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REVERSED-PHASE LIQUID CHROMATOGRAPHIC STUDIES OF NON-IONIC SURFACTANTS AND RELATED SOLUTES

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SUMMARY

Homologous series of alkyl ester, ether and amide polyoxyethylene non-ionic surfactants have been synthesized and their retention properties have been studied under reversed-phase conditions. In addition, methylene group selectivities have been determined for the three types of surfactants as well as for a homologous series of ethyl esters of alkanolic acids. In the composition range studied for a given mobile phase, methylene selectivity was nearly independent of the head group of the surfactants. This supports the idea that the retention mechanism is governed by hydrophobic interactions between the alkyl tail of the surfactant and the bonded stationary phase.

INTRODUCTION

The analytical chemistry of non-ionic surfactants has been summarized in a recently published monograph¹. Only relatively few studies have systematically dealt with the retention properties of this class of compounds. Examples of these studies may be found in refs. 2-5.

In the current investigation, homologous series of three types of alkyl oxyethylene monodispersed non-ionic surfactants with differing head groups and identical hydrocarbon tails were synthesized. The compounds which were prepared fit the general formulas: $\text{CH}_3(\text{CH}_2)_{n-1}\text{CO}_2(\text{C}_2\text{H}_4\text{O})_4\text{H}$, $\text{CH}_3(\text{CH}_2)_{n-1}(\text{OC}_2\text{H}_4)_4\text{OH}$, and $\text{CH}_3(\text{CH}_2)_{n-1}\text{CONH}(\text{C}_2\text{H}_4\text{O})_2\text{H}$. The retention behavior of these three classes of surfactants were studied under reversed-phase liquid chromatographic conditions, using aqueous methanol as the mobile phase and an octyl surface as the stationary phase. The incremental changes in retention per addition of a methylene carbon in the tail of the surfactant (*i.e.*, methylene selectivity⁶) have been determined for alkyl chain lengths varying from C₃ to C₈ for each of the three different head groups. Additionally, the changes in solute retention have been correlated with the hydrophilic/lipophil balance (HLB) determined by the Griffin equation^{7,8}.

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EXPERIMENTAL

Surfactant synthesis

All chemicals were purchased from Aldrich (Milwaukee, WI, U.S.A.).

The ether surfactants (*i.e.*, $\text{CH}_3(\text{CH}_2)_{n-1}(\text{OC}_2\text{H}_5)_m\text{OH}$, where $n = 3-8$ and $m = 2-4$) were prepared by addition of a 1:5:1 molar ratio of sodium hydroxide pellets, appropriate polyethylene glycol, and a given alkyl bromide. The resulting mixture was refluxed for several hours, cooled, and digested with water. The product was extracted with multiple portions of chloroform, and the extract was dried over anhydrous sodium sulfate. The extract was filtered, the chloroform removed in a rotary evaporator, and the remaining oily residue was fractionally distilled under reduced pressure to obtain the purified surfactant.

The amide surfactants, (*i.e.*, $\text{CH}_3(\text{CH}_2)_{n-1}\text{CONH}(\text{C}_2\text{H}_4\text{O})_2\text{H}$ where $n = 5-8$) were prepared by the method of Afzal *et al.*⁹ with a slight modification in the work-up procedure.

The ester surfactants (*i.e.*, $\text{CH}_3(\text{CH}_2)_{n-1}\text{CO}_2(\text{C}_2\text{H}_4\text{O})_4\text{H}$, where $n = 5-8$) were prepared by refluxing a given alkanolic acid with tetraethylene glycol (1:5 mol ratio) in the presence of a cation-exchange resin, which was used as a catalyst (H^+ form). A Dean-Stark trap was attached, and 50 ml of toluene were added to the flask. After *ca.* 6 h of refluxing, the toluene was distilled off; the mixture was cooled and then filtered to remove the resin. Subsequently, the mixture was digested with a saturated solution of NaCl and extracted with chloroform. The product was isolated from the chloroform in a similar fashion to that described for the ether surfactants.

In all of the above cases the purity and identity of the surfactants were established by thin-layer chromatography, infrared and nuclear magnetic resonance spectrometry.

Chromatographic experiments

All chromatographic analyses were performed on an IBM Instruments (Danbury, CT, U.S.A.) Model LC/9533 liquid chromatograph, using a 250 mm \times 4.6 mm I.D. IBM column packed with an octyl stationary phase (Part No. 8635316). The refractive index detector used was an IBM Model LC/9525 instrument. The HPLC-grade methanol was obtained from Fisher Scientific (Pittsburgh, PA, U.S.A.) and the deionized water was prepared using a Milli-Q (Millipore, Milford, MA, U.S.A.) purification system. Mobile phases were prepared on a v/v basis and degassed before using.

After switching mobile phases, the column was conditioned with at least 20-30 column volumes of the new mobile phase. Retention data were collected at a flow-rate of 1.0 ml/min. The surfactant test solutes were prepared in either methanol or in binary mixtures of methanol and water at an approximate concentration of 1.0 mg/ml. Reported capacity factors, k' , are mean values from 2-5 replicate injections, calculated using $^2\text{H}_2\text{O}$ to determine the void volume.

RESULTS AND DISCUSSION

Free energies of transfer of straight-chain solutes from water to a non-polar phase are linear with respect to the number of carbons in the chain^{10,11}. Thus, for

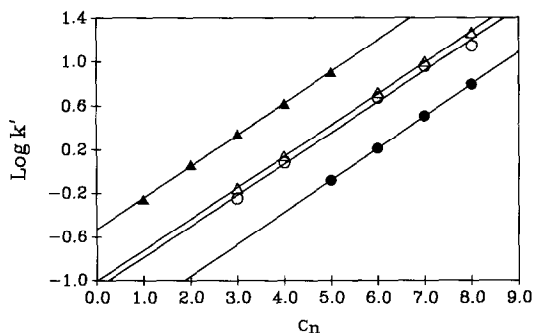


Fig. 1. $\text{Log } k'$ vs. C_n for homologous series of solutes. Mobile phase: methanol-water (55:45). Solutes: \circ = ester surfactants; \triangle = ether surfactants; \bullet = amide surfactants; \blacktriangle = ethyl alkanooates. Correlation coefficients for all plots are 0.998 or better.

homologous series of solutes $\text{log } k'$ also is linearly related to the number of carbon atoms¹²⁻²⁰. This latter relationship can be expressed as

$$\text{log } k' = aC_n + b \quad (1)$$

where the slope, a , is the incremental change in retention as a function of increasing carbon number, C_n . The intercept, b , is related to the functional groups in the solute and their influence on retention^{15,21}.

The plots of $\text{log } k'$ vs. C_n for homologous series of surfactants (ester, ether and amide) and for comparison purposes of ethyl esters of alkanolic acids using methanol-water (55:45) as the mobile phase are shown in Fig. 1. Similar plots were observed in methanol-water (65:35) and (75:25) mobile phases. Values for a and b for the three classes of non-ionic surfactants and simple esters are given in Table I. These values are consistent with those reported by others²².

The above results reflect several trends. Firstly, the methylene selectivity, a , increased directly with the water content of the mobile phase. Tanaka and Thornton²¹ have reported similar observations for homologous series of alkanes, alcohols and carboxylic acids. Secondly, the slopes were nearly constant for a given mobile phase composition, irrespective of the homologous series (*i.e.*, the ester, ether or

TABLE I
SLOPE (a) AND INTERCEPT (b) VALUES OF $\text{LOG } k'$ VS. C_n

Solute	Methanol-water					
	55:45		65:35		75:25	
	a	b	a	b	a	b
Ether surfactants	0.285	-1.005	0.235	-1.149	0.191	-1.29
Ester surfactants	0.284	-1.140	0.229	-1.136	0.196	-1.33
Amide surfactants	0.293	-1.544	0.241	-1.572	0.191	-1.68
Ethyl esters	0.282	-0.505	0.233	-0.669	0.188	-0.85

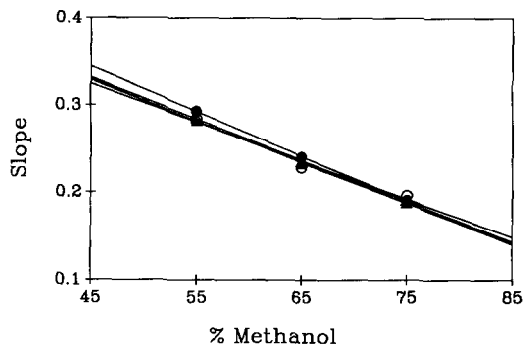


Fig. 2. Methylene selectivity vs. percent methanol. Solutes: ○ = ester surfactants; △ = ether surfactants; ● = amide surfactants; ▲ = ethyl alkanoates. The correlation coefficient is 0.992.

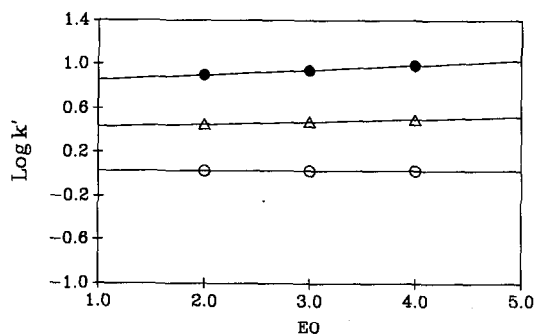


Fig. 3. Log k' vs. number of ethylene oxide (EO) units in the heptyl polyoxyethylene ethers, $\text{CH}_3(\text{CH}_2)_6(\text{EO})_m\text{OH}$. Mobile phase: methanol-water: ● = 55:45; △ = 65:35; ○ = 75:25. The correlation coefficient is 0.999.

TABLE II

CALCULATED VALUES OF HLB

Surfactant	HLB	Surfactant	HLB
$\text{C}_3\text{H}_7\text{CO}_2(\text{C}_2\text{H}_4\text{O})_4\text{H}$	16.74	$\text{C}_7\text{H}_{15}\text{O}(\text{C}_2\text{H}_4\text{O})_4\text{H}$	13.22
$\text{C}_4\text{H}_9\text{CO}_2(\text{C}_2\text{H}_4\text{O})_4\text{H}$	15.90	$\text{C}_8\text{H}_{17}\text{O}(\text{C}_2\text{H}_4\text{O})_4\text{H}$	12.61
$\text{C}_6\text{H}_{13}\text{CO}_2(\text{C}_2\text{H}_4\text{O})_4\text{H}$	14.44	$\text{C}_7\text{H}_{15}\text{O}(\text{C}_2\text{H}_4\text{O})_2\text{H}$	10.29
$\text{C}_7\text{H}_{15}\text{CO}_2(\text{C}_2\text{H}_4\text{O})_4\text{H}$	13.81	$\text{C}_7\text{H}_{15}\text{O}(\text{C}_2\text{H}_4\text{O})_3\text{H}$	12.02
$\text{C}_8\text{H}_{17}\text{CO}_2(\text{C}_2\text{H}_4\text{O})_4\text{H}$	13.23	$\text{C}_7\text{H}_{11}\text{CONH}(\text{C}_2\text{H}_4\text{O})_2\text{H}$	13.00
$\text{C}_3\text{H}_7\text{O}(\text{C}_2\text{H}_4\text{O})_4\text{H}$	16.36	$\text{C}_6\text{H}_{13}\text{CONH}(\text{C}_2\text{H}_4\text{O})_2\text{H}$	12.17
$\text{C}_4\text{H}_9\text{O}(\text{C}_2\text{H}_4\text{O})_4\text{H}$	15.44	$\text{C}_7\text{H}_{15}\text{CONH}(\text{C}_2\text{H}_4\text{O})_2\text{H}$	11.43
$\text{C}_6\text{H}_{13}\text{O}(\text{C}_2\text{H}_4\text{O})_4\text{H}$	13.88	$\text{C}_8\text{H}_{17}\text{CONH}(\text{C}_2\text{H}_4\text{O})_2\text{H}$	10.78

amide head groups). Thirdly, as shown in Fig. 2, there was a linear and nearly superimposable correlation between the methylene selectivity and volume percent of methanol in the mobile phase for all four homologous series. These latter results also demonstrate that the hydrophilic head groups do not influence the methylene selectivity.

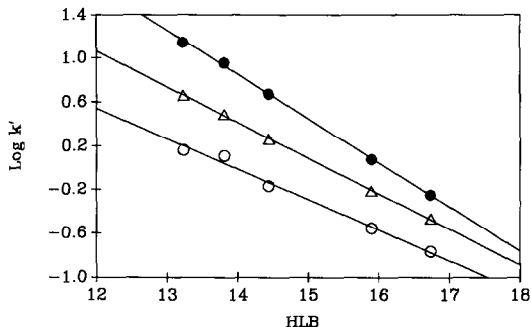


Fig. 4. $\text{Log } k'$ vs. HLB for the ester surfactants. Mobile phase: methanol-water: ● = 55:45; ▲ = 65:35; ○ = 75:25. The correlation coefficient is 0.995.

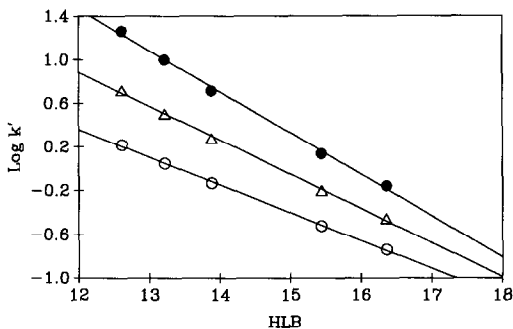


Fig. 5. $\text{Log } k'$ vs. HLB for the ether surfactants. Mobile phase: methanol-water: ● = 55:45; ▲ = 65:35; ○ = 75:25. The correlation coefficient is 0.998.

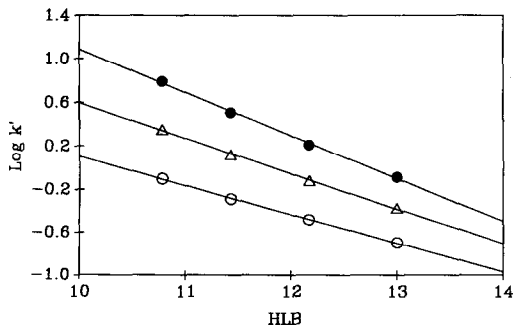


Fig. 6. $\text{Log } k'$ vs. HLB for amide surfactants. Mobile phase: methanol-water: ● = 55:45; ▲ = 65:35; ○ = 75:25. The correlation coefficient is 0.999.

The retention behavior was also studied for a series of heptyl ethers containing 2, 3 and 4 ethylene oxide units by using three different aqueous methanol mobile phase compositions. Plots of $\log k'$ vs. the number of ethylene oxide groups for methanol-water (55:45), (65:35) and (75:25) mobile phases are given in Fig. 3. The plots are nearly parallel and the slopes very small. These data further support the idea that the interactions between the hydrophobic tail of the surfactant and the stationary phase are primarily responsible for the observed changes in retention for the ethylene oxides studied.

Approximately forty years ago Griffin^{7,8} proposed an empirical relationship, which he termed the hydrophil/lipophil balance (HLB), to quantify the relationship between the two parts of a surfactant molecule, the hydrophilic and the lipophilic groups. This relationship is given in eqn. 2.

$$\text{HLB} = \frac{\text{Mol. wt. of hydrophilic part} \times 20}{\text{Mol. wt. of the surfactant}} \quad (2)$$

The HLB, which increases with increasing polarity of the molecule, has been employed in a general sense for characterizing surfactants¹.

Calculated HLB values are given in Table II for the various surfactants examined in the current study. When these values were plotted against $\log k'$, linear correlations were observed, as shown in Figs. 4-6 for the ester, ether, and amide surfactants, respectively. The overall negative slopes indicate that retention decreases with decreasing hydrophobicity of the surfactant. The nearly identical slopes between surfactant type for the compounds are consistent with the above hydrophobic retention mechanism. Further studies are needed to determine the generality of this relationship for other classes of surfactants.

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