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RETENTION OF IONIC AND NON-IONIC CATECHOLS IN CAPILLARY ZONE ELECTROPHORESIS WITH MICELLAR SOLUTIONS

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SUMMARY

The use of micellar solutions in capillary zone electrophoresis has been primarily relegated to separations of non-ionic solutes, while its applicability to cationic species has been unexplored. We have found that the use of sodium dodecyl sulfate micelles in phosphate buffer allows for tremendous gains in selectivity for several cationic and non-ionic catechols over what can be obtained with normal capillary zone electrophoresis. Complexation of catechols with boric acid alters the net charge on the solutes and changes the partitioning behavior to produce adequate selectivity with improved analysis times. Although the mechanisms of solute interaction with the micellar phase for the cationic species are not decisively known, evidence is presented supporting the existence of ion-pairing equilibria simultaneously accompanied by micellar solubilization.

INTRODUCTION

Capillary zone electrophoresis (CZE) has evolved into a high-efficiency high-resolution separation technique for small samples of ionic species[1–7]. In CZE, ionic species separate under the influence of a high-voltage (5–40 kV) potential field based on their electrophoretic mobilities. A strong electroosmotic flow created within the capillary column causes cations, non-ionic species and anions to elute at one end of the column thus facilitating use of small-volume injections and a variety of detectors[3,5,6,8–11].

Although CZE has been shown to be a very powerful separation technique for ionizable species, small ions (especially cations) do not always possess large enough differences in electrophoretic mobility to allow for adequate resolution. CZE is also lacking in its ability to resolve non-ionic species. Since non-ionic species have no electrophoretic mobilities, their migration rate is unaffected by the electric field. Such species typically migrate with a velocity equal to that of the electroosmotic flow and have therefore been used as "markers" for electroosmotic flow velocity determinations[12,13].

Two approaches have been introduced to allow resolution of non-ionic species

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with CZE. Walbroehl and Jorgenson[14] separated non-ionic organic compounds through solvophobic association with tetraalkylammonium ions to form positively charged species. The positively charged species could then be separated in an electric field based on the electrophoretic mobilities of the solvated compounds.

A second approach to improving selectivity for the separation of non-ionic species involves solubilization by micelles which are electroosmotically pumped through a capillary. This technique was introduced by Terabe *et al.*[15] and has been termed micellar electrokinetic capillary chromatography (MECC) by Burton *et al.*[16]. MECC differs from CZE in that the mechanism of separation is based primarily on partitioning phenomena rather than on electrophoretic effects.

Application of MECC to a wide variety of non-ionic compounds is well documented[15–22]. However, few reports concern selectivity enhancements for ions using MECC instead of conventional CZE[5,17]. Cohen *et al.*[5] showed that the addition of sodium dodecyl sulfate (SDS) and metal ions to the operating buffer allowed for increased resolution of anionic oligonucleotides.

We are interested in ultra-small-scale separations of catechol neurotransmitters and their analogues with CZE. At pH 7, these compounds may be cations, anions, zwitterions and, in some cases, non-ionic. Increased selectivity for separations of catechols with MECC over separations obtained with conventional CZE systems are presented in this paper. The possibility of ion-pairing of cationic catechols with surfactant monomer is discussed with regard to separation mechanism and performance. Complexation of catechols with boric acid is shown to be an effective way to dynamically alter the net charge and partitioning behavior of catechols leading to enhancements in selectivity.

EXPERIMENTAL

Electrokinetic apparatus

The apparatus employed for all electrokinetic separations with electrochemical detection has been described previously[6]. Fused-silica capillaries having inner diameters of 26 μm and outer diameters of 259 μm were obtained from Polymicro Technologies (Phoenix, AZ, U.S.A.). The columns were filled with buffered solutions via a helium-pressurized solvent reservoir at a pressure of not more than 12 p.s.i.g. (0.82 bar). Electrochemical detection was performed as previously described[6] with a single 10-μm O.D. carbon fiber cylindrical microelectrode inserted into the end of the detection capillary. The working electrode was held at a potential of 0.7 V *vs.* a sodium-saturated calomel electrode (SSCE). Injections of sample onto the column were performed by electromigration[3].

Chemicals

Dopamine (DA), norepinephrine (NE), 3,4-dihydroxybenzylamine (DHBA), epinephrine (E), L-3,4-dihydroxyphenylalanine (L-DOPA), 4-methylcatechol (4-MC) and catechol (CAT) were obtained from Sigma (St. Louis, MO, U.S.A.). Stock solutions (0.01 *M*) of catechols were prepared in 0.1 *M* perchloric acid. Samples were diluted to final concentration in operating buffer. Borate/phosphate buffers were prepared by dissolving the appropriate amounts of sodium borate (Fisher Scientific, Pittsburgh, PA, U.S.A.) and dibasic sodium phosphate (Mallinckrodt, St. Louis,

MO, U.S.A.) in doubly distilled water and by adjusting to proper pH with concentrated phosphoric acid (J. T. Baker, Phillipsburg, NJ, U.S.A.). Phosphate buffer was prepared similarly with sodium phosphate dibasic, sodium phosphate monobasic and phosphoric acid. SDS was obtained from Aldrich (Milwaukee, WI, U.S.A.). All chemicals were used as received.

RESULTS AND DISCUSSION

Retention of cationic solutes in MECC

We have recently proposed[23] that MECC might be applicable to the separation of cations through an ion-pairing mechanism with anionic surfactants. At surfactant concentrations above the critical micelle concentration (cmc), a concentration of free surfactant monomer equal to the cmc always exists[24,25]. The free monomer may ion-pair with cationic solutes to form net-neutral ion-pairs which might be solubilized by the micelles. Solubilization may take place after or simultaneously with ion-pair formation. Considerable evidence exists indicating the formation of ion-pairs in solutions of surfactants and organic cations[26–29]. We have reported evidence for ion-pairing of DA and NE cations in pre-cmc solutions of SDS (cmc 8 m*M*[25]), based on decreases in the electrochemical limiting currents with increases in SDS concentration at carbon microelectrodes[23]. Ion-pairing of catechols with alkyl sulfates and alkyl sulfonates has been used extensively in high-performance liquid chromatography (HPLC) to greatly enhance the selectivity for these compounds[30,31]. Formation of ion–ion interactions between ionic solutes and ion-pairing reagents should also prove to be a useful tool for MECC.

Selective retention in MECC arises from differential partitioning of solutes between the aqueous and micellar phases. Partitioning requires solubilization by the micelles through surface interactions or through penetration of the solute into the micelle core[32]. Non-ionic solutes are then separated based on their relative hydro-

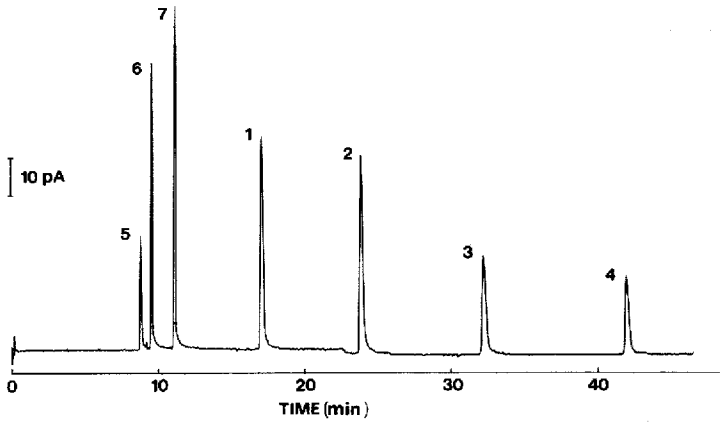


Fig. 1. Elektrokinetic separation of non-ionic and cationic catechols (see Table I for peak identification): 5 m*M* dibasic sodium phosphate–5 m*M* monobasic sodium phosphate at pH 7 with 20 m*M* SDS; separation capillary length, 66.5 cm; detection capillary length, 1.6 cm; separation potential, 20 kV (5 μA); injection, 2 s at 20 kV.

TABLE I

IONIC CHARGES OF CATECHOLS AND BORATE-COMPLEXED CATECHOLS

No.	*Compound*	*Charge*	
		pH 7	*Borate complex*
1	Norepinephrine (NE)	+1	0
2	Epinephrine (E)	+1	0
3	3,4-Dihydroxybenzylamine (DHBA)	+1	0
4	Dopamine (DA)	+1	0
5	L-DOPA	0	−1
6	Catechol (CAT)	0	−1
7	4-Methylcatechol (4-MC)	0	−1

phobicities, with the more hydrophillic species eluting first since they spend more time in the aqueous phase.

Fig. 1 shows the electrokinetic separation of several non-ionic and cationic catechols obtained with a mobile phase consisting of phosphate buffer at pH 7 and 20 m*M* SDS. The components may be identified by referring to Table I. The non-ionic catechols (4-MC, CAT) and the zwitterion L-DOPA are all less strongly retained than the cations (DA, NE, E, DHBA). If the cations were moving only under the influence of electrophoretic migration and electroosmotic flow, they would elute before the non-ionic catechols which interact with the micellar phase. It appears that the cationic solutes are retained by the micellar phase.

Hydrophobicity–retention correlations

The hydrophobicity of a compound is frequently expressed in terms of its partition ratio, *P*, between octanol and water[33,34]. Table II lists log *P* values for the non-ionic forms of the catechols studied calculated using a Prime 750 computer with ADAPT software[35]. More negative log *P* values indicate greater hydrophillicity. The elution order of the non-ionic catechols (L-DOPA, CAT, 4-MC) in Fig. 1 follows the relative hydrophobicities indicated by the log *P* values. However, when the cationic catechols are also considered, this correlation fails. The increased retention of the cationic species in the micellar phase might indicate that these molecules take on a form which is much more hydrophobic than predicted by their log *P* values. In addition, this calculation does not take into account the ionic charge on the catechols. Since ion-pairing would impart a greater hydrophobicity to the cationic compounds, we calculated log *P* values for the cations with an SDS monomer bonded to them at the ionizable functionality (a covalent bond was necessary to facilitate the calculation). The new values (Table II) show the same trend of hydrophobicity and reflect the much greater hydrophobic character which is expected for an ion-paired species. Quantitative attempts at relating log *P* values to retention were not successful for the series of compounds employed. Somewhat linear retention *vs.* log *P* relationships could be obtained for the non-ionic species alone (correlation coefficient, $r = 0.918$), and the cationic species ($r = 0.958$) by themselves, but not when these two sets of compounds were considered together. One limitation appears to be in estimating hydrophobicity for the ion-paired solutes, which are less hydrophobic than their log

TABLE II

LOG *P* FOR CATECHOLS AND ION-PAIRED CATECHOLS

Compound	*Log P*	
	Non-ionic form	*SDS ion-pair*
L-DOPA	−0.5264	
Catechol	0.8704	
4-Methylcatechol	1.535	
Norepinephrine	−0.7558	7.094
Epinephrine	−0.4372	7.784
3,4-Dihydroxybenzylamine	−0.1646	7.895
Dopamine	0.1854	8.435

P values indicate. Since ion-pairing is an equilibrium phenomenon, with no covalent bonds formed, the magnitude of the equilibrium constant would have to be accounted for in the log *P* calculation. In addition, the partitioning mechanism is likely to be different for the ion-paired cations relative to the smaller non-ionic catechols. The smaller non-ionic species are probably solubilized more into the hydrophobic interiors of the micelles, whereas the ion-paired cations might be sterically hindered from solubilization inside the micelles.

The correlation of log *P* values with retention is evidence that either the ion pairs of the cations or the cations themselves are significantly solubilized by the micelles. Many complex equilibria are thought to occur in this system and tend to make elucidation of the solubilization mechanism difficult. At least five equilibria might contribute to retention of cations in this system, including: (1) ion-pair formation in solution; (2) penetration of the ion-pair into the micelle interior; (3) solubilization of the ion-pair by insertion of the monomer end into the micelle; (4) solubilization of the ion-pair with the catechol moiety penetrating into the micelle; (5) solubilization of the free cation at the anionic surface of the micelle.

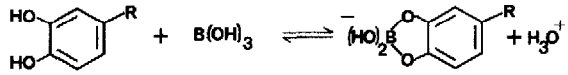
The data presented thus far suggest that equilibria 1–4 are likely occuring in this system. Process 5 may occur to some extent; however, if this were the predominant equilibria, the elution order would be based on the charge density of the cations instead of hydrophobicity.

One problem with the apparent ion-pairing of cationic solutes in MECC is that such species are highly retained. Even at low SDS concentrations (10 m*M*) DA elutes at about 25 min as compared to 6–8 min for the non-ionic solutes. It is desirable to obtain a selective and efficient separation of the components of interest without requiring extremely long analysis times. In order to meet these goals, the catechols were complexed with borate ions.

Catechol complexation with boric acid

We have altered the partitioning behavior of catechols through complexation with boric acid[36,37]. The complexation of boric acid with *ortho*-dihydroxy compounds such as catechols and certain carbohydrates has beeen studied extensive-

ly[36–38]. The complex forms via a reversible reaction with a strongly pH dependent equilibrium indicated by the reaction scheme



Of importance in this reaction is the negative charge on the boron atom which, when complexed with catechols, transforms cationic species into zwitterions and non-ionic species into anions. Table I lists the net charge of the borate complex for the compounds used within this study.

Fig. 2 shows a capillary electrophoretic separation obtained with a buffer consisting of 10 m*M* dibasic sodium phosphate and 25 m*M* sodium borate at pH 7. The first set of peaks corresponds to the cationic catechols which, as borate complexes, have a net charge of zero and migrate with a velocity near that of the electroosmotic flow. It is interesting to note that these net-neutral complexes are partially resolved, a phenomenon presumably due to differences in the equilibrium constants for complexation. The remaining peaks correspond to several non-ionic catechols which migrate as negatively charged borate complexes and therefore elute at later times than the net-neutral complexes. Borate complexation in CZE is useful for the resolution of non-ionic catechols; however, few advantages are evident for use of borate complexation with cationic catechols unless some type of differential partitioning is employed.

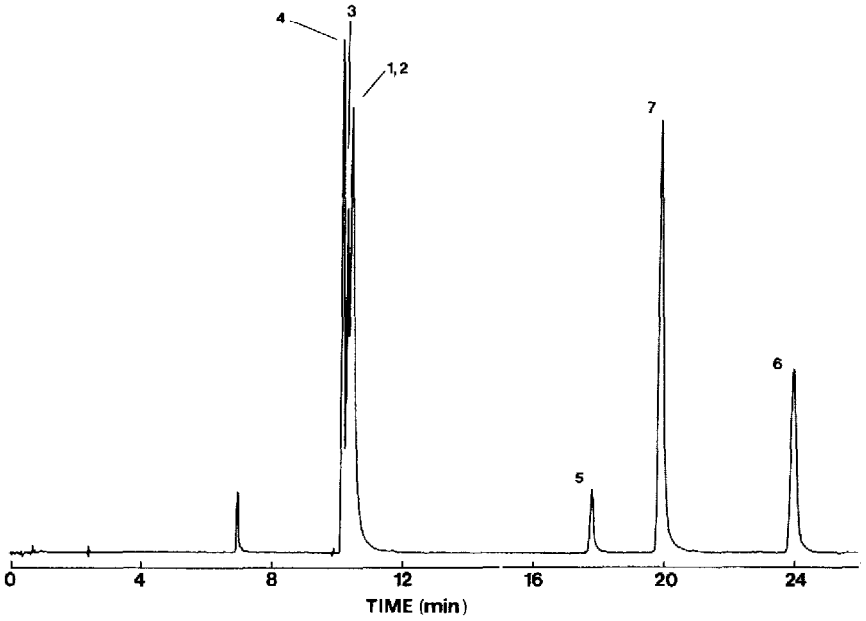


Fig. 2. Electropherogram of catechols in borate buffer: 10 m*M* dibasic sodium phosphate–25 m*M* sodium borate at pH 7; separation capillary, 68.1 cm; detection capillary, 1.7 cm; separation potential, 20 kV (12 μA); injection, 2 s at 20 kV.

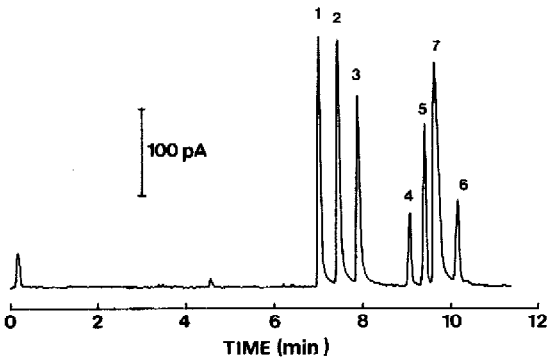


Fig. 3. Elektrokinetic separation of catechols as borate complexes: 10 m*M* dibasic sodium phosphate–6 m*M* sodium borate at pH 7 with 10 m*M* SDS; separation capillary, 64.3 cm; detection capillary, 1.7 cm; separation potential, 20 kV (7 μA); injection, 4 s at 20 kV.

MECC of borate–catechol complexes

Fig. 3 shows an electrokinetic separation of seven catechols at pH 7 in a phosphate–borate buffer containing 10 m*M* SDS. This system shows excellent selectivity for the normally cationic solutes, without excessive retention. One should also note the difference in elution order in this separation as compared to the separation shown in Fig. 1 which did not employ borate complexation. The elution order obtained for the normally cationic solutes is identical to that obtained in the phosphate buffer–SDS system (Fig. 1) and follows the trend predicted by the log *P* values. Conversely, the elution order for the normally non-ionic solutes differs from that shown in Fig. 1 and indicates that electrophoretic effects predominate for these species (net-anionic complexes).

Fig. 4 shows the dependence of solute velocity on SDS concentration for the seven borate-complexed catechols studied. The greatest SDS dependence is observed for the net-neutral borate complexes (Fig. 4a). Among the anionic complexes, CAT and L-DOPA are slightly dependent upon the micelle concentration, whereas 4-MC is more highly dependent on the micelle concentration (Fig. 4b). This may result from partial solubilization of the hydrophobic and uncharged side chain (methyl group) of 4-MC by the micelles. For anions, Otsuka *et al.*[17] have found that the degree of micellar solubilization of phenol by SDS micelles decreases with an increase of the ionization of the solute. This lowered SDS dependence is most likely a consequence of solute–micelle repulsion which limits solubilization and allows electrophoretic effects to predominate. It would appear that retention of net anionic complexes is based on both partitioning between the aqueous and micellar phases (SDS concentration dependence) and on electrophoretic effects (elution order).

Fig. 4a shows that the retention behavior of the net-neutral complexes is profoundly influenced by the concentration of SDS. This indicates that some type of interaction between the solute complex and the micelles is occurring. Retention of borate-complexed cationic catechols in this system appears to be mechanistically complicated, as in the phosphate–SDS system shown earlier. In this buffer system, the catechols are apparently complexed with borate as shown in eqn. 1. These cationic catechols form net-neutral complexes but still maintain a cationic functionality which

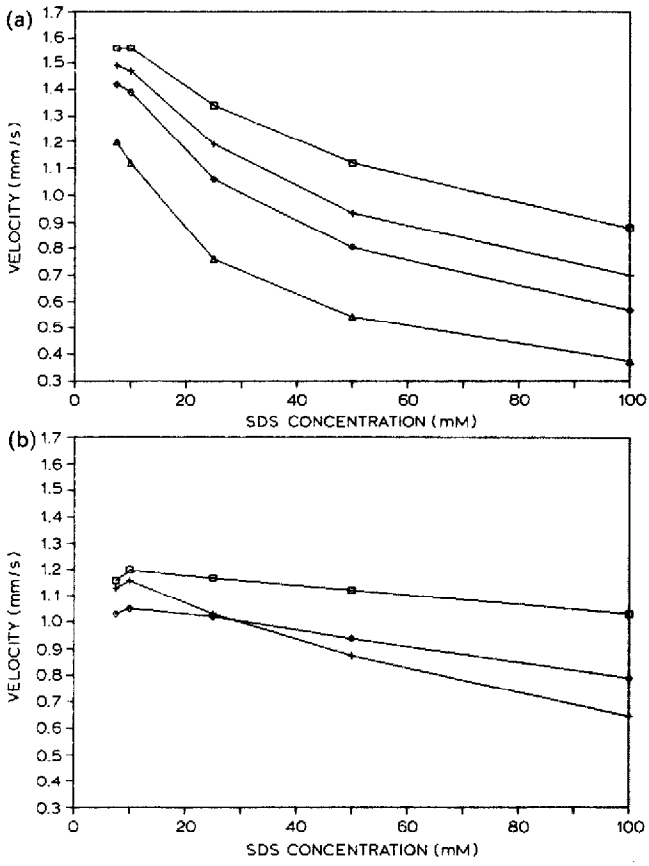


Fig. 4. Velocity of borate-complexed catechols as a function of SDS concentration. (a) Net-neutral borate complexes: □ = NE; + = E; ◇ = DHBA; △ = DA. (b) Anionic borate complexes: □ = L-DOPA; + = 4-MC; ◇ = CAT. Conditions as in Fig. 3.

can ion-pair with free surfactant monomer or interact with the Stern layer of the micelle. Thus, processes similar to those previously listed for the phosphate–SDS system may occur in separation involving borate-complexed cationic catechols. However, in this latter case, the anionic portion of the complex–ion-pair appears to reduce the partition ratio of the normally cationic catechols.

The data in Fig. 4a indicate excellent selectivity for separations of DA, NE, E, and DHBA over the entire range of SDS concentrations tested. At 7.5 m*M* SDS, all seven components are reseolved, with the net-neutral complexes eluting before the net anionic complexes. Since 7.5 m*M* SDS is below the literature value of the cmc[24,25], this behavior indicates that separation at this concentration of SDS may be based primarily on electrophoretic effects, with ion-pairing equilibria at the cationic moiety altering the mobilities in such a way to produce enhanced resolution of the components. Another possibility is that appreciable SDS aggregation occurs at this concentration. Similar results have been reported by Sepaniak and Cole[39] and can be attributed to factors such as buffer composition and ionic strength[24,25].

TABLE III

EFFICIENCY (THEORETICAL PLATES, N) AND B/A RATIO FOR MECC SEPARATION OF CATECHOLS

Conditions as listed in Fig. 1.

Compound	*10 mM SDS*		*20 mM SDS*	
	N	B/A	N	B/A
L-DOPA	201 000	2.1	70 000	3.2
CAT	142 000	1.2	114 000	2.4
4-MC	209 000	1.2	158 000	2.4
NE	45 000	5.7	50 000	2.6
E	68 000	5.0	86 000	3.4
DHBA	64 000	6.0	115 000	3.2
DA	91 000	5.0	139 000	2.6

Separation efficiency and peak shape

Although this paper concerns tailoring solution chemistry to design selective separations, peak resolution will also be affected by column efficiency. The effects of changing chemical parameters on the separation efficiency must therefore be examined.

The statistical efficiency of a chromatographic peak can be calculated from the half width of the peak using the equation:

$$N = 5.54\,(t_R/W_h)^2 \qquad (1)$$

where t_R is the retention time, and W_h is the width at half maximum. As an indication of peak asymmetry due to tailing, we include with our theoretical plate numbers a B/A ratio taken at 10% of the peak maximum[40]. A B/A ratio of 1.0 indicates a perfectly guassian peak, whereas a B/A ratio greater than 1.0 indicates a peak exhibiting tailing.

Separation efficiencies and B/A ratios for non-ionic and cationic catechols separated in the phosphate–SDS system are listed in Table III for two concentrations of SDS. At an SDS concentration of 10 mM, the efficiency for the non-ionic compounds is roughly double that obtained for the cationic solutes. At 20 mM SDS, the efficiency for the cationic solutes increases while that of the non-ionic compounds decreases. The efficiency obtained for cationic solutes is undoubtedly influenced by the many equilibria which can occur. Lowered efficiencies have been observed in HPLC separations employing secondary chemical equilibria for similar reasons[41]. This may be the case at lower SDS concentrations (*ca.* 10 mM); however, at higher SDS content (*ca.* 20 mM) the effects of these equilibria are perhaps offset by the decreased intermicelle distance[39].

In addition to equilibria factors, efficiency may also be influenced by electrostatic interactions between solutes and the negatively charged capillary walls. Such interactions are especially likely for cationic solutes and are indicated by peak tailing. Peak tailing for the cationic solutes was improved at the higher SDS concentration as indicated by the B/A ratios. This improvement is probably a consequence of in-

TABLE IV

EFFICIENCY (N) AND B/A RATIO FOR BORATE-COMPLEXED CATECHOLS AS A FUNCTION OF SDS CONCENTRATION

Conditions as in Fig. 3.

Compound	*7.5 mM SDS*		*10 mM SDS*		*25 mM SDS*		*50 mM SDS*		*100 mM SDS*	
	N	*B/A*	*N*	*B/A*	*N*	*B/A*	*N*	*B/A*	*N*	*B/A*
NE	42 000	4.8	89 000	2.6	62 000	3.2	*	*	36 000	1.9
E	44 000	6.4	71 000	3.1	40 000	*	*	*	25 000	1.7
DHBA	40 000	4.7	63 000	2.7	32 000	*	26 000	1.9	9600	1.3
DA	29 000	5.0	41 000	4.0	30 000	2.8	42 000	0.7	36 000	1.1
L-DOPA	71 000	*	108 000	1.1	*	*	*	*	71 000	1.5
4-MC	69 000	1.5	108 000	1.1	137 000	*	168 000	1.3	151 000	1.5
CAT	63 000	1.5	91 000	1.1	91 000	*	*	*	104 000	0.6

* Peak not sufficiently resolved for this measurement.

creased competition for the cationic moiety of the solute provided by the higher micelle concentrations. Conversely, for the non-ionic compounds, tailing was significantly greater at the higher SDS concentrations. At 10 mM SDS the B/A ratios for CAT and 4-MC were virtually 1.0, indicting excellent peak symmetry.

Table IV lists the efficiencies and B/A ratios obtained for the catechols run as borate complexes in the phosphate–borate–SDS system at various concentrations of SDS. Once again, the many surfactant–solute–micelle equilibria involved are sources of band broadening, especially for the species containing a positively charged moiety. The borate–catechol complexation equilibrium is also a potential source of band broadening in this system. For the net-neutral borate complexes (NE, E, DHBA, DA), best efficiency was obtained at an SDS concentration of 10 mM. Increases in SDS content served to degrade the efficiency observed for these compounds. The net-anionic borate complexes (L-DOPA, CAT, 4-MC) generally produced increased efficiency at higher SDS concentrations.

The net-neutral borate complexes (DA, NE, E, DHBA) exhibited a large degree of tailing at lower SDS concentrations. The B/A ratios approached 1.0 for these complexes as the SDS concentration increased. As in the phosphate–SDS system, this effect is presumably due to competition for the positively charged solute functionalities by the increased number of micelles. The anionic borate complexes exhibited a somewhat lesser degree of tailing throughout the entire range of SDS concentrations and this tailing was virtually independent of the SDS content. This behavior is expected for the anionic complexes since these solutes do not appear to interact significantly with the micelles.

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REFERENCES

1 R. Virtanen, *Acta Polytech. Scand. Chem. Incl. Metall. Ser.*, 123 (1974) 1.
2 F. E. P. Mikkers, F. M. Everaerts and Th. P. E. M. Verheggen, *J. Chromatogr.*, 169 (1979) 11.
3 J. W. Jorgenson and K. D. Lukacs, *J. Chromatogr.*, 218 (1981) 209.
4 H. H. Lauer and D. McManigill, *Anal. Chem.*, 58 (1986) 165.
5 A. S. Cohen, S. Terabe, J. A. Smith and B. L. Karger, *Anal. Chem.*, 59 (1987) 1021.
6 R. A. Wallingford and A. G. Ewing, *Anal. Chem.*, 59 (1987) 1762.
7 J. W. Jorgenson and K. D. Lukacs, *Science (Washington, D.C.)*, 222 (1983) 266.
8 R. A. Wallingford and A. G. Ewing, *Anal. Chem.*, 59 (1987) 678.
9 S. Hjerten, *J. Chromatogr.*, 270 (1983) 1.
10 J. S. Green and J. W. Jorgenson, *J. Chromatogr.*, 352 (1986) 337.
11 J. A. Olivares, N. T. Nguyen, C. R. Yonker and R. D. Smith, *Anal. Chem.*, 59 (1987) 1230.
12 T. Tsuda, K. Nomura and G. Nakagawa, *J. Chromatogr.*, 248 (1982) 241.
13 K. D. Lukacs and J. W. Jorgenson, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 407.
14 Y. Walbroehl and J. W. Jorgenson, *Anal. Chem.*, 58 (1986) 479.
15 S. Terabe, H. Ozaki, K. Otsuka, K. Ichikawa, A. Tsuchiya and T. Ando, *Anal. Chem.*, 56 (1984) 111.
16 D. E. Burton, M. J. Sepaniak and M. P. Maskarinec, *J. Chromatogr. Sci.*, 24 (1986) 347.
17 K. Otsuka, S. Terabe and T. Ando, *J. Chromatogr.*, 348 (1985) 39.
18 S. Terabe, H. Ozaki, K. Otsuka and T. Ando, *J. Chromatogr.*, 332 (1985) 211.
19 K. Otsuka, S. Terabe and T. Ando, *J. Chromatogr.*, 332 (1985) 219.
20 D. E. Burton, M. J. Sepaniak and M. P. Maskasrinec, *Chromatographia*, 21 (1986) 583.
21 P. Gozel, E. Gassmann, H. Michelsen and R. N. Zare, *Anal. Chem.*, 59 (1987) 44.
22 A. T. Balchunas and M. J. Sepaniak, *Anal. Chem.*, 59 (1987) 1470.
23 R. A. Wallingford and A. G. Ewing, *Anal. Chem.*, 60 (1988) 258.
24 M. J. Rosen, *Surfactants and Interfacial Phenomena*, Wiley-Interscience, New York, 1978.
25 K. L. Mittal (Editor), *Micellization, Solubilization and Microemulsions*, Vol. 1, Plenum, New York, 1977.
26 D. Lemordant, *J. Electroanal. Chem.*, 219 (1987) 125.
27 D. Meisel, M. S. Matheson and J. Rabani, *J. Am. Chem. Soc.*, 100 (1978) 117.
28 Y. Oshawa, Y. Shimazaki and S. Aoyagui, *J. Electroanal. Chem.*, 114 (1980) 235.
29 G. L. McIntire and H. N. Blount, *J. Am. Chem. Soc.*, 101 (1979) 7720.
30 S. A. Wages, W. H. Church and J. B. Justice, Jr., *Anal. Chem.*, 58 (1986) 1649.
31 F. Gerlo and R. Malfait, *J. Chromatogr.*, 343 (1985) 9.
32 K. L. Mittal (Editor), *Solution Chemistry of Surfactants*, Plenum, New York, 1979.
33 C. Hansch and A. Leo, *Substituent Constants for Correlation Analysis in Chemistry and Biology*, Wiley-Interscience, New York, 1979, pp. 18–43.
34 R. F. Rekker, *The Hydrophobic Fragmental Constant*, Elsevier, Amsterdam, 1977.
35 P. C. Jurs, J. T. Chow and M. Yuan, in E. C. Olson and R. E. Christoffereson (Editors), *Computer-Assisted Drug Design*, American Chemical Society, Washington, DC, 1979, pp. 103–129.
36 J. De Jong, C. F. M. Van Valkenburg and U. R. Tjaden, *J. Chromatogr.*, 322 (1985) 43.
37 K. Yoshino, M. Kotaka, M. Okamoto and H. Kakihana, *Bull. Chem. Soc. Jpn.*, 52 (1979) 3005.
38 H. Steinberg, *Organoboron Chemistry*, Wiley-Interscience, New York, 1964, Ch. 6.
39 M. J. Sepaniak and R. O. Cole, *Anal. Chem.*, 59 (1987) 472.
40 J. P. Foley and J. G. Dorsey, *Anal. Chem.*, 55 (1983) 730.
41 J. P. Foley, *Chromatography*, 2 (1987) 43.