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## Polymeric sulfated surfactants with varied hydrocarbon tail: I. Synthesis, characterization, and application in micellar electrokinetic chromatography

The influence of surfactant hydrocarbon tail on the solute/pseudostationary phase interactions was examined. Four anionic sulfated surfactants with 8-, 9-, 10-, and 11-carbon chains having a polymerizable double bond at the end of the hydrocarbon chain were synthesized and characterized before and after polymerization. The critical micelle concentration (CMC), polarity, and aggregation number of the four sodium alkenyl sulfate (SAIS) surfactants were determined using fluorescence spectroscopy. The partial specific volume of the polymeric SAIS (poly-SAIS) surfactants was estimated by density measurements and capillary electrophoresis (CE) was employed for determination of methylene selectivity as well as for elution window. The CMC of the monomers of SAIS surfactants decrease with increase in chain length and correlated well when fluorescence method was compared to CE. The physicochemical properties (partial specific volume, methylene selectivity, electrophoretic mobility, and elution window) increased with an increase in chain length. However, no direct relationship was found between the aggregation number and the length of hydrophobic tail of poly-SAIS surfactants. These polymeric surfactants were then used as pseudostationary phases in micellar electrokinetic chromatography (MEKC) to study the retention behavior and selectivity factor of 36 benzene derivatives with different chemical characteristics. Although variation in chain length of the polymeric surfactants significantly affects the retention of nonhydrogen bonding (NHB) benzene derivatives, these effects were less pronounced for hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) benzene derivatives. Therefore, hydrophobicity of poly-SAIS surfactants was found to be a major driving force for retention of NHB derivatives. However, for several benzene derivatives (NHB, HBA, and HBD) significantly higher selectivity factor was observed with longest chain polymeric surfactant (e.g., poly(sodium 10-undecenyl sulfate), poly-SUS) compared to shorter chain polymeric surfactant (e.g., poly(sodium 7-octenyl sulfate), poly-SOcS). In addition, the effect of the surfactant hydrophobic chain was also found to have some impact on migration order of NHB, HBA, and HBD benzene derivatives.

**Keywords:** Hydrocarbon chain length / Hydrogen bond acceptor benzene derivatives / Hydrogen bond donor benzene derivatives / Micellar electrokinetic chromatography / Nonhydrogen bonding benzene derivatives / Polymeric surfactants  
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**Abbreviations:** HBA, hydrogen bond acceptor; HBD, hydrogen bond donor; NHB, nonhydrogen bonding; poly-SAIS, poly(sodium alkenyl sulfate); poly-SDeS, poly(sodium 9-decenyl sulfate); poly-SNoS, poly(sodium 8-nonenyl sulfate); poly-SOcS, poly(sodium 7-octenyl sulfate); poly-SUS, poly(sodium 10-undecenyl sulfate); SAIS, sodium alkenyl sulfates

## 1 Introduction

Conventional micelles, e.g., sodium dodecyl sulfate (SDS), have been extensively used in micellar electrokinetic chromatography (MEKC) since the introduction of the technique [1]. Although successfully used as carriers in many separation applications, conventional micelles have some disadvantages as pseudostationary phases in MEKC. (i) Conventional micelles require higher surfactant concentrations, i.e., at least 2–10 times the critical

micelle concentration (CMC), for effective separations. However, high concentration of surfactant results in an increase in ionic strength of the system. Thus, an applied voltage across the capillary causes Joule heating that causes the temperature inside the capillary to rise. The variation in temperature may give rise to serious irreproducibilities in the migration times due to a change in CMC of the surfactant and a change in viscosity of the separation buffer. (ii) CMC of surfactants is not only influenced by parameters such as surfactant concentration, pH and ionic strength of the running buffer but also when organic solvents, urea and cyclodextrins (CDs) are added to the micellar phases [2–4]. Consequently, any unexpected changes in these parameters will cause a change in micellar structure which in turn decreases the reproducibility of migration time in MEKC. (iii) Conventional micelles cannot tolerate high organic solvent content (required for separation of highly hydrophobic compounds) due to the presence of dynamic equilibrium between the micelle and free monomers [5–7]. (iv) Presence of low-molecular-weight surfactant monomers in separation buffer makes mass spectrometric detection difficult, *i.e.*, large background signals from monomers will interfere with most solutes under study in the low-molecular-mass region. In addition, accumulation of surfactants can cause fouling of the ion source, and may limit the sensitivity in electrospray ionization-mass spectrometry [8–11].

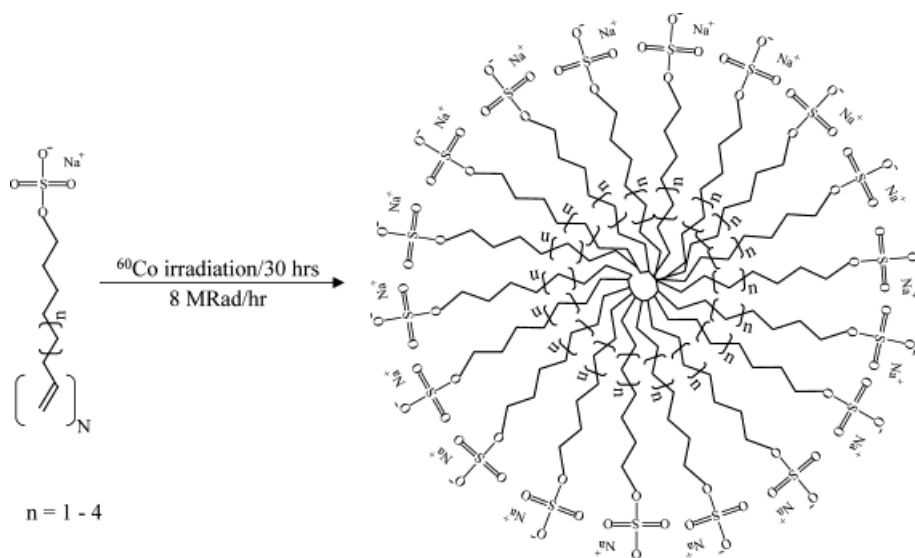
To overcome these drawbacks, polymeric surfactants (also called micelle polymers or molecular micelles) have been introduced as alternative pseudostationary phases to conventional micelles in MEKC [12–18]. Polymeric surfactants provide several advantages over conventional micelles. (i) They have zero CMC [6, 15], thus they may be used at low concentrations below the normal CMC of the monomer. (ii) Polymers are stable in the presence of high content of organic solvents. This is because monomers are covalently bonded together and organic additives do not disrupt the primary covalent structure of the micelle polymer. (iii) Due to their high molecular weight, polymeric surfactants can be conveniently used in MEKC-mass spectrometry applications without background interference from low-molecular-weight monomers.

The effect of hydrocarbon chain length of conventional surfactants on retention behavior in MEKC has been investigated by several authors who often came to different conclusions [19–22]. Crosby and El Rassi [19] utilized and compared a homologous series of cationic surfactants but no significant changes in selectivity were reported. Takeda *et al.* [20] studied the effect of alkyl chain length (*i.e.*, C11, C13, and C15) of sodium *N*-acyl sarcosinate surfactants using aniline derivatives and phthalate esters as test solutes in MEKC. They observed that the migration

window became wider as the hydrocarbon chain length of the surfactant decreased. This observation was mainly attributed to a decrease in electroosmotic velocity, which is caused by an increase of hydrophobic interaction of monomeric surfactants on capillary wall. Moreover, they observed an increase in capacity factors with an increase in alkyl chain length of surfactant. However, all three surfactants were found to give similar selectivity for hydrophilic solutes, but slightly different selectivity for hydrophobic solutes. Vitha and Carr [21] also examined the effect of hydrocarbon chain length on solute/surfactant interactions using three alkyl sulfate surfactants, *i.e.*, SDS, sodium decyl sulfate, and sodium octyl sulfate. The nature of solute/micelle interactions in these surfactant systems was found to be nearly equivalent. The influence of surfactant hydrophobic chain of sarcosinate surfactant systems on selectivity in MEKC was later examined by Trone and Khaledi [22] using a linear solvation energy relationships (LSER) model. They also investigated SDS and sodium tetradecyl sulfate to determine the chain length effect on selectivity for sodium sulfate surfactants. Their study showed that the chain length of surfactant could have an influence on selectivity in MEKC. However, this effect was reported to be mainly dependent on the nature of the surfactant head group. For example, sarcosinates, which have a larger organic head group, have more substantial effect on selectivity than sulfated surfactants.

To the author's knowledge, there have been only few reports on the use of polymeric surfactants with different alkyl chain length [23–27]. Tanaka and co-workers [23, 24] compared the use of polyallylamine (PAA)-supported pseudostationary phases with decyl groups (PAA-C<sub>10</sub>) and hexadecyl groups (PAA-C<sub>16</sub>) for separation of alkyl phenyl ketones and aromatic hydrocarbons. At lower ranges of methanol (*e.g.*, 20–40% v/v), PAA-C<sub>10</sub> provided a wider migration time window than PAA-C<sub>16</sub>. However, at higher concentrations of methanol (*e.g.*, > 60% v/v) reverse occurred [23, 24]. Recently, a new class of siloxane polymers of varying density and alkyl chain length with a range of mobilities was reported to provide different selectivity than conventional micelles [25, 26]. In addition, copolymers of 2-acrylamido-2-methyl-1-propanosulfonic acid (AMPS) and methacrylates with different pendant chain lengths (C<sub>8</sub>, C<sub>12</sub>, and C<sub>18</sub>) were investigated but no significant difference in chemical selectivity was reported [27]. However, these pseudostationary phases were found to show significant chemical selectivity differences from that of SDS.

In the present study, sodium 7-octenyl sulfate (SOcS), sodium 8-nonenyl sulfate (SNoS), sodium 9-decenyl sulfate (SDeS), and sodium 10-undecenyl sulfate (SUS) that have C8, C9, C10, and C11 hydrocarbon tails, respectively, were synthesized (Fig. 1). The four aforementioned



**Figure 1.** Scheme for polymerization of SAIS surfactants.  $N$  represents the number of repeating units (aggregation number) of the monomeric SAIS surfactants. The length of alkenyl hydrocarbon chain is represented by  $n$ , where  $n$  is 1, 2, 3, and 4 for SOcS, SNoS, SDeS, and SUS, respectively.

surfactants were then polymerized to form poly(sodium 7-octenyl sulfate) (poly-SOcS), poly(sodium 8-nonenyl sulfate) (poly-SNoS), poly(sodium 9-decenyl sulfate) (poly-SDeS), and poly(sodium 10-undecenyl sulfate) (poly-SUS). The CMC values of the monomeric surfactants, the aggregation numbers, partial specific volumes, mobility and elution window of polymeric sodium alkenyl sulfates (poly-SAIS) were determined using a variety of techniques. The surfactants were then evaluated as novel pseudostationary phases for MEKC of 36 benzene derivatives with a wide range of chemical interactions to observe the effect of the chain length on separation of the test solutes. To the best of our knowledge, this is the first systematic study of chain length effects on chemical selectivity in MEKC using polymeric sulfated surfactants. The effect of alkenyl chain length on chemical selectivity was evaluated using linear solvation energy relationships, which is the subject of part II of this series.

## 2 Materials and methods

### 2.1 Materials

All 36 benzene derivatives, alkyl phenyl ketones, 10-undecenyl alcohol, pyridine, and chlorosulfonic acid ( $\text{ClSO}_3\text{H}$ ) were obtained from Aldrich (Milwaukee, WI, USA). Disodium hydrogenphosphate ( $\text{Na}_2\text{HPO}_4$ ) and sodium dihydrogenphosphate ( $\text{NaH}_2\text{PO}_4$ ) were both obtained from EM Science (Gibbstown, NJ, USA). Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) was purchased from Lancaster Synthesis (Windham, NH, USA). The short-chain alkenyl alcohols, *i.e.*, 7-octenyl alcohol, 8-nonenyl alcohol, and 9-decenyl alcohol, were obtained from TCI America (Portland,

OR, USA). Deionized water was obtained by a water purification system from Millipore (Milford, MA, USA). All chemicals were used as received without further purification.

### 2.2 Synthesis and polymerization of sodium alkenyl sulfate surfactants

Sodium alkenyl sulfate (SAIS) monomers, which contain a sulfate ( $\text{SO}_4^-$ ) head group, with chain lengths of C8, C9, C10, and C11, were prepared according to a previously reported procedure [15–18]. The SAIS surfactants include SOcS, SNoS, SDeS, and SUS. Polymerization of SAIS monomers was achieved by preparing surfactant solutions at concentrations of nearly fourfold of CMC value of each surfactant (*i.e.*,  $\sim 1000$  mM SOcS,  $\sim 520$  mM SNoS,  $\sim 240$  mM SDeS, and  $\sim 120$  mM SUS) in triply deionized water. To find an optimum polymerization time, the surfactant solutions were exposed to a  $^{60}\text{Co}$ - $\gamma$ -radiation source (8 MRad/h) for different time periods of 18, 24, 30, and 36 h. The course of polymerization was monitored by  $^1\text{H}$ -NMR spectroscopy for absence of terminal methylene proton signals around 5–6 ppm. Polymerization was complete with exposure time of 30 h (total dose of 240 MRad) as verified by the complete absence of  $^1\text{H}$ -NMR peaks of methylene protons from the vinyl moiety. After irradiation, the polymerized surfactants, *i.e.*, poly-SOcS, poly-SNoS, poly-SDeS, and poly-SUS, were filtered and then dialyzed against triply deionized water using a regenerated cellulose dialysis membrane with 1000 Da molecular mass cutoff (Spectrum Laboratories, Rancho Dominguez, CA, USA) for 24 h. The dialyzed solutions were freeze-dried before use.

## 2.3 Characterization of polymeric surfactants

### 2.3.1 Determination of CMC using fluorescence spectroscopy and CE

Pyrene emission vibronic fine structure method was used for CMC determination of the monomeric SAIS surfactants [28–30]. This method is based on the surfactant concentration dependence of vibrational band intensities of fluorescence probe. A range of aqueous surfactant concentrations (0–310 mM SOcS, 0–180 mM SNoS, 0–90 mM SDeS, and 0–50 mM SUS) containing 0.001 mM pyrene was prepared. Fluorescence measurements were performed on a PTI QuantaMaster luminescence spectrometer (Model QM-1) (Photon Technology International, Ontario, CA, USA) at ambient temperature (~25°C). A concentration range of aqueous monomeric surfactant solutions (50–400 mM SOcS, 50–300 mM SNoS, 10–200 mM SDeS, and 5–50 mM SUS) was prepared. Measurement of CMC of each surfactant solution was carried out using Agilent CE (Agilent Technologies, Palo Alto, CA, USA). The capillary (50 μm ID, 367 μm OD) total length was 64.4 cm with an effective length of 56 cm. The capillary was activated with 1 M NaOH (30 min) and deionized water (15 min) before use. For a given surfactant solution, the capillary was rinsed for 3 min with 0.1 M NaOH, 3 min with triply deionized water and 10 min with pure surfactant solution. Once the capillary is filled with surfactant solution, a 20 kV voltage was applied for 5 min and the generated current was recorded for each concentration of the surfactant. When surfactant solution was changed, the capillary was reconditioned with triply deionized water (15 min), 0.1 M NaOH (10 min), triply deionized water (3 min), and with surfactant solution (10 min). The generated current was plotted against surfactant concentration.

### 2.3.2 Determination of aggregation number

The aggregation number,  $N$ , of the surfactants was determined by use of the fluorescence quenching method proposed by Turro and Yekta [31]. Fluorescence measurements were performed on a PTI QuantaMaster luminescence spectrometer at ambient temperature. Pyrene and cetylpyridinium chloride were used as fluorescent probe and quencher, respectively. A 1.0 mM stock solution of probe was prepared in methanol. A 2.0 mM stock solution of the quencher and a 1.0% w/v of each poly-SAIS surfactant solution were prepared separately in triply deionized water. A known volume of the probe stock solution (8 μL) was pipetted into a clean volumetric flask. Methanol was then evaporated under a gentle flow of air and then an appropriate volume of aqueous polymeric surfactant solution (4.0 mL) was added. The final concentrations of

the probe and the surfactant were 0.002 mM and 1.0% w/v, respectively (probe solution A). The solution was sonicated for 90 min and stored overnight in a dark place. Probe solution A was then divided in two halves. The first half (2.0 mL) was diluted with triply deionized water (2.0 mL) to give a 0.001 mM probe and 0.5% w/v surfactant (probe solution B). The second half (2.0 mL) was mixed with quencher stock solution (2.0 mL) to produce a solution of 1.0 mM quencher, 0.001 mM probe, and 1.0% w/v surfactant (quencher solution). The quencher solution was added to probe solution B in increasing volume increments of 40 μL and equilibrated for 20 min before collecting the fluorescent spectrum. Fluorescence intensity of the pyrene-surfactant mixture without the quencher was first measured. Decrease in emission intensity of the probe was recorded at 393 nm with the excitation at 335 nm after each aliquot of the quencher solution was added. The logarithm of fluorescence intensity ratio  $I_0/I_Q$  (where  $I_0$  and  $I_Q$  represent fluorescence intensities in the absence and the presence of quencher) was plotted against the quencher concentration,  $[Q]$ . The unknown micelle concentration in surfactant solution,  $[M]$ , was calculated using the following equation [31]:

$$\ln\left(\frac{I_0}{I_Q}\right) = \frac{[Q]}{[M]} \quad (1)$$

According to Eq. (1),  $I_0/I_Q$  vs.  $[Q]$  plot yields a straight line through the origin with a slope equal to  $1/[M]$ . The  $[M]$  is then related to the measurable total surfactant concentration,  $[S_{\text{tot}}]$ , aggregation number ( $N$ ), and CMC of the surfactant by Eq. (2).

$$[M] = \frac{[S_{\text{tot}}] - \text{CMC}}{N} \quad (2)$$

Rearranging Eq. (2) gives the following equation for calculation of  $N$  value.

$$N = \frac{1}{[M]} ([S_{\text{tot}}] - \text{CMC}) \quad (3)$$

Since polymeric surfactants have no CMC, all surfactant molecules should participate in micelle formation (*i.e.*,  $[S_{\text{tot}}] - \text{CMC} = [S_{\text{tot}}]$ ). Hence, Eq. (3) can be modified for polymeric surfactants as follows:

$$N = \frac{1}{[M]} [S_{\text{tot}}] \quad (4)$$

### 2.3.3 Determination of partial specific volume

Partial specific volume,  $\bar{v}$ , is defined as an increase in volume upon dissolving 1.0 g of a dry material (*e.g.*, surfactant) in a large volume of a solvent (*e.g.*, water) at constant temperature and pressure. The  $\bar{v}$  can be determined using Eq. (5) [32]:

$$\bar{v} = \left(\frac{1}{\rho}\right)_{\text{app}} - \frac{\partial \left(\frac{1}{\rho}\right)_{\text{app}}}{\partial W} \times W \quad (5)$$

where  $W$  is defined as the weight fraction of solvent and  $\rho$  is the density of surfactant solution. The term  $(1/\rho)_{\text{app}}$  is apparent specific volume of the surfactant. A graph of  $1/\rho$  against  $W$  allows the determination of  $\bar{v}$  from the  $y$ -intercept [33]. For density measurements, poly-SAIS surfactant solutions at eight different concentrations (*i.e.*, 0.0, 5.0, 10.0, 20.0, 30.0, 40.0, 60.0, and 70.0 mM) were prepared in triply deionized water. Density measurements were performed at 25°C using a high-precision digital DMA 4500 density meter (Paar Physica, Ashland, VA, USA).

## 2.4 CE separations

### 2.4.1 Instrumentation

An Agilent CE system (Agilent Technologies, Palo Alto, CA, USA) equipped with a diode array detector was used for MEKC separations. The system control and data handling were done using ChemStation software. The MEKC separations were performed in fused-silica capillaries (Polymicro Technologies, Tucson, AZ, USA) with dimensions of 64.4 cm total length (56 cm effective length)  $\times$  50  $\mu\text{m}$  ID (367  $\mu\text{m}$  OD). Identically activated four separate capillaries (cut to desire length from the same capillary bundle) were used for each surfactant system to eliminate possible cross contaminations.

### 2.4.2 Preparation of separation buffers and solute solution

A 100 mM solution of each of  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  was prepared by dissolving an appropriate amount of each in triply deionized water. A mixture of  $\text{NaH}_2\text{PO}_4$  solution (39.0 mL) and  $\text{Na}_2\text{HPO}_4$  solution (61.0 mL) provided a stock solution of 100 mM phosphate buffer with pH of 7.0. The solution of each pseudostationary phase was prepared by first dissolving 0.1 g of surfactant in 8.0 mL of deionized water and then adding 2.0 mL of the 100 mM stock phosphate buffer. Each surfactant solution was sonicated for 10 min, filtered through a 0.45  $\mu\text{m}$  syringe filter (Nalgene, Rochester, NY, USA), and then degassed for 3 additional min before use in MEKC experiments. All stock solute solutions were prepared in methanol with a concentration of the solutes ranging from 0.15 to 0.30 mM.

### 2.4.3 MEKC of benzene derivatives

Each new capillary was activated with 1 M NaOH (30 min at 40°C) and deionized water (20 min at 25°C) before use. For a typical MEKC run, the capillary was rinsed for 2 min

with 0.1 M NaOH followed by 3 min rinse with separation buffer between injections. Each day, the capillary was reactivated by rinsing with 1 M NaOH (10 min), triply deionized water (5 min), and the running buffer (5 min). Unless otherwise noted, the injection size was 50 mbar for 2 s.

## 2.5 Calculations

The capacity factor,  $k'$ , of neutral solutes was measured by use of the following equation [34]:

$$k' = \frac{t_{\text{R}} - t_{\text{eo}}}{t_{\text{eo}} \left[ 1 - \left( \frac{t_{\text{R}}}{t_{\text{psp}}} \right) \right]} \quad (6)$$

where  $t_{\text{R}}$ ,  $t_{\text{eo}}$  and  $t_{\text{psp}}$  are the migration times of retained solute, unretained solute (EOF), and the polymeric pseudostationary phase, respectively. Methanol was used to measure  $t_{\text{eo}}$ . An iteration method was used for  $t_{\text{psp}}$  determination [35]. Eight alkyl phenyl ketones (*i.e.*, acetophenone, propiophenone, butyrophenone, valerophenone, heptanophenone, octanophenone, decanophenone, and dodecanophenone) were used with each surfactant system under the same experimental conditions except 10% v/v acetonitrile was added to background electrolyte to increase the solubility of later eluting highly hydrophobic homologues. Then, the iteration method was applied (20–30 iterations) for  $t_{\text{psp}}$  determination of each surfactant system. By graphing  $\log k'$  versus carbon number of five alkyl benzenes (*i.e.*, benzene, toluene, ethylbenzene, propylbenzene, and butylbenzene), the methylene selectivity,  $\alpha_{\text{CH}_2}$ , (also called hydrophobic selectivity), was calculated from the antilogarithm of the slope of the regression line.

The apparent electrophoretic mobility of pseudostationary phase,  $\mu_{\text{app}}$ , was calculated at 25°C by use of Eq. (7):

$$\mu_{\text{app}} = \frac{l_t l_d}{V t_{\text{psp}}} \quad (7)$$

where  $l_t$  is the total length of capillary (cm),  $l_d$  is the length of capillary from injector to detector (cm), and  $V$  is the applied voltage (V). The retention times of pseudostationary phases were measured in s. To calculate the electroosmotic mobility,  $\mu_{\text{eo}}$ , of the buffer solution,  $t_{\text{psp}}$  term in Eq. (7) was replaced with  $t_{\text{eo}}$  as shown in Eq. (8).

$$\mu_{\text{eo}} = \frac{l_t l_d}{V t_{\text{eo}}} \quad (8)$$

By solving Eqs. (7) and (8), the effective electrophoretic mobility of pseudostationary phase ( $\mu_{\text{ep}}$ ) was calculated using Eq. (9):

$$\mu_{\text{ep}} = \mu_{\text{app}} - \mu_{\text{eo}} \quad (9)$$

The  $k'$  [Eq. (6)], is related to distribution coefficient,  $K$ , by

$$k' = K\beta = K \frac{V_{\text{psp}}}{V_{\text{aq}}} \quad (10)$$

where  $\beta$ ,  $V_{\text{psp}}$ , and  $V_{\text{aq}}$  are the phase ration, the volumes of polymeric pseudostationary phase and aqueous phase, respectively. The  $\beta$  for conventional micellar systems can be calculated by using following relationship:

$$\beta = \frac{\bar{v}([S_{\text{tot}}] - \text{CMC})}{1 - \bar{v}([S_{\text{tot}}] - \text{CMC})} \quad (11)$$

where  $\bar{v}$ ,  $[S_{\text{tot}}]$ , and CMC are the partial specific volume, the total concentration, and the CMC of the pseudostationary phase, respectively. Equation (11) can be simplified for polymeric pseudostationary phases due to a zero CMC value:

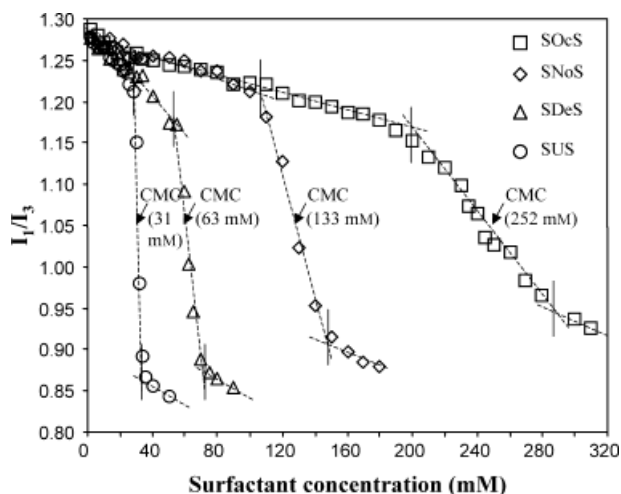
$$\beta = \frac{\bar{v}[S_{\text{tot}}]}{1 - \bar{v}[S_{\text{tot}}]} \quad (12)$$

The selectivity factor,  $\alpha$ , between neighboring solutes is determined from the ratio of the capacity factor of later eluting solute,  $k'_2$ , to the capacity factor of earlier eluting solute,  $k'_1$ . Finally, the elution window was calculated using the ratio of  $t_{\text{psp}}/t_{\text{eo}}$ .

### 3 Results and discussion

#### 3.1 Effect of hydrophobic chain on CMC

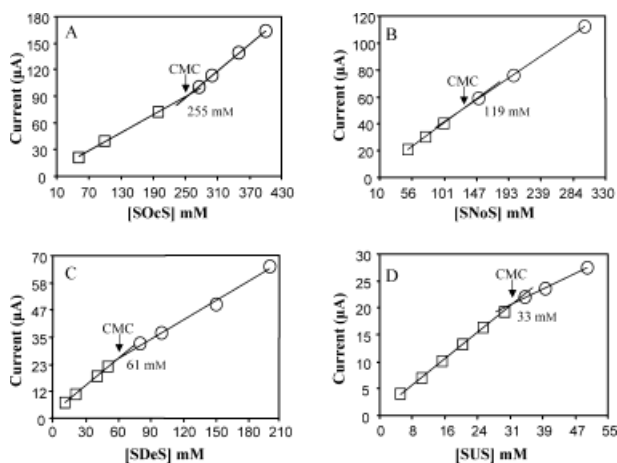
Pyrene has been commonly used as fluorescence probe; its solution shows five vibrational bands in fluorescence spectra. Intensity ratio of the first band ( $I_1$  at 373 nm) and the third band ( $I_3$  at 384 nm) shows a strong dependence on hydrophobicity of the pyrene microenvironment [28]. For example,  $I_1/I_3$  is 0.6, 1.1, and 1.8 in hydrocarbon solvents, ethanol, and water, respectively [36, 37]. Below CMC (*i.e.*, in the absence of micelles), pyrene senses a polar microenvironment; therefore the  $I_1/I_3$  value is expected to be high. In the presence of micelles (*i.e.*, above the CMC), pyrene is solubilized in the less polar micelle interior and senses more hydrophobic environment; hence the ratio  $I_1/I_3$  decreases. Upon formation of micelles, variations occur in  $I_1/I_3$  ratio of pyrene fluorescence spectra. As seen in Fig. 2, there are two distinct deviations (breaks) in  $I_1/I_3$  vs. surfactant concentration plot. The concentration range (or transition region) corresponding to between these two breaks is believed to be micellization region. It is proposed that the micellar nucleus is formed at the middle point of this transition region (*i.e.*, between the two break points). Thus, the concentration corresponding to the middle point of this transition region is accepted to be CMC. These results support the hypothesis that CMC is not a sharp transition point but a concentration region [38]. Our data suggest that each surfactant system has a different micellization concentration range (MCR). The MCR seems to be dependent on the nature of the surfactant. For instance, MCR for SUS, SDeS, SNoS, and SOcS is between 29–



**Figure 2.** Quotient of pyrene vibrational band intensities ( $I_1/I_3$ ) as a function of monomeric SAIS surfactant concentration. The CMC values and legends are shown in the plot.

34, 57–67, 107–143, and 185–284 mM, respectively. These MCR values are obtained from three linear line equations of three linear plots, *i.e.*, before the first break point, after the second break point, and between these two break points. The data show that the micellization process of relatively more hydrophobic surfactants (*e.g.*, SUS) is completed in a relatively narrow concentration range (5 mM) while that of less hydrophobic surfactant (*e.g.*, SOcS) is completed in a wider concentration range (99 mM). This is possibly due to different micellization processes of the surfactants with different carbon chains. Apparently, the dynamic of SUS monomers to and from the micelle seems to be faster than that of SOcS monomers. Thus, the ability of a hydrocarbon chain to decrease the  $I_1/I_3$  ratio follows the order: C11 > C10 > C9 > C8 which is in agreement with hydrophobic properties [32]. It is worth noting that the  $I_1/I_3$  ratio is expected to be constant up to the first break point. However, a slight but gradual decrease in  $I_1/I_3$  ratio is observed in all surfactant systems, which can be attributed to the presence of hydrophobic impurities or to pre-micellar aggregates (due to slightly higher pyrene concentration). However, as pointed out by one of the reviewers, pre-micellar aggregates can be prevented by using lower pyrene concentration.

To confirm the validity of the fluorescence method, CE method was also used for CMC determination of four SAIS surfactants (Figs. 3 A–D). The generated current at a constant applied voltage increased linearly with an increase in surfactant concentration. At a certain concentration, the line for each surfactant deviated from linearity due to micellar formation. The concentration corresponding to this deviation point is assumed to be the CMC. As



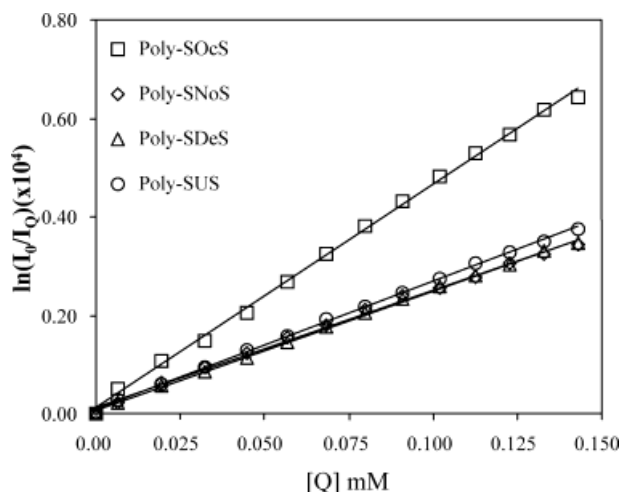
**Figure 3.** Change in capillary current as a function of (A) pure monomeric SOcS, (B) SNoS, (C) SDeS, and (D) SUS surfactant concentrations. Conditions: +20 kV applied voltage; 50  $\mu\text{m}$  ID  $\times$  64.4 cm (56 cm effective length). The CMC values are shown in the plot.

seen in Fig. 3 A, the curve shows a different pattern for SOcS surfactant (deviates sharply upwards unlike the other three surfactants). This may be due to the dissimilarity in micellar size and/or structure between SocS and other three surfactants (Figs. 3 B–D).

The CMC values determined with the fluorescence and CE method are in good agreement (Figs. 2 and 3). The CMC values determined with these two methods indicate that an increase in hydrophobicity (*i.e.*, addition of an extra  $\text{CH}_2$  group) favors formation of micelles, *i.e.*, lowers the CMC value by a factor of 2. This phenomenon agrees well with the literature. For example, the CMC values of alkyl sulfates with 8- and 10-carbon chain were reported as 133 and 33 mM, respectively, [21]. In this work, the CMC of alkenyl sulfates with the same carbon chain were found to be 250 and 61 mM, respectively, which are about two fold higher than that of saturated alkyl sulfates with the same carbon atoms [21, 38]. This divergence is not surprising because the double bond in alkenyl sulfates decreases the hydrophobicity of surfactant and hence an expected increase in the CMC.

### 3.2 Effect of hydrophobic chain on aggregation number of polymeric surfactants

Fluorescence spectra of pyrene were recorded at several quencher, cetylpyridinium chloride (CPyCl), concentrations. An increase in CPyCl concentration decreases the fluorescence intensity of pyrene molecule in aqueous poly-SAIS surfactant solution. The aggregation number,  $N$ , of each poly-SAIS surfactant was obtained from the slope of the  $\ln(I_0/I_Q)$  versus  $[Q]$  plot. As shown in Fig. 4,



**Figure 4.** Plots of  $\ln I_0/I_Q$  versus the quencher concentration,  $[Q]$ , for poly-SAIS surfactants. Legends are shown in the plot.

the slopes of the line for poly-SUS, poly-SDeS, and poly-SNoS are very similar while that of poly-SOcS is significantly higher. The experimental  $N$  values of poly-SAIS surfactants are listed in Table 1. Evaluation of  $N$  values suggests that there is no distinguishable correlation between the length of carbon chains and  $N$  values. While for poly-SOcS, which displayed the  $N$  value to be a factor of 2 higher than the others, no clear explanation is available currently to justify the  $N$  trend of these polymeric surfactants. The determined  $N$  values of poly-SAIS surfactants contradict with the findings in the literature that  $N$  values increase with increasing chain length of the hydrophobic moiety of the conventional micelles with the same head group. For example, the  $N$  values of 8-, 9-, 10-, and 12-hydrocarbon chain length sulfated micelles are 20, 31, 43, and 60, respectively [38]. The differences between the trends in  $N$  values of unpolymerized vs. polymeric surfactants are not surprising because during the polymerization the surfactant aggregates may undergo different kinetic process that may generate different aggregates.

### 3.3 Effect of hydrophobic chain on partial specific volume, polarity, and methylene selectivity of polymeric surfactants

The  $\bar{v}$  values of poly-SAIS surfactants were determined using Eq. (5). To obtain  $\bar{v}$ , the volume change of a solvent needs to be measured upon adding an infinitesimal amount of the surfactant. Direct measurement of such small volume change is nearly impossible. This, however, can be achieved by measuring the densities of a series of solutions, in which only the mass of the solute is varied. Figure 5 shows plots of inverse of the density ( $1/\rho$ ) against

**Table 1.** Physicochemical properties of the poly-SAIS surfactants

Characteristics of the polymeric surfactants	Poly-SAIS surfactants			
	Poly-SOcS (C8) <sup>a)</sup>	Poly-SNoS (C9)	Poly-SDeS (C10)	Poly-SUS (C11)
Chemical formula	C <sub>8</sub> H <sub>15</sub> NaO <sub>4</sub> S	C <sub>9</sub> H <sub>17</sub> NaO <sub>4</sub> S	C <sub>10</sub> H <sub>19</sub> NaO <sub>4</sub> S	C <sub>11</sub> H <sub>21</sub> NaO <sub>4</sub> S
Molecular mass (g·mol <sup>-1</sup> )	230.26 <sup>b)</sup> 2.28 × 10 <sup>4</sup> <sup>c)</sup>	244.28 1.20 × 10 <sup>4</sup>	258.31 1.21 × 10 <sup>4</sup>	272.34 1.31 × 10 <sup>4</sup>
CMC (mM)	0 <sup>d)</sup>	0	0	0
Aggregation number <sup>e)</sup> ( <i>N</i> )	99 (±2.5)*	49 (±1.9)	47 (±1.5)	48 (±2.0)
Partial specific volume <sup>f)</sup> , $\bar{v}$ (mL·g <sup>-1</sup> )	0.692 (±0.003)	0.717 (±0.002)	0.736 (±0.002)	0.775 (±0.003)
Electroosmotic mobility <sup>g), h)</sup> , $\mu_{eo}$ (10 <sup>-4</sup> cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	4.15 (±0.04)	4.01 (±0.03)	4.23 (±0.07)	4.11 (±0.03)
Apparent electrophoretic mobility <sup>g), i)</sup> , $\mu_{app}$ (10 <sup>-6</sup> cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	56.28 (±2.84)	29.16 (±2.46)	17.41 (±1.25)	9.64 (±0.7)
Effective electrophoretic mobility <sup>g), j)</sup> , $\mu_{ep}$ (10 <sup>-4</sup> cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	-3.58 (±0.04)	-3.72 (±0.03)	-4.07 (±0.06)	-4.02 (±0.04)
Methylene-group selectivity <sup>g), k)</sup> ( $\alpha_{CH_2}$ )	1.30 (±0.02)	1.39 (±0.03)	1.44 (±0.02)	1.54 (±0.04)
Migration-time window <sup>g), l)</sup> ( $t_{psp}/t_{eo}$ )	7.4 (±0.2)	13.8 (±0.8)	24.4 (±1.4)	42.6 (±2.7)
Polarity <sup>m)</sup> ( $I_1/I_3$ ratio)	1.45 (±0.01)	1.38 (±0.02)	1.27 (±0.01)	1.20 (±0.01)

a) Number of carbons in the hydrocarbon tail of each surfactant are shown in parentheses

b) Molecular mass of a single surfactant monomer

c) Molecular mass of polymeric surfactant =  $N \times$  molecular weight of monomer

d) Polymeric surfactants do not have a CMC (*i.e.*, CMC = 0)

e) Determined in deionized water by fluorescence quenching method at ambient temperature (~25°C)

f) Calculated from density values of surfactant solutions

g) Data were collected with 64.4 cm (56 cm effective length) × 50 μm ID capillary with an applied voltage of +30 kV using a running buffer containing 20 mM phosphate buffer (pH 7.0), 0.5% w/v polymeric surfactant, at 25°C.

h) Calculated from Eq. (8)

i) Calculated from Eq. (7)

j) Calculated from Eq. (9)

k) Calculated from the antilogarithm of the slope of the regression line of log  $k'$  vs. carbon number of alkyl benzene homologues

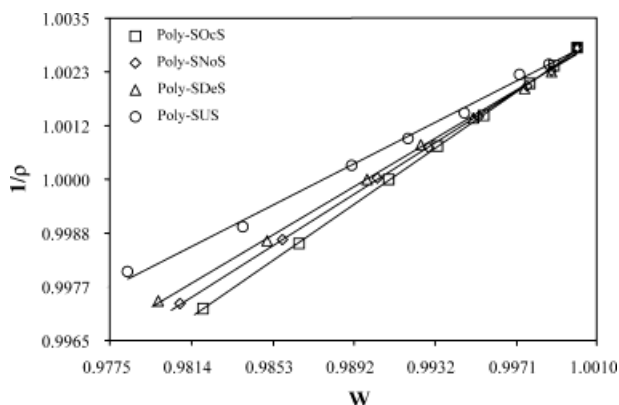
l) Obtained from the ratio of micellar phase retention time over electroosmotic retention time

m) Determined by fluorescence spectroscopy using the ratio of the first and the third band of pyrene molecule in a 0.5% w/v surfactant solution

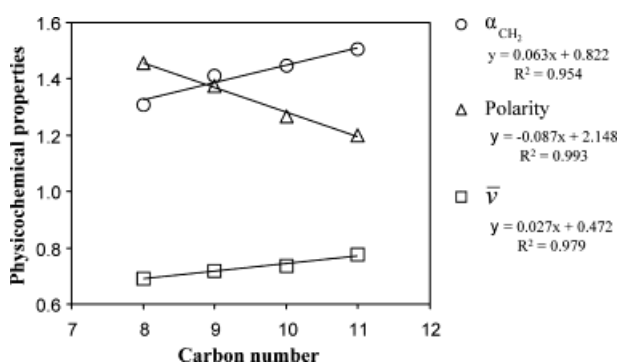
\* Standard deviations are given in parentheses.

W at 25°C. It can be seen from the  $\bar{v}$  values (Table 1) that an increase in carbon chain length of polymeric surfactant leads to an increase in  $\bar{v}$  value (*i.e.*,  $\bar{v}_{C11} > \bar{v}_{C10} > \bar{v}_{C9} > \bar{v}_{C8}$ ). The data suggest that surfactants with a shorter hydrocarbon chain (*e.g.*, poly-SOcS) have a relatively more compact structure than those with a longer hydrocarbon chain (*e.g.*, poly-SUS). Accordingly, poly-SUS micelles have a more open and flexible structure among all surfactants.

The  $\alpha_{CH_2}$  values for the four polymeric surfactant systems at 25°C are listed in Table 1. As expected, the  $\alpha_{CH_2}$  value increases with an increase in carbon chain length of the polymers. The longest alkyl chain poly-SUS provided the most hydrophobic environment (highest  $\alpha_{CH_2}$  value) and poly-SOcS provided the least hydrophobic environment for alkylbenzene molecules. The  $\alpha_{CH_2}$  values for poly-SAIS surfactants agree well with polarity values obtained



**Figure 5.** Plot of  $1/\rho$  (mL/g) as a function of  $W$  [( $g_{\text{solvent}}/g_{\text{solvent}} + g_{\text{surfactant}}$ )]. Legends are shown in the plot.



**Figure 6.** Change in methylene selectivity, polarity, and partial specific volume of poly-SAIS surfactants as a function of carbon number of the hydrocarbon tail.

from fluorescence measurements. Relationship between  $\alpha_{\text{CH}_2}$ ,  $\bar{v}$ , and polarity as a function of carbon number of polymeric surfactants is plotted in Fig. 6 to show correlations between these three parameters.

### 3.4 Effect of hydrophobic chain on electrophoretic mobility and elution window

The electroosmotic mobility ( $\mu_{\text{eo}}$ ), apparent electrophoretic mobility ( $\mu_{\text{app}}$ ), and effective electrophoretic mobility ( $\mu_{\text{ep}}$ ) as well as the migration-time window of poly-SAIS surfactants are listed in Table 1. No correlation was observed between the length of carbon chain and  $\mu_{\text{eo}}$ . It is worth mentioning that poly-SDeS has the highest and poly-SNoS has the lowest  $\mu_{\text{eo}}$  value, while poly-SOcS and poly-SUS have modest but very similar  $\mu_{\text{eo}}$  values. This may be attributed to a possible viscosity difference between these polymeric surfactant solutions. Poly-SUS and poly-SDeS have very similar but highest effective mobility. On the other hand, as expected, poly-SOcS has the lowest, and poly-SNoS has an effective mobility larger

than poly-SOcS but smaller than poly-SUS or poly-SDeS. Furthermore, the determined elution window follows the decreasing order: poly-SUS > poly-SDeS > poly-SNoS > poly-SOcS. Thus, highly hydrophobic surfactant (poly-SUS) provides the widest, while the least hydrophobic surfactant (poly-SOcS) provides the narrowest elution window.

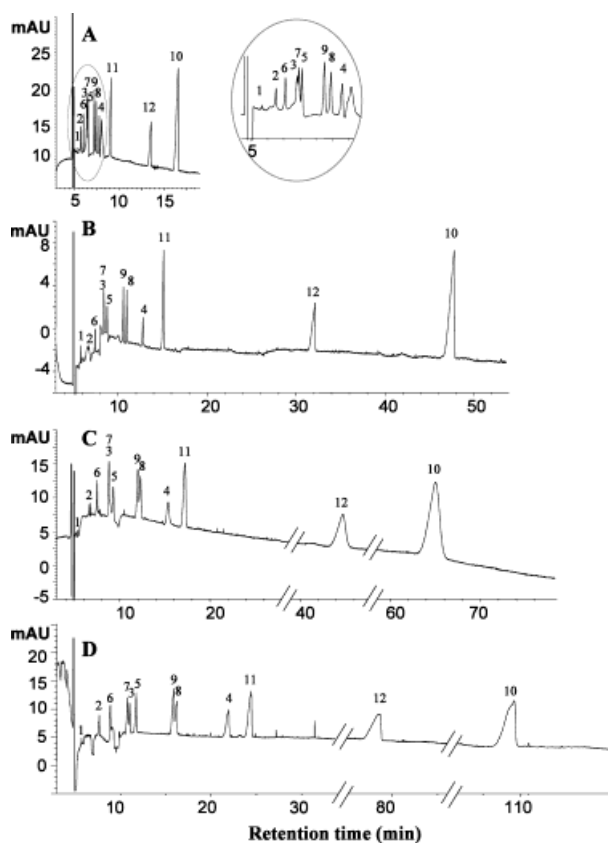
### 3.5 Effects of hydrophobic chain in micellar electrokinetic chromatography

To understand the mechanisms of solute interaction with the four polymeric pseudostationary phases, the retention behavior of 36 benzene derivatives with different properties was studied. The benzene derivatives in Table 2 can be characterized as nonhydrogen bond donors (NHBs, solutes 1–12), hydrogen bond acceptors (HBAs, solutes 13–24), and hydrogen bond donors (HBD, solutes 25–36). The NHB solutes that include alkyl- and halo-substituted benzenes and polyaromatic hydrocarbons do not have any hydrogen-bonding functional groups; however, due to the aromatic ring(s), they are considered to be weak hydrogen bond acceptors. The HBA solutes possess only hydrogen bond accepting functional groups on the aromatic ring, whereas, HBD solutes have both hydrogen bond donating and hydrogen bond accepting functional groups. The capacity factors,  $k'$ , of all 36 test solutes were calculated using Eq. (6). Once the phase ratio ( $\beta$ ) is known (Eq. 12), the partitioning coefficients,  $K$ , of the solutes were then calculated using Eq. (10). The test solutes and their  $K$  values in poly-SAIS surfactants are presented in Table 2. The  $K$  values of all NHB solutes increase with increasing hydrocarbon chain length of polymeric surfactant. There are, however, some exceptions in HBA and HBD solutes. For example, the  $K$  values of acetophenone, benzonitrile, nitrobenzene, methylbenzoate, ethylbenzoate, 4-nitrotoluene, benzyl alcohol, phenol, and 4-methylphenol in poly-SNoS are slightly higher than those in poly-SDeS.

Four micellar electrokinetic chromatograms of 12 NHB benzene derivatives are depicted in Fig. 7. The identities of these 12 NHB solutes are listed in Table 2 along with their  $K$  values. Some changes in elution order were observed. For example, as shown in Fig. 7, bromobenzene (solute 7) eluted before ethyl benzene (solute 3) in poly-SUS, while the elution order of these two solutes reverses when poly-SOcS is used as a pseudostationary phase. However, these two solutes remained unresolved in poly-SNoS and poly-SDeS. In addition, note that iodobenzene (solute 8)/4-chlorotoluene (solute 9) pair is well resolved in poly-SOcS and poly-SNoS, whereas the same pair is partially resolved in poly-SDeS and poly-SUS. Although other NHB benzene derivatives do not

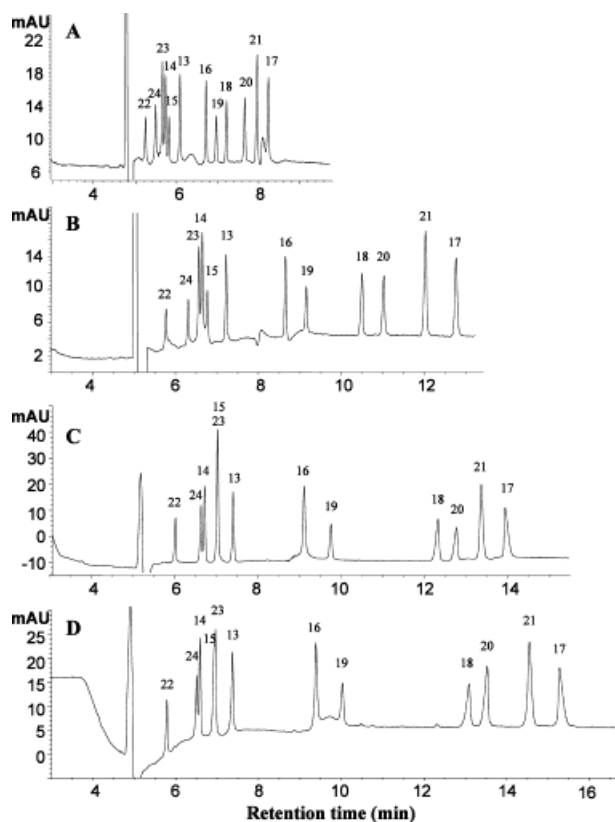
**Table 2.** NHB, HBA, and HBD benzene derivatives and their distribution coefficients (*K*) in poly-SAIS

Solutes	Surfactant systems			
	Poly-SOcS	Poly-SNoS	Poly-SDeS	Poly-SUS
<b>NHB solutes</b>				
1 Benzene	113	174	190	211
2 Toluene	214	379	439	514
3 Ethylbenzene	374	755	922	1176
4 Propylbenzene	730	1946	2448	3746
5 <i>p</i> -Xylene	409	846	1030	1314
6 Chlorobenzene	283	512	630	746
7 Bromobenzene	385	755	922	1128
8 Iodobenzene	637	1414	1723	2302
9 4-Chlorotoluene	585	1311	1654	2229
10 Biphenyl	3967	25205	30312	45194
11 Naphthalene	1090	2700	2909	4441
12 1-Methyl-naphthalene	2609	10284	12409	23477
<b>HBA solutes</b>				
13 Acetophenone	312	460	419	459
14 Benzonitrile	226	336	289	312
15 Nitrobenzene	246	362	347	377
16 Methyl benzoate	468	778	746	848
17 Ethyl benzoate	879	1783	1709	2072
18 4-Chloroanisole	598	1211	1371	1597
19 4-Nitrotoluene	532	893	864	974
20 4-Chloroacetophenone	718	1339	1456	1686
21 Methyl 2-methylbenzoate	802	1592	1587	1910
22 Phenyl acetate	111	153	156	164
23 3-Methylbenzyl alcohol	208	319	347	381
24 Phenethyl alcohol	169	264	272	297
<b>HBD solutes</b>				
25 Benzyl alcohol	111	156	146	171
26 Phenol	111	156	146	171
27 4-Methylphenol	207	319	312	376
28 4-Ethylphenol	379	672	676	842
29 4-Fluorophenol	144	203	200	231
30 4-Chlorophenol	328	559	609	729
31 4-Bromophenol	450	812	896	1099
32 4-Chloroaniline	259	452	502	599
33 3-Chlorophenol	336	559	597	712
34 3-Methylphenol	207	319	312	368
35 3-Bromophenol	450	795	857	1046
36 3,5-Dimethylphenol	379	672	676	842

**Figure 7.** Comparison of (A) poly-SOcS, (B) poly-SNoS, (C) poly-SDeS, and (D) poly-SUS for separation of NHB benzene derivatives. MEKC separation conditions: 0.5% w/v each surfactant in 20 mM phosphate buffer (pH 7.0); pressure injection, 50 mbar for 2 s; applied voltage, +30 kV; temperature, 25°C; UV detection, 200 nm. The inset represents the expanded electrokinetic chromatogram of the first nine solutes in poly-SOcS surfactant system. Peak identifications are same as listed in Table 2.

show any additional elution order change, it does improve the separation selectivity between later eluting NHB benzene derivatives. Moreover, significantly longer retention times of later eluting NHB solutes (*i.e.*, solutes 10–12) are realized upon varying the chain length of the poly-SAIS surfactants.

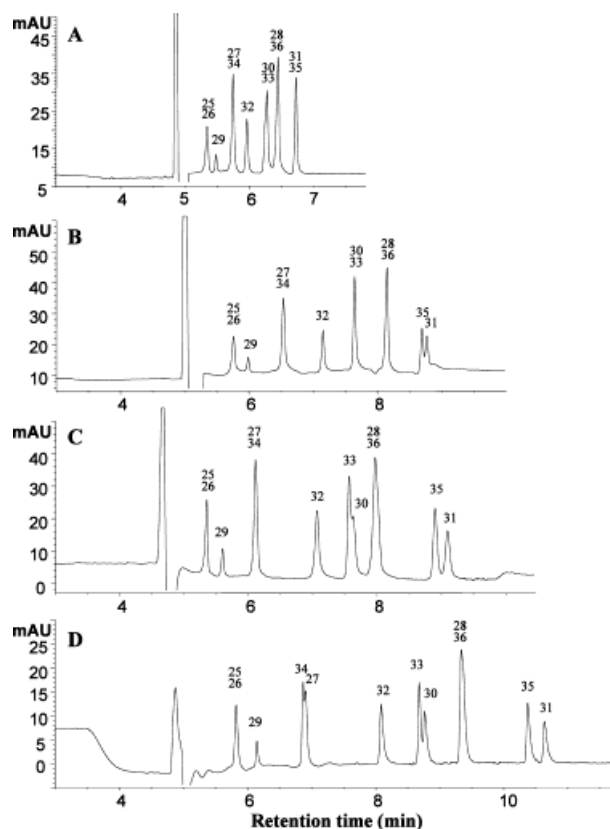
The major difference between the four poly-SAIS surfactants is the separation selectivity or resolution between neighboring peak pairs of HBA (Fig. 8) and HBD (Fig. 9) solutes. The HBA solutes have essentially the same migration orders among all four surfactant systems with few exceptions. For example, peak 23 (3-methylbenzyl alcohol) eluted before peak 14 (benzonitrile) in both poly-SOcS (Fig. 8A) and poly-SNoS (Fig. 8B). However, using poly-SDeS (Fig. 8C) and poly-SUS (Fig. 8D), the order of these two HBA solutes reversed, the former moved ahead of the later, and merged with peak 15 (nitrobenzene).



**Figure 8.** Comparison of (A) poly-SOcS, (B) poly-SNoS, (C) poly-SDeS, and (D) poly-SUS for separation of HBA benzene derivatives. The MEKC separation conditions are as in Fig 7. Peak identifications are the same as listed in Table 2.

Some selectivity differences between the polymeric surfactants toward the later eluting HBA solutes are observed. For example, the selectivity factor ( $\alpha = k'_2/k'_1$ ) between solute 18 (4-chloroanisole) and solute 19 (4-nitrotoluene) is found to be 1.12, 1.36, 1.59, and 1.64 in poly-SOcS, poly-SNoS, poly-SDeS, and poly-SUS systems, respectively. Poly-SUS and poly-SDeS have the same  $\alpha$  (1.06) toward the pair of solute 18/solute 20, but poly-SOcS and poly-SNoS show higher  $\alpha$  values (1.20 and 1.11) for the same solute pair. Similarly, the  $\alpha$  value between solute 20 (4-chloroacetophenone) and solute 21 (methyl 2-methylbenzoate) are 1.12, 1.19, 1.09, and 1.13 in poly-SOcS, poly-SNoS, poly-SDeS, and poly-SUS surfactant systems, respectively. Some minor differences in  $\alpha$  between the four polymeric surfactants were also observed toward solute pairs of solute 17 (ethylbenzoate)/solute 21 and solute 16 (methylbenzoate)/solute 19.

The HBD analytes showed similar migration order in all surfactant systems. Although, the solute pairs of 25/26 (benzyl alcohol/phenol) and 28/36 (4-ethylphenol/3,5-dimethylphenol) were not resolved in all four surfactant



**Figure 9.** Comparison of (A) poly-SOcS, (B) poly-SNoS, (C) poly-SDeS, and (D) poly-SUS for separation of HBD benzene derivatives. The MEKC separation conditions are as in Fig 7. Peak identifications are the same as listed in Table 2.

systems, some differences in  $\alpha$  values were obtained. The solute pair 30/33 (4-chlorophenol/3-chlorophenol) was fairly resolved in poly-SUS and poorly resolved in poly-SDeS, but not resolved in poly-SNoS and poly-SOcS. In addition, solute pair 27/34 (4-methylphenol/3-methylphenol) was slightly resolved in poly-SUS while comigrated in other three poly-SAIS surfactants. Similarly, solute pair 31/35 (4-bromophenol/3-bromophenol) is baseline-resolved in poly-SDeS and poly-SUS, partially resolved in poly-SNoS and coeluted in poly-SOcS.

#### 4 Concluding remarks

The unsaturated SAIS surfactants with hydrocarbon tails of 8, 9, 10, and 11 carbon atoms were synthesized. The CMC values determined with fluorescence and CE methods correlated well and suggested that an addition of an extra methylene group to the hydrocarbon chain of monomeric sulfated surfactant lowered the CMC value by a factor of 2. In addition, the experimental CMC data obtained in this work showed that the CMC values of

unsaturated alkenyl sulfate surfactants are about twofold higher than the reported CMC of saturated alkyl sulfates with the same carbon atoms [21, 38]. All four monomers of SAIS were polymerized in the micellar form with  $^{60}\text{Co}$   $\gamma$ -radiation under identical conditions. The partial specific volume, elution window, and hydrophobicity (*i.e.*, methylene selectivity) of poly-SAIS surfactants were found to increase with an increase in hydrocarbon chain length. In addition, fluorescence spectroscopy indicated that the poly-SAIS surfactant with a shorter hydrocarbon tail (*e.g.*, poly-SOcS) showed a more polar character than that with a longer hydrocarbon tail (*e.g.*, poly-SUS). The aggregation numbers ( $N$ ) of polymeric surfactants were very similar, except for the poly-SOcS that provided about twofold higher  $N$  value than the other three polymeric surfactants. However, no direct relationship was found between aggregation number and the length of hydrophobic tail.

Hydrophobic interaction between solute and pseudostationary phase plays an important role in solute migration in MEKC as seen in electrokinetic chromatograms of NHB, HBA, and HBD solutes. All three groups of the solutes (*i.e.*, NHB, HBA, and HBD) eluted longer in relatively more hydrophobic poly-SUS due to its relatively stronger interaction with the solutes. The longest migration time with poly-SUS can also be attributed to the greatest (most negative) effective electrophoretic mobility of this longer chain polymer. On the contrary, least hydrophobic poly-SOcS provided faster separation of all solutes among all surfactant systems. For example, the total separation time with poly-SOcS was found to be about seven times shorter for 12 NHB benzene derivatives than that with poly-SUS. This is because the former surfactant provided narrow peak spacing while the latter surfactant gave wide peak spacing resulting in longer analysis time but better separation. Since the NHB solutes retained longer than HBA and HBD solutes, the effect of chain length on retention of NHB solutes was more pronounced. The interaction of poly-SAIS surfactants for HBA solutes was stronger than that for HBD solutes. This observation shows that hydrogen bonding is also a significant force in retention of solutes when comparing the polymeric surfactants with different chain length. Therefore, the chain length can still have an influence on chemistry of the head group through water molecules, which reside in palisade and/or Stern layers of the micelle. Previous investigations showed that a significant amount of water is present in palisade and Stern layers of the conventional micelles [39, 40]. It has been suggested that these water molecules can influence the polarity and the hydrogen-bonding characteristics of the micelle [40, 41]. Variation of the hydrocarbon chain was found to influence the equilibrium aggregate structure and hence the

molecular packing of the micelle [42, 43]. This, in turn, will affect the chemistry of the water localized in the palisade layer [40, 42, 43]. This seems to be a reasonable explanation for the observed selectivity differences between poly-SAIS surfactants, since all poly-SAIS surfactants have the same head group (*i.e.*, sulfate).

Finally, results obtained in this study show also that polymeric surfactants can be successfully employed in MEKC as pseudostationary phases at exceptionally low concentrations. For example, the amount of each poly-SAIS surfactant, *i.e.*, 0.5% w/v, used in MEKC experiments is equivalent to 21.74 mM mono-SOcS, 20.49 mM mono-SNoS, 19.38 mM mono-SDeS, and 18.38 mM mono-SUS. These concentrations are obviously far below the CMC of monomeric surfactants. It should be noted that in order to achieve successful separations with conventional micelles in MEKC the concentrations at least 3- to 4-fold above the CMC must be utilized. Under such conditions, surfactant with a high CMC value (250 mM), such as SOcS, would generate high currents in MEKC that would make it unfeasible as a pseudostationary phase. However, this report shows that polymeric surfactants with even shorter chain length can be conveniently employed in MEKC. The following paper (Part II) expands this study to include further analysis of the sulfated surfactants using linear solvation energy relationships.

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