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Alkyl modified anionic siloxanes as pseudostationary phases for electrokinetic chromatography
I. Synthesis and characterization

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Abstract

Anionic water soluble siloxane polymers have been synthesized and characterized for electrokinetic chromatography. Siloxane polymers are of interest in electrokinetic chromatography because of the wide variety of chemistries that can be developed based on these backbones, including much of the stationary phase chemistry developed in the last 30 years. The siloxanes in this study have a sulfonate functional group. The siloxanes have different length alkyl chains (C_8, C_{12}, C_{18}) attached to the backbone in differing densities. The methylene selectivity generally increases with increasing alkyl chain length and with increasing alkyl chain density. The electrophoretic mobility appears to pass through a maximum as more alkyl chain is added to the siloxane backbone. The efficiency also would seem to pass through a maximum as more alkyl chain is added. The chemical selectivities of the siloxane polymers are very different from sodium dodecyl sulfate but are similar to each other.

Keywords: Pseudostationary phases; Electrokinetic chromatography; Siloxane pseudostationary phases; Ketones; Surfactants

1. Introduction

Introduced by Terabe et al. in 1984 [1], micellar electrokinetic chromatography (MEKC) has proven to be a powerful tool for separating neutral analytes in an electrophoretic environment [2–6]. The migration of an analyte is determined by its affinity for the micelle versus the buffer and all neutral analytes will elute between the migration time of the electroosmotically driven buffer (t_0) and the micelle (t_{mc}). A variety of pseudostationary phases have been developed and characterized for MEKC. Micelles are most commonly employed, but their very nature as equilibrium self-assemblies limits their application in many cases. Limited micellar stability makes the separation of hydrophobic compounds difficult [7–9], and it is difficult to utilize mass spectrometric detection with micellar phases [10]. Surfactants which provide a variety of chemical selectivity have been applied to MEKC [6,11–15], but the diversity of surfactant that can be used is limited by the requirement of a low critical micellar concentration (CMC).

Polymeric surfactants have been employed as pseudostationary phases in electrokinetic chromatography and offer several advantages over normal micelles [16–22]. These advantages include the ability to act without effects of co-micellization

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[23,24], stability in high concentrations of organic modifiers [16,20,25,26], unique chemical selectivity and the ability to be applied with mass spectrometric detectors [10,27,28]. Polymers based on a single backbone with varied side chain chemistry also can provide unique selectivity [23,29].

Recent studies have demonstrated the applicability of water soluble anionic siloxane polymers (sometimes called silicones) to electrokinetic chromatography [30–32]. Siloxanes have many potential advantages in application to electrokinetic chromatography. Siloxane polymers are commercially available or can be easily synthesized in a full range of molecular masses and structures. Much of the chemistry of conventional chromatography is based on silica or siloxanes. Application of siloxanes to MEKC would allow these previously developed and tested chemistries to be employed to achieve selective separations [33,34]. Initial studies had significant difficulties in solubilizing siloxanes [30]. Much of the work that has been done to make siloxanes water soluble has been for industrial applications [33,34]. The main route to obtain water soluble siloxanes is by attaching sufficient amounts of hydrophilic groups to the siloxane backbone [35–37].

We have recently demonstrated the utility of anionic water soluble siloxanes as pseudostationary phases [31]. Another recent study has demonstrated that water soluble siloxanes can be synthesized with a wide range of anionic functionalities, leading to different electrophoretic and chromatographic properties [32]. It was also demonstrated previously that it is possible to introduce alkyl chains into a siloxane to produce different selectivity [32]. To produce these phases, commercially available methylhydrosiloxanes are modified with various terminal vinyl compounds with the aid of platinum catalysts [36–38]. Epoxy functional groups added to the siloxane backbone in this manner are then converted to a variety of side groups [32,39] including an amino functional sulfonate [32,40]. *n*-Alkenes can also be added to the siloxane to produce a copolymer with higher lipophilic character [32,41].

In this study we have synthesized various alkyl-substituted anionic siloxanes with sulfonate functional groups. The alkyl chains that have been attached are 1-octene (C_8), 1-dodecene (C_{12}) and 1-octadecene (C_{18}). These alkyl chains have been added to the siloxane backbones in different densities from 10 to 25% of the silicon centers, with the remainder having the sulfonate groups. The siloxanes synthesized are soluble in water at relatively high concentrations and are demonstrated to achieve selective separations in electrokinetic chromatography. The results show that a family of pseudostationary phases based on siloxane chemistry can be produced with varied chemical selectivity.

2. Experimental

2.1. Synthesis of anionic siloxane surfactants

All siloxanes were synthesized starting with polymethylhydrosiloxane obtained from United Chemical Technologies (Bristol, PA, USA), which had an average initial molecular mass of 1500 g/mol. The synthetic procedure used is similar to one described previously [41]. A total of 5 ml of the siloxane (0.0033 mol; 0.08 mol SiH) was placed in a three-neck round bottomed flask equipped with a stir bar, N_2 flow, thermometer and reflux condenser. To this was added 25 ml of distilled toluene (Aldrich, Milwaukee, WI, USA) and 10 μl of platinum divinyl complex catalyst (United Chemical Technologies). To this was added 50% of the terminal alkene (1-octene, 1-dodecene, 1-octadecene; Acros, Pittsburgh, PA, USA) that was to be added to the siloxane backbone. After 2 h of stirring at 35°C, the full amount of allyl glycidyl ether (Aldrich) that was to be attached to the siloxane backbone was added to the reaction and was allowed to react for ~5 h at 80°C. The remaining portion of the terminal alkene was then added and the solution was allowed to react for another 16 h. The solvent was removed by rotary evaporation. The epoxy functionalites were then modified with *N*-methyltaurine to produce a hydrophilic sulfonate functionality. The siloxane was placed in a round bottomed flask equipped with a stir bar, and condenser. To the product was added 10 ml of ethanol (Aldrich). An excess of *N*-methyltaurine (Alfa Aesar, Ward Hill, MA, USA) was added as a solution in water with the pH adjusted to 10.5 using hydrochloric acid. This mixture was allowed to reflux for 4 h, and the solvents were removed by rotary evaporation. The product was purified by

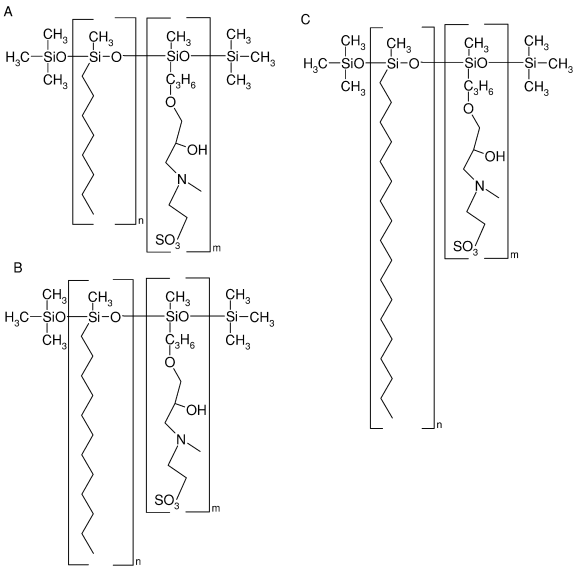

Fig. 1. Structure of anionic siloxane surfactants used in this study. (A) OAGENT (C_8), (B) DAGENT (C_{12}), (C) SAGENT (C_{18}).

dialysis for 24 h against distilled deionized water using dialysis tubing with a 2000 molecular mass cut-off (Spectrum, Houston, TX, USA). After dialysis, the water was removed by freeze drying. Three different siloxanes were produced and were given the names OAGENT (C_8), DAGENT (C_{12}), and SAGENT (C_{18}). The structure of these compounds is given in Fig. 1. The amount of alkyl chain that was added was varied from 10 up to 30%.

2.2. Characterization of siloxane polymers

The structure of all polymers was confirmed from spectroscopic data. Infrared spectra of the polymers were collected on a Nicolet Avatar 360 Fourier transform- (FT)-IR instrument (Madison, WI, USA). The spectra were collected as KBr (Acros) pellets. NMR spectra were collected on a Jeol (Peabody, MA, USA) 300-MHz spectrometer. Spectra were collected in deuterium oxide (Aldrich) at a polymer concentration of 1% (w/v).

2.3. Chromatography

All electrokinetic chromatography experiments were performed using a Hewlett-Packard (Palo Alto, CA, USA) ^{3D}CE capillary electrophoresis instrument. Fused silica capillaries (Polymicro Technologies, Phoenix, AZ, USA) of 50 μm (effective length of 42 cm)×50-μm I.D. were used for all studies. The detector was operated at 214 and 254 nm. An electric field of 20 kV was applied for all separations unless otherwise noted. The temperature was maintained at 25°C. The polymer was dissolved in buffers at 1% (w/v) unless otherwise noted. This concentration of polymer was chosen because it gives a phase ratio approximately equivalent to a 40-m*M* sodium dodecyl sulphate (SDS) solution. Borate (50 m*M*) buffers of pH 9.2 were prepared from sodium borate (Sigma, St. Louis, MO, USA) and distilled deionized water. All buffers were filtered through 0.45-μm filters (Whatman, Clifton, NJ, USA) prior to use. All solutes were obtained from Aldrich. Samples were prepared by dissolving the solutes in the run buffer. Analytes were injected by applying a pressure of 40 mbar for 2 s. For the selectivity study, four analytes were injected for each sample. Analytes were identified using a spectral library, and if the spectral library was not conclusive the unidentified analytes were run individually to identify them by migration times. The values of t_{mc} were determined by measuring the migration times of a homologous series of alkyl phenyl ketones (C_1–C_6) and estimating t_{mc} using the reiterative calculation procedure of Bushey and Jorgenson [42]. A BASIC program was used to perform the reiterative calculation, and the calculation was repeated until the change in t_{mc} from the previous iteration was less than 0.1% or the correlation coefficient exceeded 0.9999. The methylene selectivities were calculated from the slope (m) of the plot of the logarithm of the capacity factor versus carbon number ($\alpha_{CH2}=10^m$) and thus represent an average for the entire homologous series.

3. Results and discussion

3.1. Synthesis and characterization

Synthetic yield for the polymer modifications was above 50%. Most of the synthetic products had sufficient water solubility for application in MEKC. Exceptions were C_{18} phases with substitution of 25% and above, and the C_8 and C_{12} phases substituted at

concentrations of 30% and above. The molecular masses of the products vary from 7250 to 8565, based on the initial molecular mass of the methylhydrosiloxane polymers. FT-IR was used to confirm that the methylhydrosiloxanes were 100% substituted by observing the disappearance of the SiH stretch (2165 cm^{-1}). Proton NMR results for each polymer had the anticipated resonances. OAGENT: δ 0.11 ppm (SiC**H**$_3$), δ 0.62 ppm (SiC**H**$_2$), δ 0.85 ppm (CH_2C**H**$_3$), δ 1.25 ppm (alkyl C**H**$_2$), δ 1.64 ppm ($SiCH_2C$**H**$_2$), δ 2.43 ppm (SC**H**$_2$), δ 2.97 (NC**H**$_2$), δ 3.46 ppm (C**H**$_2$O), δ 3.94 ppm (C**H**OH). DAGENT: δ 0.10 ppm (SiC**H**$_3$), δ 0.62 ppm (SiC**H**$_2$), δ 0.85 ppm (CH_2C**H**$_3$), δ 1.24 ppm (alkyl C**H**$_2$), δ 1.64 ppm ($SiCH_2C$**H**$_2$), δ 2.44 ppm (SC**H**$_2$), δ 3.04 (NC**H**$_2$), δ 3.47 ppm (C**H**$_2$O), δ 3.95 ppm (C**H**OH). SAGENT: δ 0.18 ppm (SiC**H**$_3$), δ 0.61 ppm (SiC**H**$_2$), δ 0.90 ppm (CH_2C**H**$_3$), δ 1.29 ppm (alkyl C**H**$_2$), δ 1.67 ppm ($SiCH_2C$**H**$_2$), δ 2.43 ppm (SC**H**$_2$), δ 3.04 (NC**H**$_2$), δ 3.47 ppm (C**H**$_2$O), δ 3.98 ppm (C**H**OH).

NMR was used to measure the density of alkyl chains substituted on the siloxane backbone (Table 1). Substitution is generally at or just below the expected level. There remains no SiH stretch in the IR spectra, which indicates that the siloxane is fully substituted. Allyl glycidyl ether was added in exact amounts and the alkyl chains were added in slight excess. All this evidence indicates that the siloxanes are substituted with the expected amount of alkyl chains.

3.2. Chromatographic and electrophoretic performance

The siloxanes produced were used to separate a

Table 1
Properties of siloxanes in this study

Pseudostationary phase	Alkyl chain density (%)[b]	Methylene selectivity	$10^4\times$ Electrophoretic mobility ($cm^2/V\,s$)	Efficiency (plates/m)	Ratio of efficiencies	Correlation (r^2)
SDS (30 m*M*)	n/a	2.33±0.04	−4.05±0.02	311 000±93 000	1.19±0.06	1.000
AGENT[a]	n/a	1.66±0.05	−5.3±0.5	330 000±240 000	2.7±0.5	0.5253
PAGENT[a] (20% C_5)	19.7	1.84±0.01	−4.75±0.06	268 000±121 000	1.9±0.7	0.7042
OAGENT (10% C_8)	6.4	1.94±0.01	−4.74±0.09	160 000±120 000	9.8±2.3	0.5151
OAGENT (15% C_8)	11.2	2.131±0.006	−5.52±0.05	147 000±58 000	6.1±3.2	0.6063
OAGENT (20% C_8)	16.5	2.20±0.02	−4.19±0.04	320 000±118 000	2.4±0.5	0.6702
OAGENT (25% C_8)	22.6	2.466±0.005	−3.86±0.02	166 679±142 000	9.9±0.6	0.6560
DAGENT (10% C_{12})	10.3	1.942±0.005	−4.59±0.06	157 000±77 000	4.4±0.9	0.6759
DAGENT (15% C_{12})	12.3	2.29±0.03	−3.897±0.009	223 000±90 000	3.2±0.2	0.6873
DAGENT (20% C_{12})	18.3	2.28±0.01	−4.133±0.007	319 000±103 000	2.6±0.5	0.6960
DAGENT (25% C_{12})	23.2	2.57±0.04	−3.79±0.03	254 000±142 000	5.4±0.4	0.6892
SAGENT (10% C_{18})	11.5	1.940±0.005	−7.2±0.2	269 000±155 000	6.3±2.7	0.5167
SAGENT (15% C_{18})	13.4	2.244±0.005	−4.83±0.07	196 000±75 000	3.3±0.4	0.6282
SAGENT (20% C_{18})	17.2	2.63±0.05	−3.78±0.04	304 000±148 000	4.4±0.3	0.6702

[a] Data from Ref. [32].
[b] As determined by NMR.

homologous series of six alkyl phenyl ketones. A representative separation using three siloxanes with different alkyl chain lengths is given in Fig. 2. The siloxanes clearly separate the homologous series with good selectivity. Siloxanes without lipophilic substitution have been previously reported to suffer from non-linear band broadening which was reduced when the siloxane was substituted with alkyl chains [32].

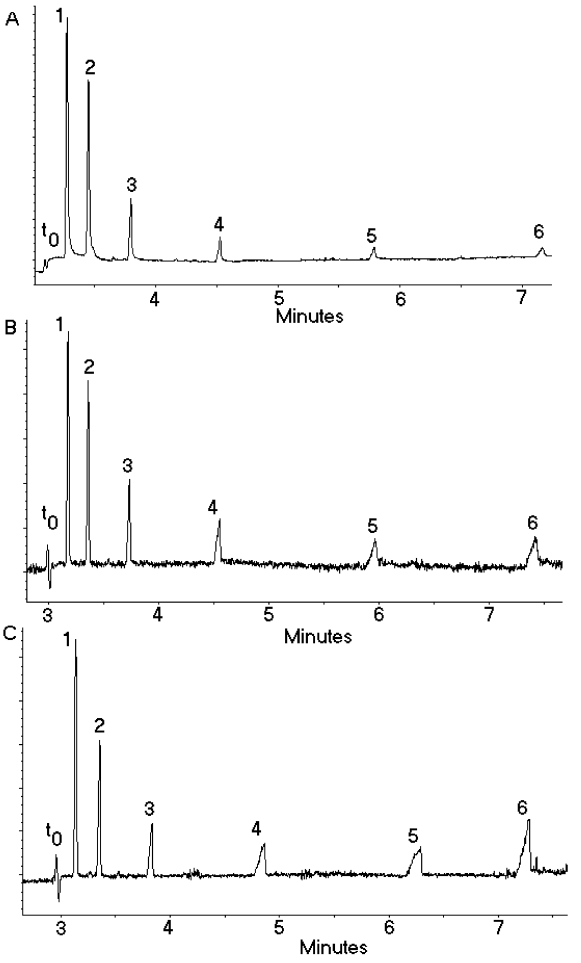

Fig. 2. Separation of six alkyl phenyl ketones for (A) OAGENT, (B) DAGENT, and (C) SAGENT. Each siloxane backbone has alkyl chains substituted at 20% of the silane sites. All separations with 1% (w/v) of siloxane, 50 m*M* borate buffer, and 20 kV applied voltage. Peak t_0 acetone; 1, acetophenone; 2, propiophenone; 3, butyrophenone; 4, valerophenone; 5, hexanophenone; 6, heptanophenone. All analytes injected at a concentration of 30 ppm for A and 50 ppm for B and C. Detection at 214 nm.

While there is some peak fronting present in Fig. 2, it is not as much of a problem as previously observed [32]. In Fig. 2 the peak asymmetries are above 0.76 for heptanophenone. The peak fronting is quite pronounced for OAGENT ($s=0.76$), but is less problematic for DAGENT ($s=0.86$) and SAGENT ($s=0.88$). The peak fronting was more pronounced at higher solute concentrations and for later eluting peaks, indicating the peak fronting is a result of sample overloading. The chromatographic properties are somewhat better for the longer alkyl chain modified siloxanes. This implies that the siloxanes modified with longer alkyl chains are more able to provide a larger and more flexible hydrophobic domain for the solvation of hydrophobic compounds, particularly those with long alkyl chains. This is consistent with the observation that the solvation capacity of poly-soaps is directly related to the extent of substitution with hydrophobic moieties [32,43]. Fig. 3 shows the separation of alkyl phenyl ketones for DAGENT at different amounts of alkyl chain added from 10 to 25%. In Fig. 3 the performance in the separation improves as more alkyl chain is attached to the siloxane backbone, especially between 10% (157 000 plates/m) and 20% (319 000 plates/m).

The electrophoretic and chromatographic properties of the siloxanes used in this study are given in Table 1. These properties are derived from the separation of the homologous series of alkyl phenyl ketones.

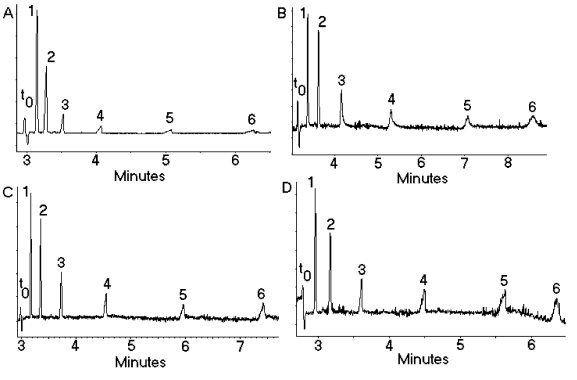

Fig. 3. Separation of six alkyl phenyl ketones for DAGENT substituted with different amounts of alkyl chain. (A) 10%, (B) 15%, (C) 20%, (D) 25%. Separation conditions and analytes numbered as in Fig. 2.

The methylene selectivities vary significantly, from being less than SDS to being more than SDS. As expected, the methylene selectivity increases with density of alkyl chains and with increasing alkyl chain length added to the siloxane. These data clearly demonstrate that the methylene selectivity can be adjusted by adding different lengths and amounts of alkyl chains to the siloxane backbone.

The electrophoretic mobilities of the siloxanes also vary significantly. In most cases, the mobilities are higher than SDS. Trends in electrophoretic mobilities with substitution and alkyl chain length are not easily discerned. The results suggest that the electrophoretic mobilities for these polymers pass though a maximum as alkyl chain is added to the backbone. The maximum appears between 10 and 20% substitution for OAGENT, at ~10% substitution for DAGENT, and at 10% substitution or less for SAGENT. The chain density at which the maximum occurs appears to be dependant on the alkyl chain length being added, with maxima for longer alkyl chain lengths occurring at lower substitution. This complex behavior likely results from changes in polymer conformation and extent of ionization with chain length and extent of substitution.

The average plate numbers obtained for the homologous series are presented in Table 1. For the octyl and dodecyl modified siloxanes the efficiency at 10% modification is significantly lower than SDS, increases to a maximum at 20% modification and decreases again at 25% modification. There is an optimal concentration (~20% modification) at which the efficiency is highest and approaches that observed with SDS micelles. The efficiency for the C_{18} modified siloxane starts high at 10% modification, drops for the 15% modified polymer and increases again at 20% modification. Also presented are the ratios of the plate counts for acetophenone (first eluted) to heptanophenone (last eluted). This ratio is a measure of the variation in plate number with migration time and hydrophobicity of the solutes. The ratio passes through a minimum for all phases at 15–20% alkyl chain substitution. There is an optimum alkyl chain density of ~15–20% at which the efficiency over the entire migration window is maximized.

The selectivity differences between the pseudostationary phases were studied by determining the retention factor for the homologous series and a group of 12 additional substituted benzene and naphthalene compounds. A sample separation for each chain length at 15% density is given in Fig. 4. The log of the retention factor for each pseudostationary phase was plotted versus the log of the retention factor for SDS. The correlation coefficients for these plots are given in Table 1. A correlation of 1 indicates identical selectivity as SDS. All of the pseudostationary phases show significant differences

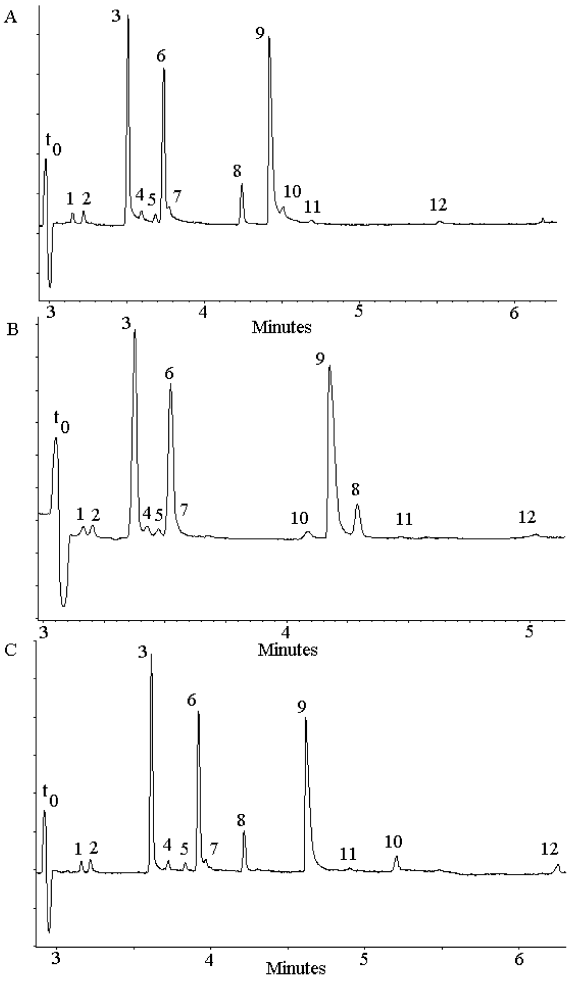

Fig. 4. Representative separation of 12 solutes using (A) 1% OAGENT, (B) 1% DAGENT, and (C) 1% SAGENT. Separations carried out in 50 m*M* borate buffer with an applied potential of 20 kV. Peak t_0 acetone; 1, nitrobenzene; 2, nitroaniline; 3, naphthalene methanol; 4, anisole; 5, naphthylamine; 6, naphthaleneethanol; 7, naphthalene; 8, 2-naphthol; 9, *p*-xylene; 10, dihydroxynaphthalene; 11, 1-naphthol; 12, phenyl ether. All analytes injected at a concentration of ~25 ppm. Detection wavelength was 214 nm.

in selectivity compared to SDS. There is an increase in the correlation as more alkyl chain is added to the siloxane backbones, with what may be a maximum at ~20% substitution. Using similar plots, it was found that the selectivity of the various siloxanes is similar (average $r^2=0.937$). In some cases, however, significant differences in selectivity were observed between polymers (e.g. 10% DAGENT vs. 25% DAGENT, $r^2=0.784$). The greatest differences are observed between polymers with low and high alkyl chain densities.

4. Conclusions

A series of water-soluble anionic siloxane polymers have been synthesized and employed as pseudostationary phases in electrokinetic chromatography. The siloxanes had different length alkyl chains (C_8, C_{12}, C_{18}) attached to the backbone in different densities. The alkyl chain attached and its concentration on the siloxane backbone have a significant effect on the methylene selectivity, which can be adjusted from being less than SDS to being greater than SDS. The electrophoretic mobility varies in a complex manner as the density and length of alkyl chains added to the backbone is varied, possibly passing through a maximum at 10–15% substitution. The efficiency also varies with the amount and length of alkyl chain added, passing through a maximum at 15–20% substitution. The chemical selectivity of the various substituted siloxanes is very different from SDS micelles, especially for polymers with lower alkyl chain density. The chemical selectivity does not vary greatly between the various polymers.

The dodecyl-modified polymer with alkyl substitution of 15–20% provides the best overall performance in terms of electrophoretic mobility, solubility, average efficiency, and efficiency over the entire migration range. This polymer also provides significantly different chemical selectivity from SDS micelles.

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