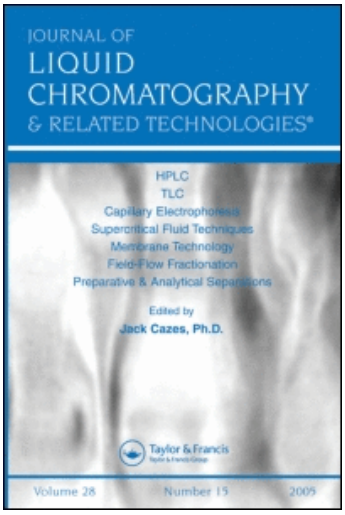

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Pseudophase Liquid Chromatography: Applications to TLC

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PSEUDOPHASE LIQUID CHROMATOGRAPHY: APPLICATIONS TO TLC

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ABSTRACT

The technique of pseudophase liquid chromatography is described. In this type of separation, a substance does not partition to the bulk mobile phase but rather to discreet aggregates or other substances (i.e., micelles or cyclodextrins) which are dissolved in the mobile phase. Advantages of this technique include high selectivity, low cost, and low volatility and toxicity of the mobile phase. Appropriate previous TLC separations are reviewed and new data on the separation of quinones are presented.

INTRODUCTION

The search for more efficient and effective chromatographic separations has produced a number of techniques without which much of modern chemical research would be difficult. In liquid chromatography, as in g.l.c., a great deal of work has been done to alter, improve, and/or discover new stationary phases which might produce better separations. Indeed, much of this work has resulted in improved separations. Research on the mobile phase is less extensive and generally consists of an intuitive, trial and error type mixing of two or more solvents in various ratios. Eventually one obtains a mobile phase of "appropriate polarity" which produces an adequate separation. There are, of course, variations on this theme. One could add soluble acids or bases to the mobile phase so that appropriate solutes could be chroma-

tographed in their respective protonated or unprotonated forms. In addition, one might add buffers or salts to control pH and ionic strength of water-based mobile phases. Overall, the study and development of the mobile phase seems to have been secondary to that of the stationary phase. This is somewhat understandable considering the limited number of things one can do with a solvent (vide supra).

Mobile phases have recently been developed wherein partitioning does not occur to the bulk solvent but rather to highly selective species dissolved in the solvent. Aqueous solutions of micelle forming surfactants are good examples of this type of mobile phase (1-4). A variety of hydrophobic molecules, which are weakly soluble or insoluble in water, partition to aqueous micelles. Aqueous solutions of cyclodextrins produce analogous results because of their ability to bind aromatic molecules in a hydrophobic cavity (5).

The partitioning of many molecules to the cyclodextrin and micellar pseudophase can be highly selective, much more so than partitioning to simple solvent or mixed solvent systems. A simple micelle offers a variety of environments, from its organic core, to the more viscous polar region toward the edge of the hydrophobic core, to the highly polar and charged (in the case of micelles formed from ionic surfactants) Stern layer. This ability to interact with molecules both electrostatically and hydrophobically cannot be duplicated by any pure or mixed solvent system (6). Solutions of cyclodextrins have another advantage. The diameter of their hydrophobic cavity physically limits the size of the molecule that can be bound. Thus by choosing different cyclodextrins one can chromatograph molecules of different size. Solutions of cyclodextrins, therefore, can act as mobile molecular sieves in TLC and other forms of liquid chromatography.

It seems that superior separations might eventually be achieved using a highly selective mobile phase in conjunction with a compatible, highly selective stationary phase. In this

work, the uses of micellar and cyclodextrin mobile phases in TLC are summarized.

EXPERIMENTAL

Exact experimental methods have been published previously (2,3,5). Polyamide stationary phases were found to be the most useful in pseudophase thin layer chromatography (PTLC). Alumina stationary phases could also be used in many cases. Silanized silica gel stationary phases can be used with reversed micellar solutions (2,3). In general, no purification of surfactants or cyclodextrins is necessary when using solutions of these compounds in PTLC. In cases where the mobile phase must be spectroscopically pure (i.e., HPLC) one can purify the surfactant or cyclodextrin by recrystallization from appropriate high purity HPLC grade solvents (4).

RESULTS AND DISCUSSION

A variety of compounds have been separated via PTLC. A list of R_f values of several selected compounds is given in Table 1. In general, it appears that cetyltrimethylammonium bromide (CTAB) solutions give separations comparable to those of sodium dodecyl sulfate (SDS) solutions but at a somewhat lower concentration. This may be due, in part, to the fact that CTAB's critical micelle concentration is almost an order of magnitude less than that of SDS (7). At identical molar surfactant concentrations, solutions of SDS and CTAB contain different numbers of micelles. In addition, the micelles are of different size. CTAB micelles have a positive fraction of charge on their surface while SDS micelles have a negative fraction of charge. This difference in surface charge might affect some separations (where electrostatic interactions are important) while not affecting others (where the interactions are strictly hydrophobic). In the case of p,p-DDD there appears to be a much greater partitioning to the CTAB micelle relative to the SDS micelle. This may be due in part to

TABLE 1

A Comparison of the R_f Values of Several Selected Compounds that were Separated via PTLC using Different Mobile Phases.[a]

Compound	Mobile Phase Composition[i]	R_f Value	Reference
naphthalene	0.4 M SDS[f]	1.00	3
pyrene	0.4 M SDS[f]	0.37	3
pyrenecarboxaldehyde	0.4 M SDS[f]	0.50	3
benzo(α)pyrene	0.4 M SDS[f]	0.14	3
decachlorobiphenyl	0.4 M SDS[f]	0.00	2
decachlorobiphenyl	0.1 M CTABg	0.00	2
p,p'-DDE[b]	0.4 M SDS[f]	0.26	2
p,p'-DDE[b]	0.1 M CTABg	0.20	2
p,p'-DDD[c]	0.4 M SDS[f]	0.06	2
p,p'-DDD[c]	0.1 M CTABg	0.18	2
o-bromobenzoic acid	0.1 M α-cyclodextrin	0.16	5
m-bromobenzoic acid	0.1 M α-cyclodextrin	0.41	5
p-bromobenzoic acid	0.1 M α-cyclodextrin	0.67	5
1,4-naphthaquinone	0.4 M SDS[h]	0.66	9
1,4-naphthaquinone	0.3 M CTABg	0.65	9
1,4-naphthaquinone	0.1 M α-cyclodextrin	0.14	9
anthraquinone	0.4 M SDS[h]	0.29	9
anthraquinone	0.3 M CTABg	0.28	9
anthraquinone	0.1 M α-cyclodextrin	0.11	9
vitamin K_5[d]	0.4 M SDS[h]	0.69	9
vitamin K_5[d]	0.2 M CTABg	0.67	9
vitamin K_5[d]	0.1 M α-cyclodextrin	0.41	9
vitamin K_1[e]	0.4 M SDS[h]	0.80	9
vitamin K_1[e]	0.1 M α-cyclodextrin	0.00	9

[a]All mobile phases were aqueous solutions and all stationary phases were Brinkmann Polyamide-6 UV_{254} thin layer sheets.
[b]2,2-bis(p-chlorophenyl)-1,1-dichloroethylene.
[c]2,2-bis(p-chlorophenyl)-1,1-dichloroethene.
[d]4-amino-2-methyl-1-naphthol
[e]2-methyl-3-phytyl-1,4-naphthaquinone.
[f]sodium dodecyl sulfate (from Sigma Chemical Co.).
[g]cetyltrimethylammonium bromide (from Sigma Chemical Co.).
[h]sodium dodecyl sulfate (from BioRad Laboratories).
[i]Surfactants purchased from different chemical companies can vary widely in purity. This variation in purity can cause significant differences in the R_f values of many substances.

electrostatic interactions (2). The R_f values of polynuclear-aromatic hydrocarbons (using micellar mobile phases) tend to decrease with the increasing molecular weight of the solute (Table 1). The addition of a polar functional group (as in pyrenecarbox-

aldehyde) tends to increase the R_f values of the polynuclear aromatic compounds.

Both vitamin K_1 and K_5 appear to partition well to SDS micelles but their R_f values are close enough to make separation difficult. With an α-cyclodextrin mobile phase, separation is simplified since vitamin K_1 is totally excluded from the cyclodextrin cavity (causing it to remain at the origin) while vitamin K_5 is not. Conversely 1,4-naphthaquinone and anthraquinone have similar R_f values when chromatographed with an α-cyclodextrin mobile phase. Both CTAB and SDS mobile phases, however, effectively separate the quinones. α-cyclodextrin mobile phases are particularly effective at separating ortho, meta and para substituted benzene derivatives (see o, m and p-benzoic acid, Table 1).

One's choice of mobile phase depends largely on the type of compounds being separated. Cyclodextrin solutions seem to be most effective when used in the separation of aromatic compounds. Micellar solutions tend to have a more general applicability. Despite the encouraging results obtained thus far, much more research must be done before the full potential and limitations of pseudophase chromatography are realized.

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