

CHROM. 18 481

Note

Determination of alkyl sulfonates by liquid chromatography with indirect photometric detection

J. R. LARSON

Analytical Laboratories, The Dow Chemical Company, 574 Building, Midland, MI 48667 (U.S.A.)

(Received December 30th, 1985)

Indirect photometric liquid chromatography (IPC) is the name given to a technique which uses a UV-absorbing counter-ion in an ion-exchange mode with an UV detector to determine ionic species. IPC, as described in detail by Small and Miller^{1,2}, was first used for the determination of inorganic ions. Later Larson and Pfeiffer used IPC for the determination of UV-transparent quaternary ammonium salts³, and alkylamines and alkanolamines⁴. This paper describes an IPC technique for the determination of a class of UV-transparent organic anions, *viz.* alkyl sulfonates. In the past these compounds have been determined by time-consuming derivatization techniques⁵. More recently, reversed-phase ion-pair chromatography with UV-absorbing ion-pair reagents has been used for determination of these compounds^{6–8}.

EXPERIMENTAL

Chemicals

Distilled-in-glass acetonitrile was obtained from Burdick and Jackson Labs. (Muskegon, MI, U.S.A.). Potassium biphthalate was obtained from Aldrich (Milwaukee, WI, U.S.A.). Sulfosalicylic acid and *m*-sulfobenzoic acid were obtained from ICN Pharmaceuticals (Plainview, NY, U.S.A.).

High-performance liquid chromatographic conditions

The liquid chromatograph used consisted of a Laboratory Data Control Constametric III pump, a Rheodyne Model 7125 injection valve equipped with a 20- μ l loop, a Perkin-Elmer LC-75 variable-wavelength UV detector and a Sargent-Welch Model SRG recorder. The column used was a 250 \times 4.6 mm I.D. Partisil 10 SAX (Whatman).

RESULTS AND DISCUSSION

In IPC the UV-absorbing counter-ion has the dual role of (1) selectively displacing the sample ions from the ion-exchange column and (2) revealing the UV-transparent sample ions as negative peaks in an elevated baseline as they are displaced from the column. Three compounds, potassium biphthalate, sulfosalicylic acid and *m*-sulfobenzoic acid were evaluated for use as the UV-absorbing counter-ion for the

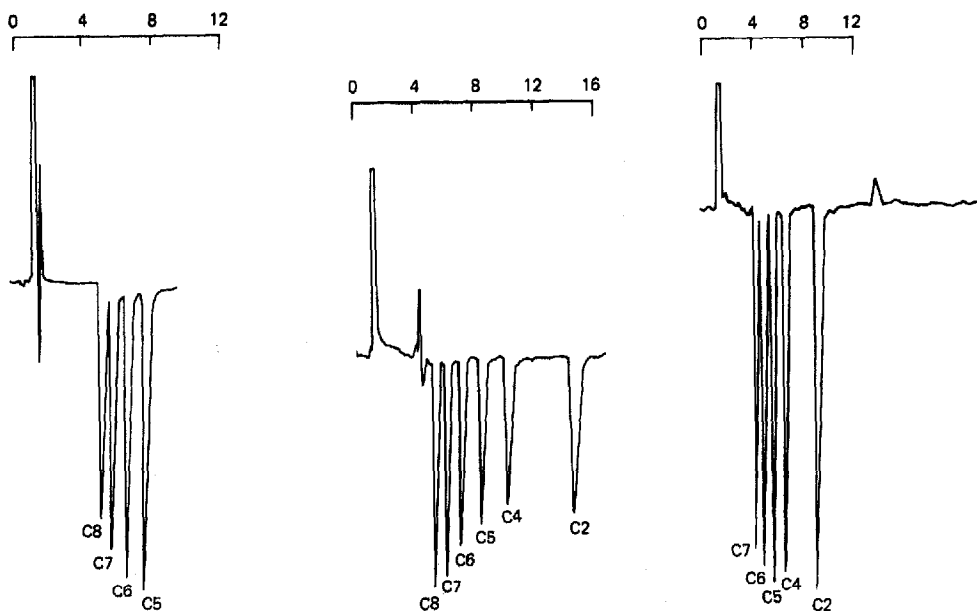


Fig. 1. Separation of octanesulfonate (C8), heptanesulfonate (C7), hexanesulfonate (C6) and pentanesulfonate (C5). Column: 250 × 4.6 mm I.D. Partisil-10 SAX. Mobile phase: acetonitrile-water (60:40) with 0.005 *M* potassium biphthalate, pH 5; flow-rate, 2.0 ml/min. Detection: UV at 297 nm and 0.16 a.u.f.s. Injection: 20 μ l of 1.0 mg/ml of each alkylsulfonate in mobile phase.

Fig. 2. Separation of octanesulfonate (C8), heptanesulfonate (C7), hexanesulfonate (C6), pentanesulfonate (C5), butanesulfonate (C4) and ethanesulfonate (C2). Mobile phase: acetonitrile-water (60:40) with 0.005 *M* sulfosalicylic acid, pH = 2.4. Detection: UV at 320 nm and 0.16 a.u.f.s. Other conditions as in Fig. 1.

Fig. 3. Separation of heptanesulfonate (C7), hexanesulfonate (C6), pentanesulfonate (C5), butanesulfonate (C4), and ethanesulfonate (C2). Mobile phase: acetonitrile-water (60:40) with 0.005 *M* *m*-sulfobenzoic acid, pH = 3.6. Detection: UV at 298 nm and 0.16 a.u.f.s. Other conditions as in Fig. 1.

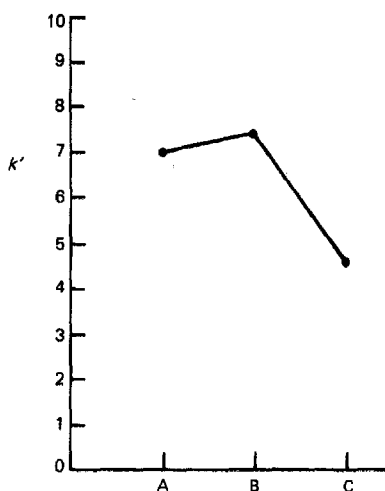


Fig. 4. k' of pentanesulfonate with: (A) biphthalate; (B) sulfosalicylic acid; (C) *m*-sulfobenzoic acid.

separation of alkyl sulfonates. Separations obtained using identical counter-ion and organic modifier concentrations are shown in Figs. 1-3. As illustrated in Fig. 4, which is a plot of capacity factor (k') versus choice of counter-ion, *m*-sulfobenzoic acid is the strongest counter-ion while potassium biphthalate and sulfosalicylic are approximately equal in strength. Thus, for speed of analysis *m*-sulfobenzoic acid would be the counter-ion of choice.

As noted by Small and Miller¹, the sensitivity of IPC improves as the concentration of counter-ion decreases up to the point where increased k' and band spreading negate this beneficial effect. This means that *m*-sulfobenzoic acid could also be used for increased sensitivity, since its concentration in the mobile phase could be reduced and still maintain k' equivalent to the other two counter-ions.

A linear response and constant k' were observed for the alkyl sulfonates over a range of 10-1000 ppm with a detection limit of 0.3 μg .

The IPC approach has several advantages compared to a reversed-phase ion-pair technique using a UV-absorbing ion-pair reagent⁷. These include improved peak shape, increased linear range, ease of calibration (peak height or peak area), and selectivity. Since retention times using the ion-pair approach decrease as volume injected or concentration injected increases, peak identification is difficult and calibration is limited to peak areas. Since the mode of separation in IPC is ion exchange, ionic compounds are retained while neutral compounds elute on the solvent front. This selectivity of IPC for ionic compounds is also an advantage, because alkyl sulfonates are often used in complex non-ionic matrixes.

REFERENCES

- 1 H. Small and T. E. Miller, *Anal. Chem.*, 54 (1982) 462.
- 2 *U.S. Pat.*, No. 4,414,842.
- 3 J. R. Larson and C. D. Pfeiffer, *Anal. Chem.*, 55 (1983) 393.
- 4 J. R. Larson and C. D. Pfeiffer, *J. Chromatogr.*, 259 (1983) 519.
- 5 T. Nakagawa, K. Miyajima and T. Uno, *J. Gas Chromatogr.*, 6 (1968) 292.
- 6 M. Denkert, L. Hackzell, G. Schill and E. Sjögren, *J. Chromatogr.*, 218 (1981) 31.
- 7 B. Sachok, S. N. Deming and B. A. Bidlingmeyer, *J. Liquid Chromatogr.*, 5 (1982) 389.
- 8 B. A. Bidlingmeyer and F. V. Warren, Jr., *Anal. Chem.*, 54 (1982) 2351.