after IHA
calib after DHA
calib after LFA
calib after SFA
Theory
(a)
10-8
10-6
10-4
10-2
DPC Conc. (M)

Fig. 6(a)

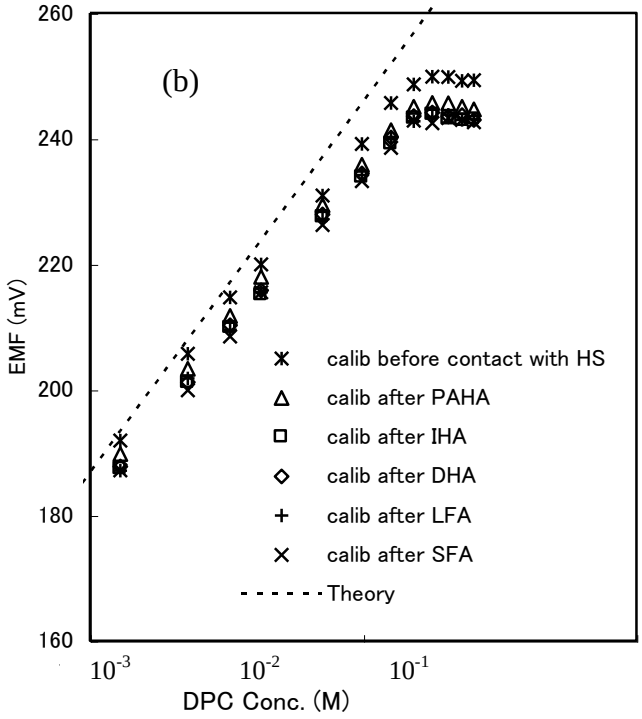

(b)
260
240
220
200
180
160
EMF (mV)
10^{-3}
10^{-2}
10^{-1}
DPC Conc. (M)
calib before contact with HS
calib after PAHA
calib after IHA
calib after DHA
calib after LFA
calib after SFA
Theory

Fig. 6(b)

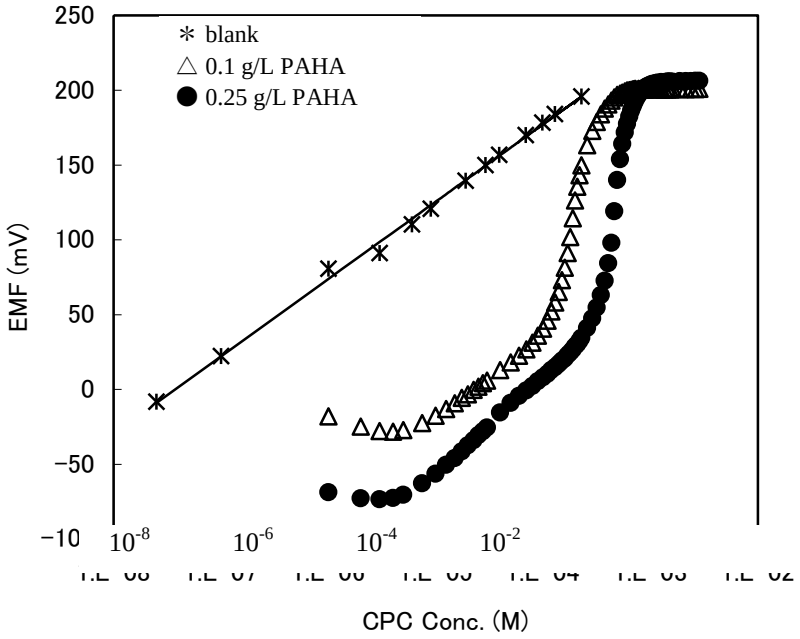

250
200
150
100
50
0
−50
−10
EMF (mV)
∗ blank
△ 0.1 g/L PAHA
● 0.25 g/L PAHA
10-8
10-6
10-4
10-2
CPC Conc. (M)

Fig. 7

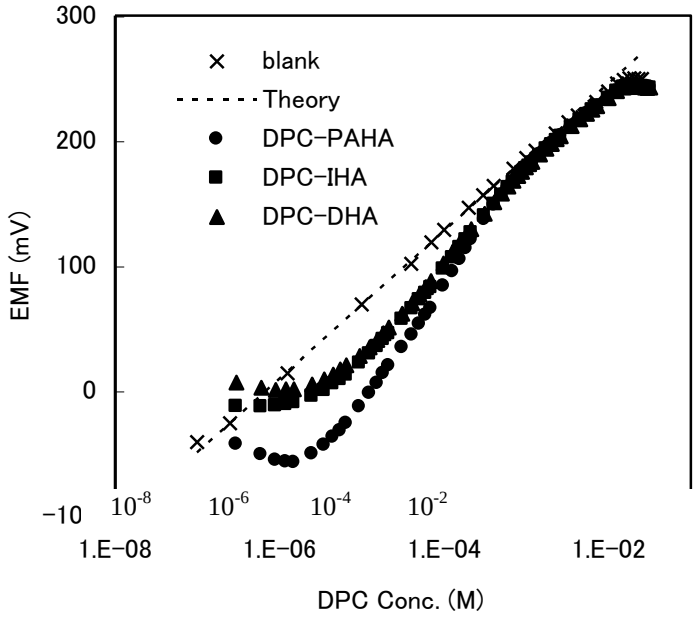
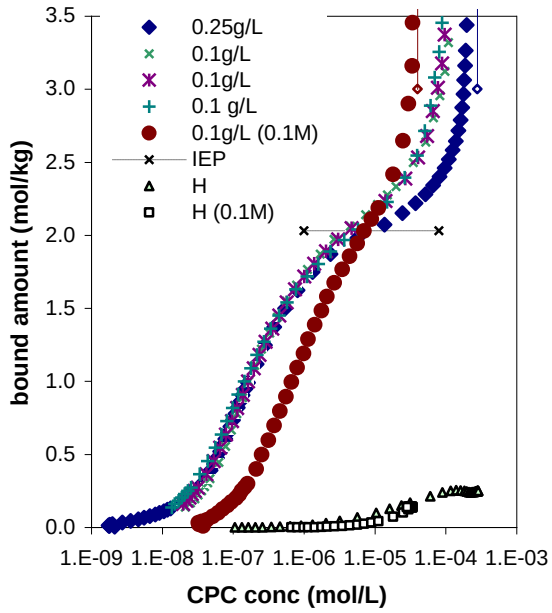
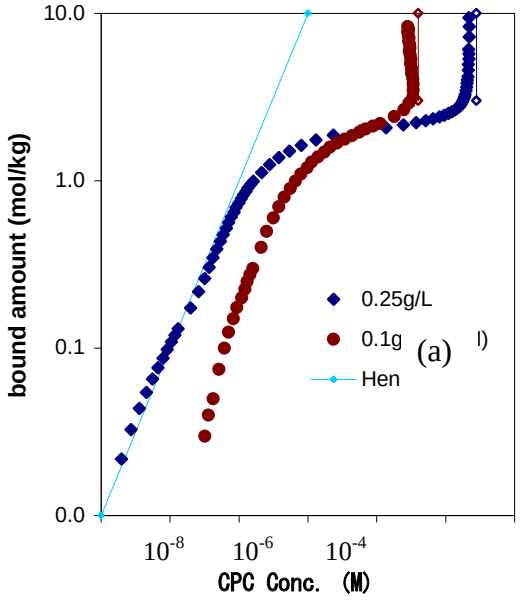

300
200
100
0
−10
EMF (mV)
blank
Theory
DPC−PAHA
DPC−IHA
DPC−DHA
10-8
10-6
10-4
10-2
1.E−08
1.E−06
1.E−04
1.E−02
DPC Conc. (M)

Fig. 8


0.25g/L
0.1g/L
0.1g/L
0.1 g/L
0.1g/L (0.1M)
IEP
H
H (0.1M)
bound amount (mol/kg)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.E-09 1.E-08 1.E-07 1.E-06 1.E-05 1.E-04 1.E-03
CPC conc (mol/L)


bound amount (mol/kg)
10.0
1.0
0.1
0.0
0.25g/L
0.1g
Hen
(a)
10-8
10-6
10-4
CPC Conc. (M)

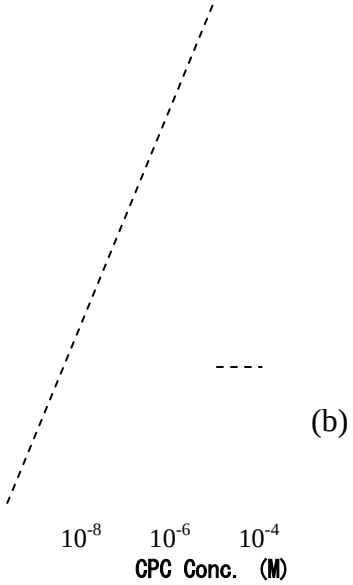

(b)
10-8
10-6
10-4
CPC Conc. (M)

Fig. 9

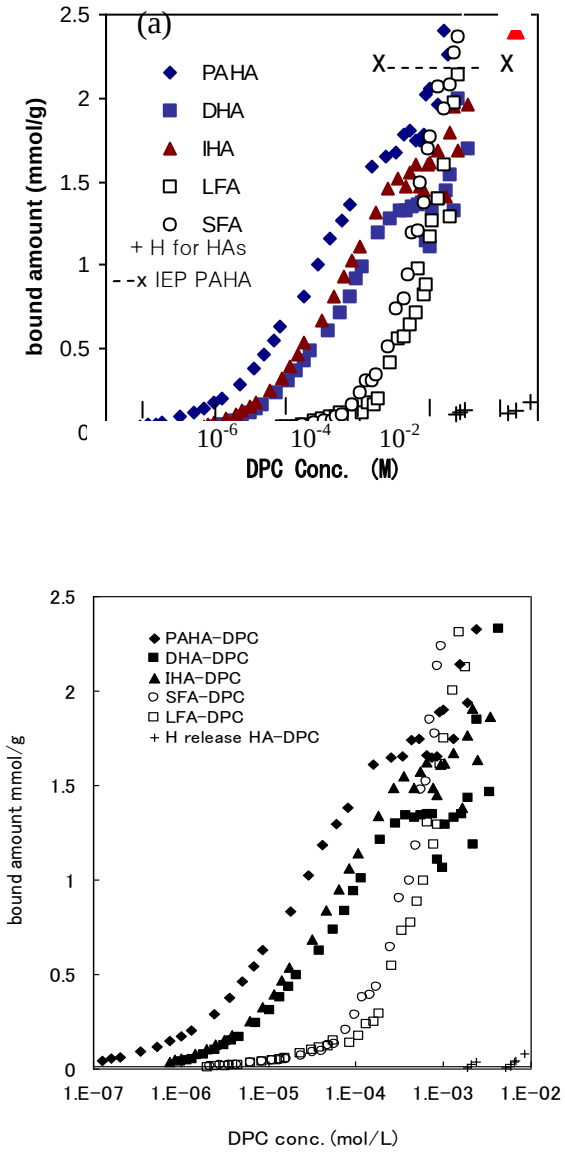

(a)
PAHA
DHA
IHA
LFA
SFA
+ H for HAs
--x IEP PAHA
bound amount (mmol/g)
DPC Conc. (M)
2.5
2
1.5
1
0.5
0
10-6
10-4
10-2
PAHA-DPC
DHA-DPC
IHA-DPC
SFA-DPC
LFA-DPC
+ H release HA-DPC
bound amount mmol/g
DPC conc. (mol/L)
1.E-07
1.E-06
1.E-05
1.E-04
1.E-03
1.E-02

Fig. 10(a)

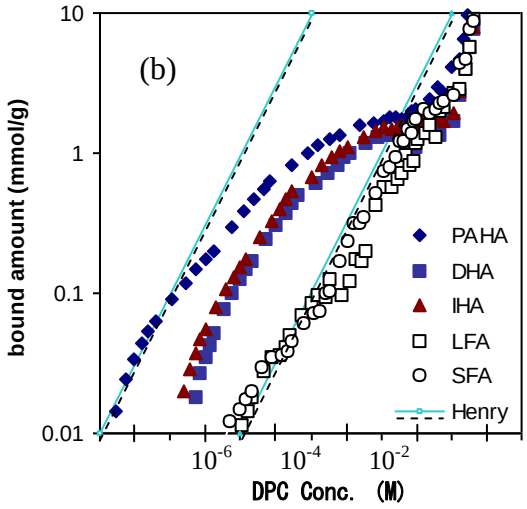
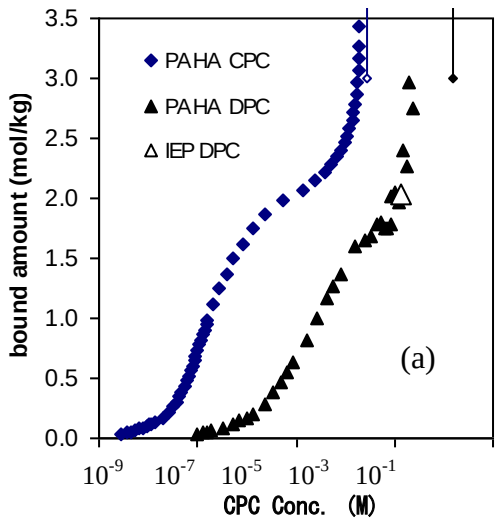

(b)
bound amount (mmol/g)
10
1
0.1
0.01
10^{-6}
10^{-4}
10^{-2}
DPC Conc. (M)
PAHA
DHA
IHA
LFA
SFA
Henry

Fig. 10(b)


3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
bound amount (mol/kg)
PAHA CPC
PAHA DPC
IEP DPC
(a)
10-9
10-7
10-5
10-3
10-1
CPC Conc. (M)

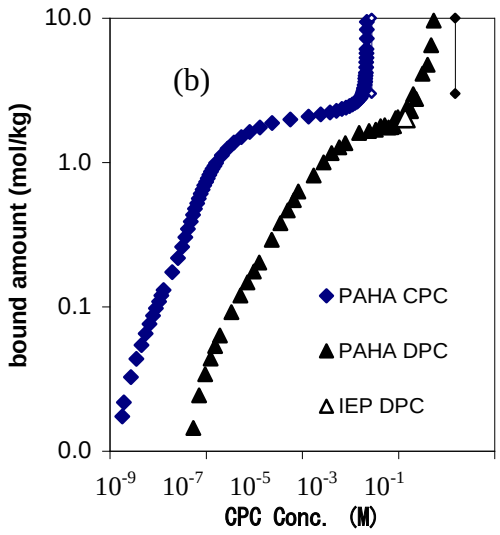

10.0
1.0
0.1
0.0
bound amount (mol/kg)
(b)
PAHA CPC
PAHA DPC
IEP DPC
10-9
10-7
10-5
10-3
10-1
CPC Conc. (M)

Fig.11