Waters
Lab Highlights
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ADVANCES IN PAIRED-ION CHROMATOGRAPHY

III. EFFECT OF IONIC STRENGTH ON RETENTION AND DETECTOR RESPONSE

Previous Lab Highlights of this series (LAH 0075, 0099) have discussed the ion-interaction model and the new technique of UV-Visualization liquid chromatography. Further efforts at understanding and applying the UV-Visualization technique have continued at Waters. The influence of inorganic salts added to the mobile phase has been most recently studied, using the chromatographic conditions shown in Table 1. A series of eluents was prepared in which the concentration of inorganic salt was varied from 10^{-5} M to 10^{-2} M. The salts used in two separate experiments were KCl and KH_2PO_4. For both salts, a similar effect was observed: as the ionic strength of the eluent was increased, additional cetylpyridinium chloride (CPC) reagent was adsorbed onto the C_{18} stationary phase. This rather unexpected result is summarized in Figure 1, which shows the accumulation of adsorbed CPC reagent as a function of increasing salt concentration.

The dramatic changes indicated by Figure 1 would be expected to influence the retention of ionic samples. To test this, a mixture of alkylsulfonates was analyzed by UV-Visualization at three concentrations of KH_2PO_4. Figure 2 shows the resulting chromatograms. Changes in retention and detector response are immediately apparent.

Retention of alkylsulfonates is seen to decrease as ionic strength increases, despite the fact that more positively-charged CPC reagent is present on the C_{18} surface at higher concentrations of salt. In addition, peaks which are positive at low ionic strength become negative at higher ionic strength (Figure 2 B,C). The switch from positive to negative occurs as the peak moves from elution after the reagent peak to elution before the reagent peak. Finally, the relative peak magnitudes for the alkylsulfonates vary as ionic strength is increased. Consider, for example, the relative peak heights of the C_7 and C_8 peaks in Figure 2 (A-C).

These behaviors are explained in part in a recent publication from the Waters Application Lab (1). For the system shown in Table 1, eluent ionic strength was shown to be a powerful variable for paired ion chromatography. The role of ionic strength remains an open question for other paired ion systems, but it is clear that control of eluent ionic strength is essential for reproducible chromatography. Users of paired ion systems may want to explore the additional control of retentivity which can be achieved through the manipulation of ionic strength.

TABLE 1

Column:	μBONDAPAK™ C_{18}	Temperature:	Ambient
Mobile Phase:	60% Methanol	Flow Rate:	2.0 ml/min
	40% Water	Detector:	Model 440,254 nm,
	0.2 mM Cetylpyridinium Chloride		0.05 AUFS

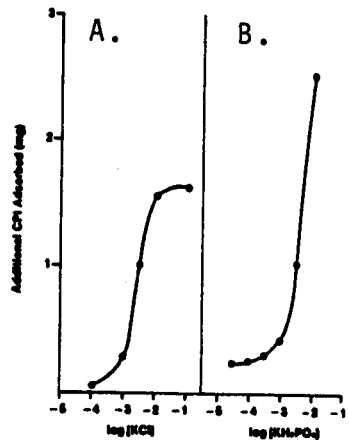

Figure 1. The effect of ionic strength upon the adsorption of cetylpyridinium ion onto the stationary phase: (A) using potassium chloride; (B) using monobasic potassium phosphate. Eluent was the same as in Table 1.

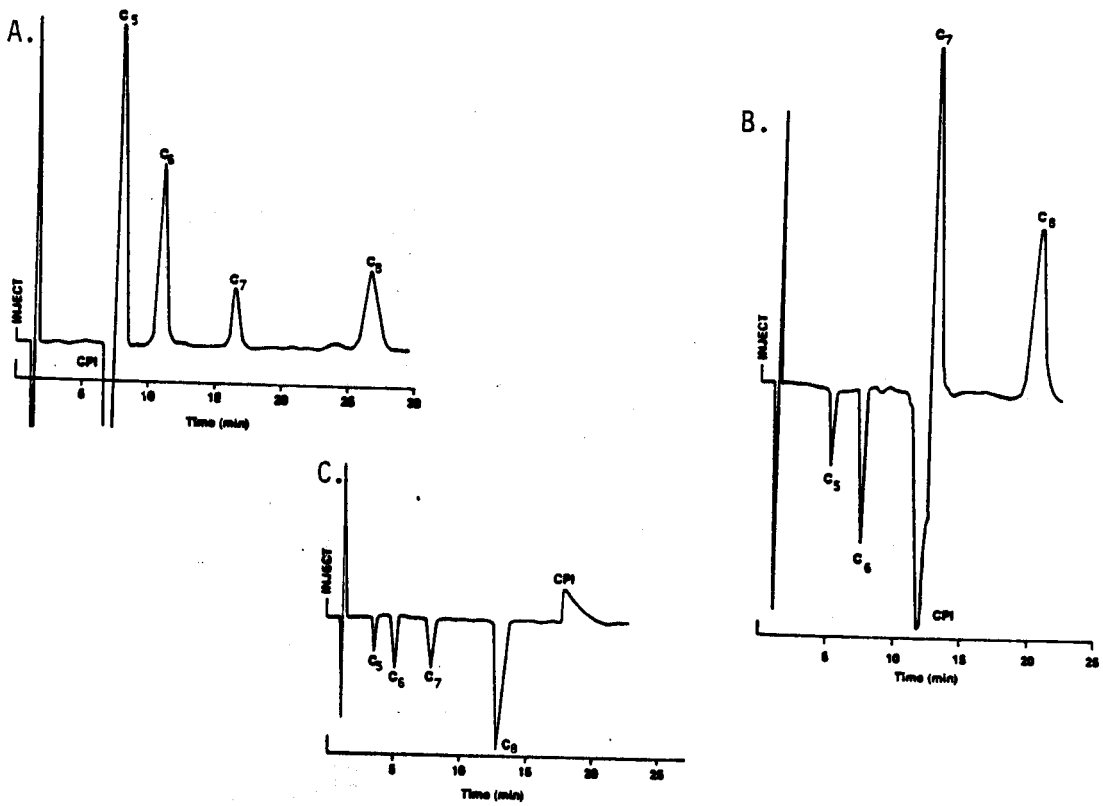

Figure 2. Chromatographic response of alkylsulfonates (C_5, C_6, C_7, C_8) in eluents of different ionic strength. (CPI denotes cetylpyridinium reagent.) The chromatographic conditions are the same as in Table 1 with a noted amount of dibasic potassium phosphate: (A) is 10^{-5} M, (B) is 10^{-3} M, (C) is 10^{-2} M.

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1. B. A. Bidlingmeyer and F. V. Warren, Jr. Anal. Chem., 54 (1982) 2351.