NOVEL CHROMATOGRAPHIC TECHNIQUE FOR STUDYING PRESSURE AND SECONDARY SURFACE EFFECTS ON THE CRITICAL MICELLE CONCENTRATION

R. K. GILPIN*, A. KASTURI and G. WERNER*

Department of Chemistry, Kent State University, Kent, OH 44242 (U.S.A.)

(First received February 13th, 1986; revised manuscript received May 1st, 1986)

SUMMARY

A high-performance liquid chromatographic method has been developed to study micelle formation. A maximum is observed at the critical micelle concentration (CMC) when the chromatographic selectivity factor for solute pairs of different polarity is plotted as a function of surfactant concentration. The values obtained for the CMC are about 10–15% higher than those reported for ambient pressures but are much closer to elevated pressure data.

INTRODUCTION

Surfactants are used widely in chemistry to alter the properties and activities of various systems. At high concentrations aggregate units (micelles) are formed which are roughly spherical to elliptical in shape typically consisting of 40–100 monomers. The narrow range of concentration at which these aggregates become detectable is the critical micelle concentration (CMC) and is probably the simplest means of characterizing the colloid and surface behavior of a surfactant[1]. The concentration at which micelles become detectable depends on the experimental approach[1]. To date a variety of techniques have been used to determine the CMC and include measurements of surface tension, colligative and transport phenomena, electrical conductivity, light scattering and calorimetric properties. Likewise, spin-lattice relaxation times and chemical shifts determined by NMR have also been used[2–4].

Several applications of micellar systems in high-performance liquid chromatography (HPLC) have been reported[5,6]. Armstrong and Henry[7] were the first to utilize the approach for the separation of selected phenols and polynuclear aromatic hydrocarbons with an aqueous micellar mobile phase of sodium dodecyl sulfate. Subsequently, others have used micelle systems to enhance both selectivity and detection[8–12]. Recently, Dorsey and co-workers[13,14] have studied the influence of temperature and small amounts of organic modifier on chromatographic performance. Likewise these same investigators have described a method for determining the CMC

* Present address: Karl-Marx University, Leipzig, G.D.R.

from biphasic changes in plots of the capacity factor *versus* surfactant concentration[13]. However, ambiguities using this approach have been observed[15,16]. An alternative HPLC method has been developed based on changes in relative retention between solute pairs.

EXPERIMENTAL

Equipment

All chromatographic experiments were carried out with a Laboratory Data Control (Riviera Beach, FL, U.S.A.) Model Constametric III pump and Model spectromonitor III UV detector. An IBM (Danbury, CT, U.S.A.) Model 9000 computer system was used to record and process the data. Columns (25 cm × 4.6 mm I.D. octyl- and octadecyl-silica) also were obtained from IBM and were maintained at 25.0 ± 0.1°C in a thermostated waterbath. The flow-rate was monitored with a Phase Separations (Queensferry, U.K) Model FLOSOA electronic flowmeter.

Reagents

Sodium octyl sulfonate, sodium octyl sulfate and sodium decyl sulfate were reagent-grade obtained from Eastman-Kodak (Rochester, NY, U.S.A.). Sodium dodecyl sulfate was electrophoresis-grade from Fisher Scientific (Pittsburgh, PA, U.S.A.). All were used as received. The methanol was HPLC-grade from MCB (Norwood, OH, U.S.A.).

Procedure

Each mobile phase was prepared by dissolving the appropriate amount of surfactant in distilled water. A test mixture of uracil, sulfanilamide, resorcinol and phenol was also prepared in water. Prior to use each column was conditioned with at least 100 ml of methanol and washed thoroughly with copious quantities of water. All runs were carried out starting with 100% water and successively increasing the concentration of surfactant in the mobile phase. At each new mobile phase concentration the surface was equilibrated with a sufficient volume until constant solute retention was obtained. A minimum of four injections were made for each mobile phase. The void volume was determined at each surfactant concentration by several repetitive injections of [^{2}H]water.

RESULTS AND DISCUSSION

The retention behavior of four neutral solutes of differing polarities was studied on two reversed-phase surfaces as a function of increasing surfactant concentration. The capacity factor ratio, selectivity, for solute pairs was calculated and plotted against the concentration of surfactant in the mobile phase. Representative data are shown in Fig. 1A. These results were obtained for sodium dodecyl sulfate on the octyl and octadecyl columns using uracil–phenol as the solute pair and on the octyl column for phenol–sulfanilamide. At low surfactant concentrations, the selectivity remained relatively constant, started to increase in the intermediate pre-micellar region, and reached a maximum at the CMC. Shown in Fig. 1B is the incremental change in selectivity with respect to change in concentration ($\Delta S/\Delta C$) *versus* mean
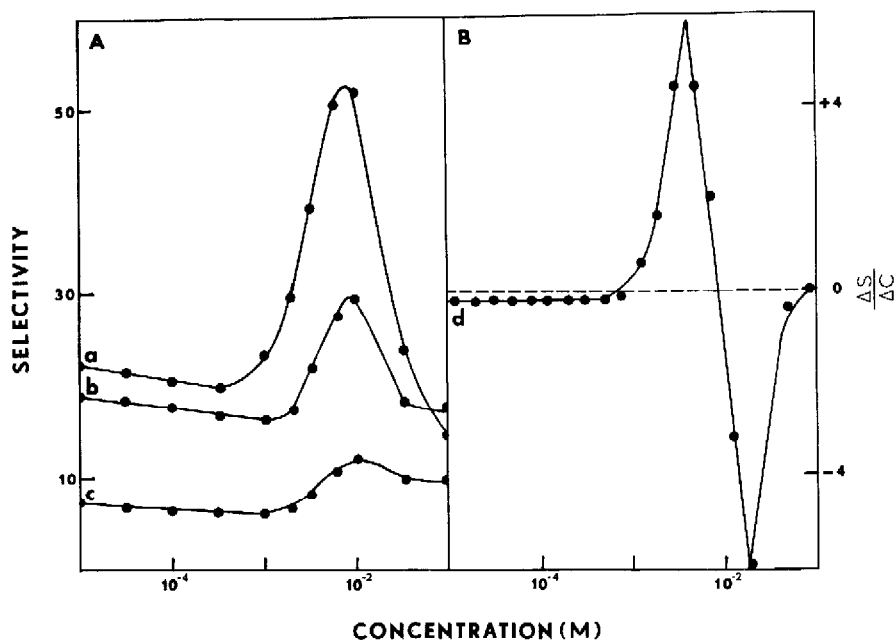
Fig. 1. Changes in selectivity *versus* surfactant concentration for sodium dodecyl sulfate. (a) Column, octadecyl; solute pair, phenol–uracil. (b) Column, octyl; solute pair, phenol–uracil. (c) Column, octyl; solute pair, phenol–sulfanilamide. (d) Derivative plot of curve b. For A and B, see text.

concentration. This derivative plot was determined graphically from Fig. 1A and intersects the concentration axis at the CMC. Immaterial of solute and surface, the selectivity reached a maximum at the CMC. However, there are large differences in magnitude for the curves. Among the four neutral solutes studied, phenol and uracil were, respectively, the least and most polar and the selectivity maximum for this solute pair was the greatest. Likewise, the maximum change in selectivity (Fig. 1) was greater on the octadecyl column than on an octyl column for a given solute pair. These results imply that the more hydrophobic the stationary phase the greater the change in selectivity. This dependency on the bonded hydrocarbon chain length has been attributed to structuring–solvation effects which reach a maximum at the critical micelle concentration[16]. Similarly for a given hydrophobic surface changes in selectivity (*i.e.*, applied to the determination of the CMC) can be maximized via selection of a suitable neutral solute pair which differ in polarity.

The CMC for sodium dodecyl sulfate determined by the current method using different solute pairs and column types are listed in Table I. The CMC obtained chromatographically is about 10–15% higher than reported[1] ambient pressure values but is much closer to elevated pressure data. With this correction the values in Table I are only about 5% higher.

Fig. 2 shows selectivity *versus* concentration plots for the solute pair, phenol–resorcinol on the octyl surface for various surfactants. Similar agreement between reported and chromatographically measured results was obtained for sodium decyl sulfate. Unfortunately, because of problems of poor column stability and

TABLE I

CMC FOR SODIUM DODECYL SULFATE DETERMINED BY HPLC SELECTIVITY METHOD

Solute pair	Column	CMC (M)*
Phenol–uracil	C_8	$9.6 \cdot 10^{-3}$
Phenol–sulfanilamide	C_8	$9.8 \cdot 10^{-3}$
Resorcinol–uracil	C_8	$9.7 \cdot 10^{-3}$
Phenol–resorcinol	C_8	$9.5 \cdot 10^{-3}$
Phenol–uracil	C_{18}	$9.4 \cdot 10^{-3}$
Phenol–sulfanilamide	C_{18}	$9.4 \cdot 10^{-3}$
Resorcinol–uracil	C_{18}	$9.6 \cdot 10^{-3}$
Phenol–resorcinol	C_{18}	$9.1 \cdot 10^{-3}$

* Measured at 25°C. Literature CMC: $8.1–8.4 \cdot 10^{-3}$ M at atmospheric pressure; $9.1–9.4 \cdot 10^{-3}$ M at elevated pressure. (From ref. 1.)
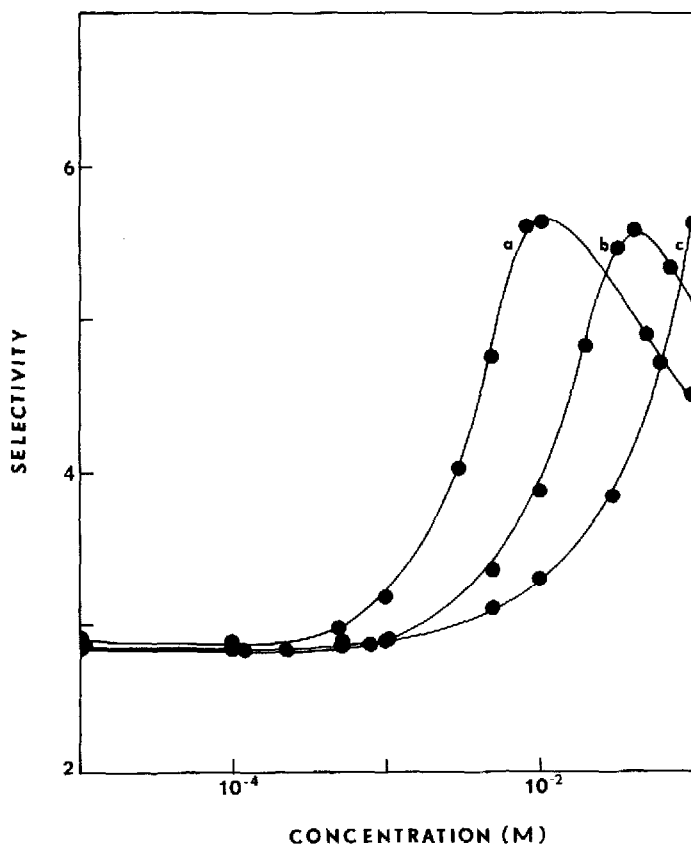

Fig. 2. Changes in selectivity *versus* surfactant concentration for different surfactants. Column, octyl; solute pair, phenol–resorcinol; (a) sodium dodecyl sulfate; (b) sodium decyl sulfate; (c) sodium octyl sulfate.

increased detector noise resulting from foaming, the upper surfactant concentrations were limited to approximately 0.1 M. Since the CMC values for both octyl surfactants are near these experimental limits, they could not be determined.

Based on the statistics of the current data it is not possible to assert whether chromatographically determined CMC values are within experimental error of reported elevated pressure data or are slightly high due to secondary solute–surface effects. Since each of these can be distinguished experimentally, a number of studies are now in progress and will be reported in the future.

REFERENCES

1 P. Muskeriee and K. J. Mysels, *Ciritical Micelle Concentrations of Aqueous Surfactant Systems, NSRDS-NBS 36*, United States Department of Commerce, Washington, DC, 1971, p. 222.
2 H. Okabayashi, T. Yoshida, K. Matsushita and Y. Terada, *Chem. Scr.*, 20 (1982) 117.
3 K. Matsushita and H. Okabayashi, *Chem. Scr.*, 15 (1980) 69.
4 K. Matsushita, Y. Terada, T. Yoshida and H. Okabayashi, *Z. Naturforsch.*, 38 (1983) 1149.
5 J. A. Graham and L. B. Rogers, *J. Chromatogr. Sci.*, 18 (1980) 614.
6 L. J. Cline Love, J. G. Habarta and J. G. Dorsey, *Anal. Chem.*, 56 (1984) 1132A.
7 D. W. Armstrong and S. J. Henry, *J. Liq. Chromatogr.*, 3 (1980) 657.
8 D. W. Armstrong and F. Nome, *Anal. Chem.*, 53 (1981) 1662.
9 P. Yarmchuk, R. Weinberger, R. F. Hirsch and L. J. Cline Love, *Anal. Chem.*, 54 (1982) 2233.
10 P. Yarmchuk, R. Weinberger, R. F. Hirsch and L. J. Cline Love, *J. Chromatogr.*, 283 (1984) 47.
11 D. W. Armstrong, W. L. Hinze, K. H. Bui and H. N. Singh, *Anal. Lett.*, 14 (1981) 1659.
12 R. Weinberger, P. Yarmchuk and L. J. Cline Love, *Anal. Chem.*, 54 (1982) 1552.
13 J. G. Dorsey, M. T. DeEchegaray and J. S. Landy, *Anal. Chem.*, 55 (1983) 924.
14 J. S. Landy and J. G. Dorsey, *J. Chromatogr. Sci.*, 22 (1984) 68.
15 A. Kasturi and R. K. Gilpin, presented at the *American Chemical Society 17th Central Regional Meeting, Akron, OH, 1985*.
16 A. Katuri and R. K. Gilpin, *J. Chromatogr. Sci.*, in press.