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Comparison of monomeric and polymeric amino acid based surfactants for chiral separations

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Abstract

To better understand chiral recognition with polymeric amino acid based surfactants, the chromatographic performance of 18 monomeric and polymeric surfactants were compared for chiral analytes with various charge states and hydrophobicities. In this study, four amino acids (glycine, L-alanine, L-valine, and L-leucine) were chosen, and all possible combinations of the chiral single amino acid and dipeptide surfactants were synthesized. The results indicate that polymeric surfactants usually provide better chiral resolution for enantiomers of lorazepam, temazepam, 1,1′-bi-2-naphthol, and propranolol as compared to monomeric surfactants. In contrast, monomers perform better for chiral recognition of the 1,1′-bi-2-naphthyl-2,2′-diyl hydrogenphosphate enantiomers.

Keywords: Enantiomer separations; Enantiomer separation; Background electrolylte composition; Pseudostationary phases; Surfactants; Binaphthol; Lorazepam; Binaphthyl dihydrogenphosphate; Temazepam; Propanolol; Amino acids; Peptides

1. Introduction

Micelles are aggregates of surfactant molecules that assemble above a certain concentration referred to as the critical micelle concentration (CMC). Normal micelles are aggregates with a dynamic equilibrium existing between the micelles and the surfactant monomers [1,2]. In addition, complexation of micelles with a given solute is also a dynamic interaction [3,4], which can be altered by the equilibrium that exists between micelle and the surfactant monomer. Thus, the dynamic micellar system may have a negative influence on the efficiency of the chiral interaction.

Exposure of aqueous solutions of micelles, which contain a terminal double bond at the end of the hydrophobic chain, to γ-radiation, results in formation of covalently linked polymeric surfactants [5–10]. Polymerization eliminates the dynamic equilibrium between the monomer and the micelle [1–10]. This, in turn, may result in increased mass transfer of the solute with the chiral pseudostationary phases (CPSPs). In addition, covalent stabilization in polymeric surfactants results in a more structured phase with greater constraints than the unpolymerized micelle. It should be mentioned that in conventional micelles, surfactant molecules open up and reorganize themselves to provide hydrophobic pockets for the solute. Polymerized micelles, on the other hand,

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have a rigid structure. This rigidity may diminish the ability of the polymer to create proper hydrophobic pockets for organic compounds [8].

Although several papers, which investigate the potential of polymeric surfactants in chiral recognition, have been published [10–22], not much work has been done comparing the performance of monomeric and polymeric chiral surfactants. Wang and Warner demonstrated several advantages of polymeric amino acid based chiral surfactants as compared to monomeric chiral surfactants in 1994 [10]. In that study, the authors discussed the enantioselectivity of sodium *N*-undecanoyl L-valinate (SUV). It was shown that polymeric surfactants of SUV separated the enantiomers of 1-1′-binaphthyl-2,2′-diol better than its corresponding monomer. Later, Dobashi et al. used a similar polymer to separate the enantiomers of 3,5-dinitrobenzoyl amino acid isopropyl ester [22,23].

Billiot et al. have examined the performance of a series of dipeptide surfactants [14]. The monomeric sodium *N*-undecanoyl (L,L) valyl-leucinate provided resolution of the enantiomers of 1,1′-bi-2-naphthyl-2,2′-diyl hydrogenphosphate (BNP), while the polymer of this surfactant exhibited no enantioselectivity. In contrast, polymeric sodium *N*-undecanoyl (L,L) leucyl-valinate separated enantiomers of BNP better than its corresponding monomer. In the study presented here, a comparison is made of the performance of a variety of monomeric and polymeric amino acid based surfactants in chiral separations.

2. Experimental

2.1. Chemicals

Single amino acids and dipeptides were obtained from Sigma (St. Louis, MO, USA). The racemates of 1,1′-bi-2-naphthol (BOH), (BNP lorazepam (LR), temazepam (TM), and propranolol (Prop), were also purchased from Sigma. The structures of the chiral analytes under study are provided in Fig. 1.

2.2. Synthesis of polymeric dipeptide chiral surfactants

Surfactant monomers were synthesized from the

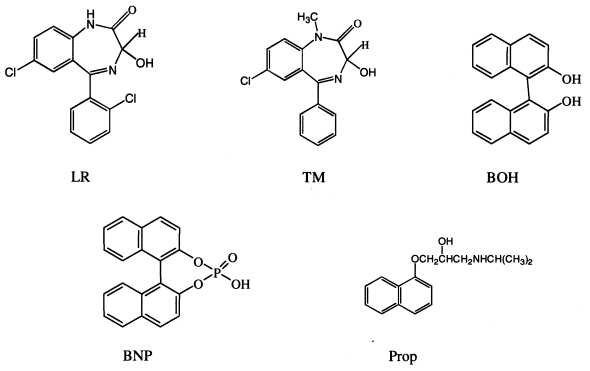
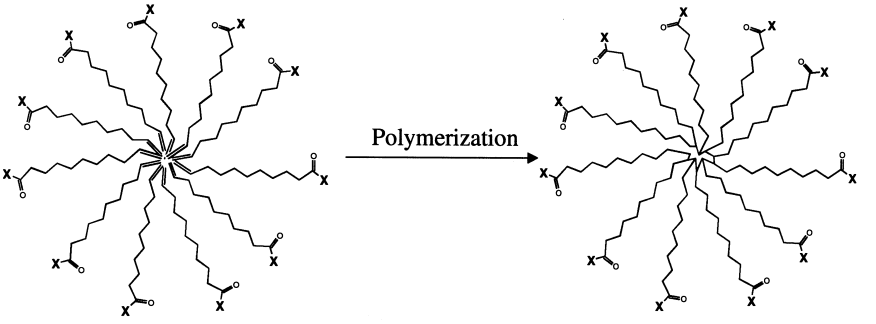


Fig. 1. Structure of chiral analytes.

N-hydroxysuccinimide ester of undecylenic acid according to a previously reported procedure [10]. The dipeptide surfactants synthesized for this purpose are all possible dipeptide combinations of glycine, L-alanine, L-valine, and L-leucine. The six single-chiral center, dipeptide surfactants examined in this study are sodium *N*-undecanoyl (L,L) glycyl-alaninate (SUGA), sodium *N*-undecanoyl L-alanyl-glycinate (SUAG), sodium *N*-undecanoyl L-glycyl-valinate (SUGV), sodium *N*-undecanoyl L-valyl-glycinate (SUVG), sodium *N*-undecanoyl L-glycyl-leucinate (SUGL), and sodium *N*-undecanoyl L-leucyl-glycinate (SULG). The nine dual-chiral center dipeptide surfactants used in this study are sodium *N*-undecanoyl (L,L) alanyl-alaninate (SUAA), sodium *N*-undecanoyl (L,L) alanyl-valinate (SUAV), sodium *N*-undecanoyl (L,L) alanyl-leucinate (SUAL), sodium *N*-undecanoyl (L,L) valyl-alaninate (SUVA), sodium *N*-undecanoyl (L,L) valyl-valinate (SUVV), sodium *N*-undecanoyl (L,L) valyl-leucinate (SUVL), sodium *N*-undecanoyl (L,L) leucyl-alaninate (SULA), sodium *N*-undecanoyl (L,L) leucyl-valinate (SULV), and sodium *N*-undecanoyl (L,L) leucyl-leucinate (SULL). In addition, three single amino acid surfactants, sodium *N*-undecanoyl L-alaninate (SUA), sodium *N*-undecanoyl L-valinate (SUV), and sodium *N*-undecanoyl L-leucinate (SUL) were studied. The structures of these surfactants are illustrated in Fig. 2.

A 100-m*M* solution of each monomer, in sodium salt form, was then polymerized by use of ^{60}Co γ-radiation. After polymerization, proton NMR spectroscopy was used to confirm polymerization.



R1	R2	Surfactant
CH_3	NA	SUA
$CH(CH_3)_2$	NA	SUV
CH_2-$CH(CH_3)_2$	NA	SUL
H	CH_3	SUGA
H	$CH(CH_3)_2$	SUGV
H	CH_2-$CH(CH_3)_2$	SUGL
CH_3	H	SUAG
CH_3	CH_3	SUAA
CH_3	$CH(CH_3)_2$	SUAV
CH_3	CH_2-$CH(CH_3)_2$	SUAL
$CH(CH_3)_2$	H	SUVG
$CH(CH_3)_2$	CH_3	SUVA
$CH(CH_3)_2$	$CH(CH_3)_2$	SUVV
$CH(CH_3)_2$	CH_2-$CH(CH_3)_2$	SUVL
CH_2-$CH(CH_3)_2$	H	SULG
CH_2-$CH(CH_3)_2$	CH_3	SULA
CH_2-$CH(CH_3)_2$	$CH(CH_3)_2$	SULV
CH_2-$CH(CH_3)_2$	CH_2-$CH(CH_3)_2$	SULL

single amino acid
X=NH-CH(R1)-C-ONa
O

dipeptide
X=NH-CH(R1)-C-NH-C(R2)-C-ONa
O O

Fig. 2. Structure of amino acid based surfactants.

Radiated polymers were dialyzed with a 2000 molecular mass cutoff dialysis membrane and then lyophilized to obtain the dry product. All surfactants were found to be 99% pure or better as calculated from elemental analysis.

2.3. Micellar capillary electrophoresis procedure

Micellar electrokintetic chromatography (MEKC) separations were performed by use of a Hewlett-Packard (HP) ^{3D}CE model G1600AX. The fused-silica capillary, 63.5 cm (effective length 55 cm to detection window)×50 μm I.D. was purchased from Polymicron Technologies (Phoenix, AZ, USA) and mounted in an HP capillary cartridge. The cartridge temperature was maintained at 25°C for the separation of BNP and BOH and 12°C for LR, TM, and Prop separations. The running background electrolytes (BGEs) were prepared in triply distilled water; surfactants were added and the pH was adjusted by adding either HCl or NaOH to the BGE. All solutions were filtered through a 0.45-μm membrane filter before use.

A new capillary was conditioned for 30 min with 1 *M* NaOH at 60°C, followed by 10 min with triply distilled water. The capillary was then flushed with buffer for 2 min prior to injecting the sample. All analyte standard solutions were prepared in methanol–water (1:1) at 0.1–0.5 mg/ml. Samples were injected for 5 s at 10 mbar pressure. Separations were performed at +30 kV, with UV detection at 220 nm.

2.4. Background electrolyte conditions

The MEKC conditions for optimum enantiomeric resolution were previously determined [18] using amino acid based surfactants as follows: (1) LR and TM: 25 m*M* Tris, 25 m*M* sodium borate, pH 9.2 at 12°C; (2) BNP and BOH: 10 m*M* sodium borate, 100 m*M* Tris, pH 10.0 at 25°C; (3) Prop: 50 m*M* sodium borate, 300 m*M* CAPS, pH 8.5 at 12°C.

3. Results and discussion

Chiral recognition with amino acid based surfactants can largely be attributed to electrostatic, hydrophobic, and steric interactions, as well as hydrogen bonding. Hydrophobic forces dictate the depth of penetration of the analyte into the micellar core. This, in turn, plays a major role in chiral recognition of charged, as well as neutral enantiomers [21]. It has been previously shown that positively charged analytes interact preferentially with negatively charged surfactants at the surface of the micelle due to electrostatic interactions, while hydrophobic neutral analytes penetrate deeper into the micellar core [19]. It should be mentioned that enantiomers of BNP are one of the few anionic analytes that have been separated by use of this class of surfactant. The successful enantiomeric resolution of BNP with the negatively charged micelles examined in this study suggest that the presence of the naphthyl moiety in this analyte provides strong enough hydrophobic forces to overcome the charge repulsion between BNP and the anionic head group of the surfactants. In addition, BNP is an atropisomer, since it does not possess a chiral center, but rather a chiral plane. The chiral plane is another possible factor which contributes to the successful enantiomeric separation of BNP with the anionic surfactants we examined.

More recent studies in our laboratory using fluorescence spectroscopy have shown that the aggregation numbers of monomeric surfactants are significantly larger than the number of repeat units of the micelle polymers [24]. The aggregation number of the monomeric surfactants were between 38 and 358, while repeating units of the polymers were between 20 and 33. These differences suggest that the chiral interactions of monomeric and polymeric CPSPs may be different. In addition to the differences discussed above, joule heating caused by non-polymerized micelles can be problematic in CE. For example, we have observed that at equivalent monomer concentrations (EMC), monomeric surfactants produce more current than their corresponding polymers. The polymeric CPSPs examined in this study always provided lower currents, with higher theoretical plate numbers as compared to monomeric CPSPs. In addition, we have observed that at higher surfactant concentrations (i.e. 50 m*M*), normal micelles often produce bubbles inside the capillary, resulting in spikes and unstable baseline during the electrokinetic run. This problem was not observed with the polymers.

To evaluate the chromatographic performance of monomeric and polymeric surfactants in terms of their chiral recognition, chiral separations of five test analytes were performed at two different concentrations: (1) the optimum polymer concentrations; and (2) the concentration at which the monomer (unpolymerized micelle) provided the optimum selectivity. It should be mentioned that the optimum concentration of all the monomers is the same essentially for all the surfactants examined in this study. The same situation was observed with the polymers. In other words, while the optimum concentration may not be the same for the monomers as compared to the polymers, the optimum concentration was the same for all monomers, as well as for all polymers studied. It can thus be stated that, for the surfactants examined in this study, the optimum concentration is analyte dependent not surfactant dependent.

3.1. Enantioseparation of neutral analytes

In this section, the enantioselectivity of three neutral analytes (LR, TM, and BOH) are examined. Prior to comparison of the various surfactants, optimum monomer and polymer concentrations were determined. Optimum enantiomeric resolutions of LR, TM, and BOH for the various polymers were achieved at 12, 20, and 6 m*M* EMC, respectively. In contrast, the optimum concentration for the monomers were 45 m*M* for LR and TM and 50 m*M* for BOH. The optimum monomer concentration was more than twice the concentration of the corresponding polymers for TM and LR and around eight times greater for BOH. It should be mentioned that the CMC of the single amino acid and dipeptide surfactants were determined to be about 20 and 7 m*M*, respectively. Although 12 and 20 m*M* are above the CMC of the dipeptide surfactants, the enantiomers of LR and TM coeluted with the electroosmotic flow (EOF) at this concentration of monomers. In fact, for dipeptide monomeric surfactants at 20 m*M*, only 65% of surfactants are in the micellar state, while the polymeric surfactants ex-

amined in this study are in ''micellar'' form at any concentration. However, it is acknowledged that the micellar configuration will likely change at concentrations below the normal CMC.

Presumably, the diastereomeric complexes formed between the enantiomer and monomeric CPSPs are less stable as compared to that of the polymeric phase. The success of chiral recognition depends, in part, on the strength of the chiral interaction of the enantiomers with the CPSPs [25]. Covalent linkage among the hydrophobic tail of the surfactants results in a more organized phase with greater steric constraints than the unpolymerized phases [8]. This greater structural rigidity of the former may result in enhanced enantioselectivity for neutral analytes.

As shown in Fig. 3, the polymeric surfactants always provide better chiral separation for LR as compared to the monomeric form of the same surfactant. For example, the polymers of SULV, SUAG and SUVA separated the enantiomers of LR with resolution values of 3.11, 1.83, and 2.94, respectively. However, no chiral recognition of these enantiomers was achieved even when the concentrations of the corresponding monomers were increased to as high as 45 m*M*. Examination of the data for the single amino acid and dipeptide surfactants investigated in this study, indicate that only six monomers were able to show any chiral recognition for LR (i.e. SUL, SUAA, SUAL, SUVG, SUVL and SULG). In addition, examination of selectivity data, shown in Table 1, indicates that the polymeric surfactants always provide better enantioselectivity for enantiomers of LR.

Fig. 4 shows the chromatographic data for enantiomers of TM. Note the structural differences of LR and TM (Fig. 1). The main difference is the methyl group located on the nitrogen in the seven membered ring of TM and the chlorine in the ortho position of the lower benzene ring of LR. Examination of these data for the single amino acid surfactants reveals that poly SUV and SUL were able to separate the enantiomers of TM with resolution values of 2.32, and 2.68, respectively, while no chiral recognition was obtained using the monomeric forms of the same surfactants. In contrast, mono SUA provided slight resolution of the enantiomers of TM (R_s of 0.36), while no enantiomeric resolution of TM was observed using poly SUA.

When comparing single-chiral center dipeptide surfactants with the chiral center at the *N*-terminal position, i.e. SUAG, SUVG, SULG, monomeric surfactants provided either the same or better chiral

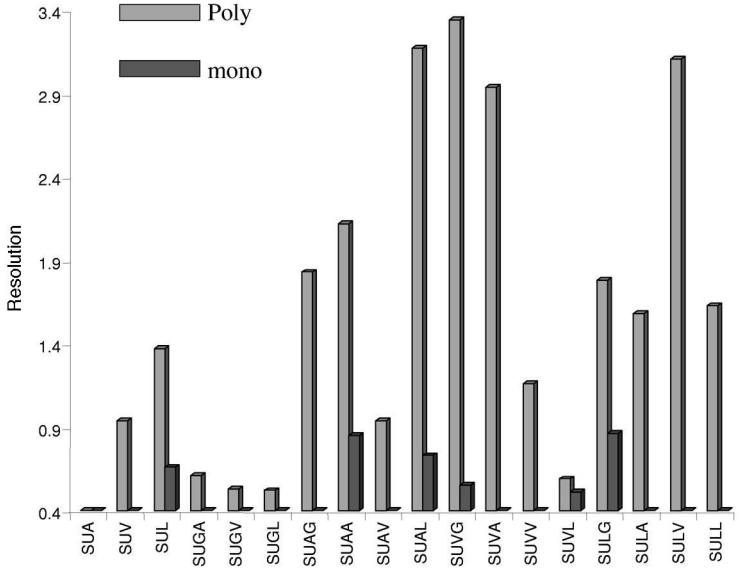


Fig. 3. Enantiomeric separation of LR: Buffer; 25 m*M* Tris, 25 m*M* sodium borate pH 9.2, +30 kV applied voltage, 215 nm UV detection, sample concentration; 0.1 mg/ml, surfactant concentrations; poly 12 m*M* of EMC, mono, 45 m*M*.

Table 1
Chiral selectivity of the neutral compounds for polymeric and monomeric surfactants[a]

	LR		TM		BOH	
	Poly	Mono	Poly	Mono	Poly	Mono
SUA	1	1	1	1.013	1.094	1.046
SUV	1.009	1	1.021	1	1.057	1.028
SUL	1.014	1.012	1.031	1	1.068	1.019
SUGA	1.005	1	1.031	1.023	1.041	1
SUGV	1.006	1	1.051	1.023	1.004	1.012
SUGL	1.006	1	1.054	1.037	1	1.009
SUAG	1.023	1	1.019	1.052	1.078	1.012
SUAA	1.022	1.011	1	1.010	1.078	1.038
SUAV	1.100	1	1.014	1	1.015	1
SUAL	1.029	1.013	1.045	1.032	1.0100	1.005
SUVG	1.039	1.009	1	1.019	1.062	1.030
SUVA	1.027	1	1.010	1	1.097	1.021
SUVV	1.012	1	1	1	1.044	1.022
SUVL	1.025	1.007	1.030	1.017	1.026	1.008
SULG	1.021	1.010	1.015	1.008	1.088	1.037
SULA	1.019	1	1.033	1.013	1.088	1.032
SULV	1.028	1	1.043	1.019	1.062	1.018
SULL	1.016	1	1.053	1.037	1.043	1.038

[a] Average standard deviation, ±0.001.

selectivity for TM as compared to the polymers (Table 1). However, as shown in Fig. 4, resolution values of the aforementioned polymers are always better than the monomers. This is due in part to the better efficiency of the polymers as compared to the monomers. The plate number for polymers were between 110 000 and 130 000. This value is significantly higher than the plate number obtained for monomers (i.e. 65 000–97 000). The more flexible configuration of the monomer could allow rearrangement of the polar head group enabling the chiral center of TM to more strongly interact with the inside amino acid of the monomeric surfactants as compared to the polymers.

Similar to the single amino acid surfactant SUA, some enantioselectivity of TM was observed with the monomeric dipeptide surfactant SUAA, while no chiral selectivity was achieved using poly SUAA. It is not clear why monomers of SUAA and SUA provide better chiral interactions for enantiomers of TM. However, one possible explanation could be the differences in aggregation number of the polymers and the monomers. The aggregation number of monomeric SUAA, determined by use of a steady state fluorescence quenching technique, is greater than 300, while the number of repeat units of the polymeric form is about 25 [24]. The higher aggregation number of mono SUAA may provide a better chiral interaction of TM enantiomers with monomeric surfactants as compared to the polymer. Fur-

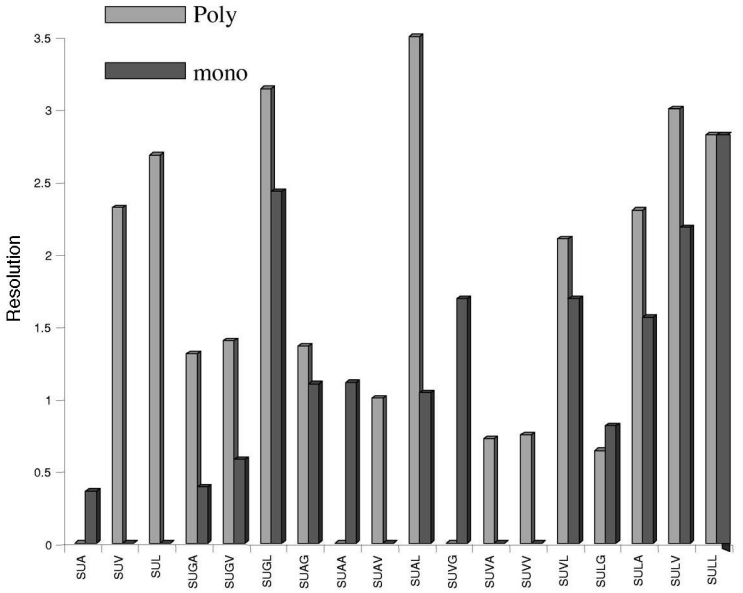


Fig. 4. Enantiomeric separation of TM: Surfactant concentrations; poly 20 m*M* of EMC, mono; 45 m*M*. Other conditions same as Fig. 3.

ther experiments using spectroscopic techniques are being conducted to better understand the chiral interaction of SUA and SUAA with enantiomers of TM.

The best enantioseparation for enantiomers of TM was attained using poly SUAL (R_s of 3.50) with two chiral centers. Except for the surfactants that were discussed earlier, polymeric surfactants always provided better chiral separations for enantiomers of TM as compared to their monomeric counterparts. Three of the 18 monomeric surfactants (SUA, SUAA, SUVG) provided better chiral resolution toward enantiomers of TM compared to that of the polymer.

The third neutral analyte examined in this study is BOH. The difference between this analyte and LR and TM is that BOH has a chiral plane, while the other two analytes contain a chiral center (Fig. 1). In addition, BOH is very hydrophobic and the optimum polymeric concentration (ca. 6 m*M* EMC) for this analyte is significantly lower than for LR and TM (12 and 20 m*M* EMC, respectively). As illustrated in Fig. 5, poly SUGA and poly SUAV provided R_s values of 1.32 and 1.36 for the enantiomers of BOH, respectively, while no chiral recognition was observed using the corresponding monomers. Monomeric surfactants of SUGV and SUGL provided R_s (and α) values of 1.71 (α of 1.012) and 0.53 (α of 1.009), respectively, while poly SUGV resolution (and α) value was 0.77 (α of 1.004), and poly SULG was not able to enantiomerically resolve BOH. We have previously reported that enantiomers of BOH preferentially interact with the N-terminal amino acid of the dipeptide surfactant. It is believed that the looser configuration of the monomers allow the enantiomers of this analyte to interact stronger with the C-terminal amino acids of the monomeric surfactants as compared to the polymers.

A comparison of the selectivity factors for neutral analytes reported in Table 1, indicates that polymers generally provide better enantioselectivity than the corresponding non-polymerized form. From the chromatographic data presented here, it is clear that polymeric surfactants are better CPSP reagents for enantiomeric separation of the neutral compounds examined in this study than the corresponding monomers.

3.2. Enantioseparation of charged analytes

In an effort to compare the chromatographic

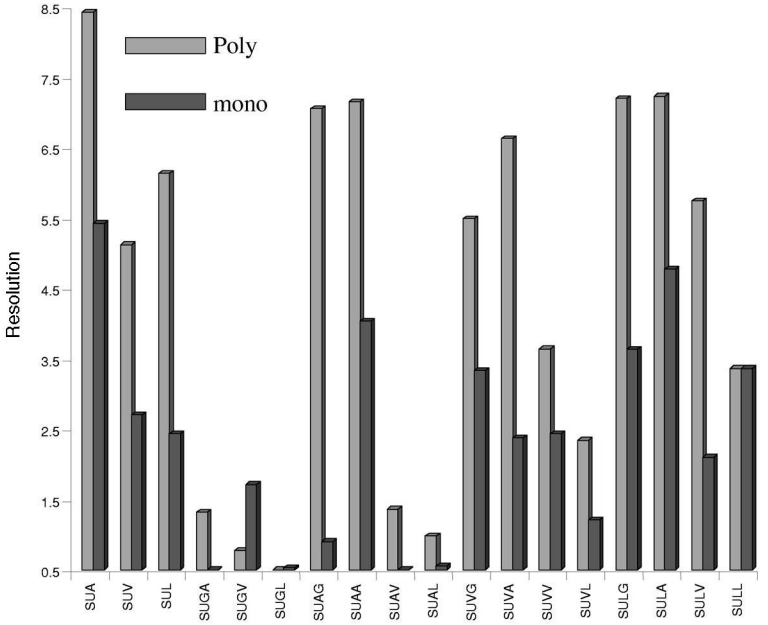


Fig. 5. Enantiomeric separation of BOH: Buffer; 100 m*M* Tris, 10 m*M* sodium borate pH 10, +30 kV applied voltage, 215 nm UV detection, sample concentration; 0.1 mg/ml, surfactant concentrations; poly 6 m*M* of EMC, mono, 50 m*M*.

performance of monomeric and polymeric surfactants for the enantiomeric separation of charged analytes, Prop (positively charged) and BNP (negatively charged) were examined. The optimum enantioseparation of Prop enantiomers using polymeric surfactants was achieved at 18 m*M* of EMC. However, at this concentration, no chiral separation was observed using monomeric surfactants. Much higher concentrations of monomeric surfactants were needed to achieve optimum separation (i.e. 50 m*M*). The optimum concentration of both monomeric and polymeric forms of the surfactants for the enantiomeric separation of BNP was determined to be 30 m*M* [14].

Comparisons of the enantioresolution of Prop for various surfactants are illustrated in Fig. 6. Again, in most cases, R_s values of Prop obtained with polymeric surfactants were higher than those achieved with the corresponding non-polymerized ones. However, when the chiral center of the single-chiral center dipeptide surfactant is located at the N-terminal amino acid (e.g. SUVG and SULG), the monomer performed better than the polymer. As can be seen in Fig. 6, no chiral resolution was observed with the polymeric form of SUVG, and poly SULG provided a R_s value of 0.3, while the monomers separated the enantiomers of Prop with R_s values of 0.31, and 0.7, respectively. This apparent anomaly is probably due to differences in depth of penetration of Prop into the hydrophobic core of the micelle, as compared to the polymer.

It has previously been shown that Prop interacts preferentially with the outside (C-terminal) amino acid of polymeric dipeptide surfactants. Electrostatic interactions between the positively charged Prop and the negatively charged dipeptide surfactants are likely to be the primary factor in binding of this class of compound to the polar head of the micelle [19]. Thus, chiral selectivity is assumed to be dependent primarily on the C-terminal amino acid. However, steric interactions of the benzene ring of this positively charged analyte with the N-terminal amino acid's R group of the dipeptide surfactants need to be considered as well.

Examination of the selectivity factors of Prop enantiomers shown in Table 2 indicates that monomers always provide better or approximately the same chiral selectivity for enantiomers of this posi-

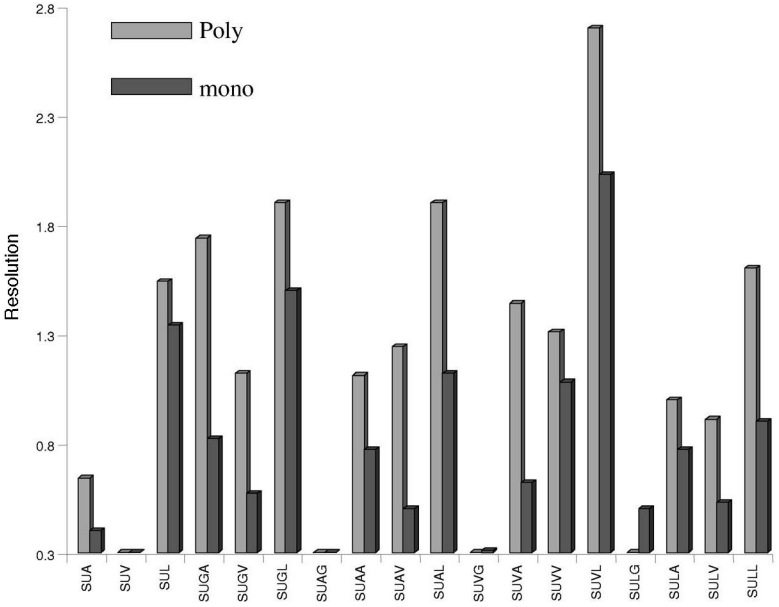


Fig. 6. Enantiomeric separation of Prop: Buffer; 300 m*M* 3-cyclohexylamino-1-propanesulfonic acid (CAPS), 50 m*M* sodium borate pH 8.5, +30 kV applied voltage, 215 nm UV detection, sample concentration; 0.1 mg/ml, surfactant concentrations; poly 12 m*M* of EMC, mono, 45 m*M*.

Table 2
Chiral selectivity of the charged compounds with polymeric and monomeric surfactants[a]

	Prop		BNP	
	Poly	Mono	Poly	Mono
SUA	1.005	1.032	1	1
SUV	1	1	1	1.011
SUL	1.013	1.014	1.019	1.009
SUGA	1.010	1.011	1.016	1
SUGV	1.013	1.017	1.027	1.024
SUGL	1.022	1.023	1.047	1.049
SUAG	1	1	1	1.013
SUAA	1.012	1.022	1.008	1
SUAV	1.014	1.029	1	1
SUAL	1.024	1.025	1.009	1.008
SUVG	1	1.007	1.026	1.022
SUVA	1.015	1.024	1.050	1.036
SUVV	1.019	1.026	1.020	1
SUVL	1.033	1.038	1	1.037
SULG	1.004	1.015	1.096	1.097
SULA	1.011	1.013	1.073	1.102
SULV	1.011	1.012	1.066	1.036
SULL	1.018	1.044	1.059	1.042

[a] Average standard deviation, ±0.001.

tively charged analyte. Again, this is possibly due to the fact that the looser configuration of the monomers allows a better chiral interaction of the Prop enantiomers, as compared to the polymers. As noted earlier, higher resolution values are usually obtained with polymers due to an increase in the efficiency of the polymeric over the monomeric micelles.

Chromatographic data for the enantiomeric separation of BNP are reported in Fig. 7. In contrast to the other analytes examined in this study, optimum monomeric and polymeric concentrations for chiral selectivity of BNP are similar (i.e. 30 m*M*). As mentioned earlier, so far BNP is one of a few negatively charged analytes that has been enantiomerically separated in our laboratory using anionic amino acid based surfactants. This is most likely due to the fact that this analyte is an atropisomer and also possesses a very hydrophobic moiety, which can penetrate into the micellar core and compete with charge repulsion.

As shown in Table 2, both the monomeric and the polymeric forms of 10 surfactants (SUL, SUGV, SUGL, SUAL, SUVG, SUVA, SULG, SULA, SULV, and SULL), were able to separate the enantiomers of BNP. Out of these 10 surfactants, half of the monomers provided either better or approximately the same chiral recognition for the enantiomers of BNP. In addition, monomers of SUV, SUAG, and SUVL separated the enantiomers of BNP with R_s

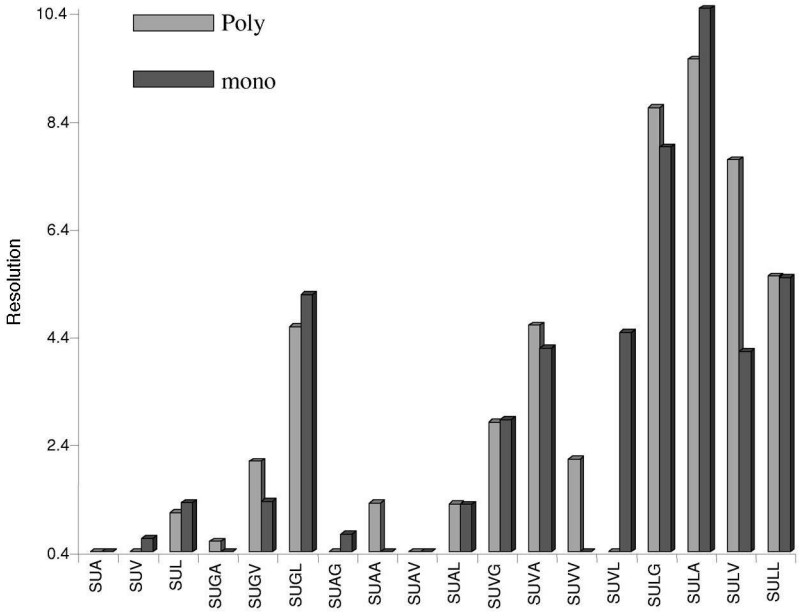


Fig. 7. Enantiomeric separation of BNP: 30 m*M* of EMC, mono; 30 m*M*. Other conditions same as Fig. 5.

values (and α) of 0.64 (α of 1.011), 0.72 (α of 1.013), and 4.46 (α of 1.037), respectively, while the corresponding polymers did not show any enantioselectivity toward the enantiomers of BNP. It is worth noting that the polymers of SUAA, SUVV, and SUGA separated the enantiomers of BNP with R_s values (and α) of 1.3 (α of 1.008), 1.2.11 (α of 1.02), and 0.59 (α of 1.016), respectively, whereas no selectivity was achieved with the monomers of these surfactants. In general, it can be concluded that monomeric surfactants are better chiral stationary phases for BNP than the polymers.

In conclusion, chromatographic data presented in this manuscript suggest that polymeric surfactants are generally much better chiral selectors for enantiomers of neutral as well as cationic compounds. In our laboratory, we are presently using a variety of techniques to further investigate the interaction of enantiomers with amino acid based surfactants. Some of the techniques include fluorescence and NMR spectroscopy. It is believed that these investigation will lead to a deeper understanding of chiral interaction with amino acid based surfactants and thus to chiral interactions in general with amino acid based compounds.

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