

Notes

CHROM. 3390

The influence of electrolytes on the gas-liquid chromatography of hydrocarbons and alcohols

The recent literature records examples of the use of electrolytes dissolved in the stationary phase to produce unusual resolutions in gas chromatography. For example, alkenes and dienes show remarkable retention times with a stationary phase containing silver nitrate¹⁻³. Amines and hydrazines can be separated on polyethylene glycol treated with KOH⁴⁻⁶. In the first case the silver ions exert a specific interaction with the double bonds, in the second case the base inhibits the formation of hydrogen bonds. However, effects of the addition of electrolytes to the partition liquid are not limited to specific chemical interactions. In fact, the presence of an electrolyte can cause a new type of interaction to take place: ion-molecule of the solute and ion-molecule of the solvent. The consequence of these physical and chemical phenomena is a considerable variation in the solubility of non-electrolytes in solvents containing various dissolved electrolytes⁷.

Experimental

The effect of lithium chloride dissolved in Carbowax 400 on the retention times of *n*-alkanes, alcohols, and benzene was examined and related to the change in the stationary phase containing the dissolved electrolyte. We used a Fractovap GV chromatograph (C. Erba, Milan) equipped with a filament detector and steel columns (1-2 m length, 6 mm diameter).

TABLE I

EFFECT OF ADDED LiCl ON RETENTION TIMES WITH RESPECT TO BENZENE

	<i>Carbowax 400</i>	<i>Carbowax 400 + LiCl (0.186 M)</i>	<i>Carbowax 400 + LiCl (0.766 M)</i>
<i>n</i> -Hexane	0.08	0.08	0.07
<i>n</i> -Heptane	0.16	0.15	0.13
<i>n</i> -Octane	0.31	0.29	0.26
<i>n</i> -Nonane	0.59	0.55	0.49
<i>n</i> -Decane	1.10	1.03	0.90
Methanol	1.22	1.46	2.16
Ethanol	1.54	1.75	2.40
1-Propanol	2.92	3.20	4.20
Benzene	1.00	1.00	1.00
V_R Benzene	68.9	63.8	53.1

The support was 60–80 mesh silanized Chromosorb P treated with a stationary phase (20 % by weight) containing, in separate experiments: 0.186 and 0.766 molal salt concentrations. We employed helium as a carrier gas at a flow rate of 1 c.c./sec (at 0° and 760 mm Hg). The results (see Table I) are recorded as ratios of the retention times to that of benzene at 78°. In the same table, for comparison, the ratios obtained on Carbowax 400 without added electrolyte are recorded. (The behavior of the standard, benzene, is shown as specific retention volumes V_g .)

When the salt concentration in the stationary phase was increased benzene showed a decrease in solubility. A more remarkable decrease is shown by the alkanes and is reflected in the decreasing retention values. Since the effect of added salt is greater for alkanes than for benzene an inversion in the elution order of the benzene–decane pair occurs.

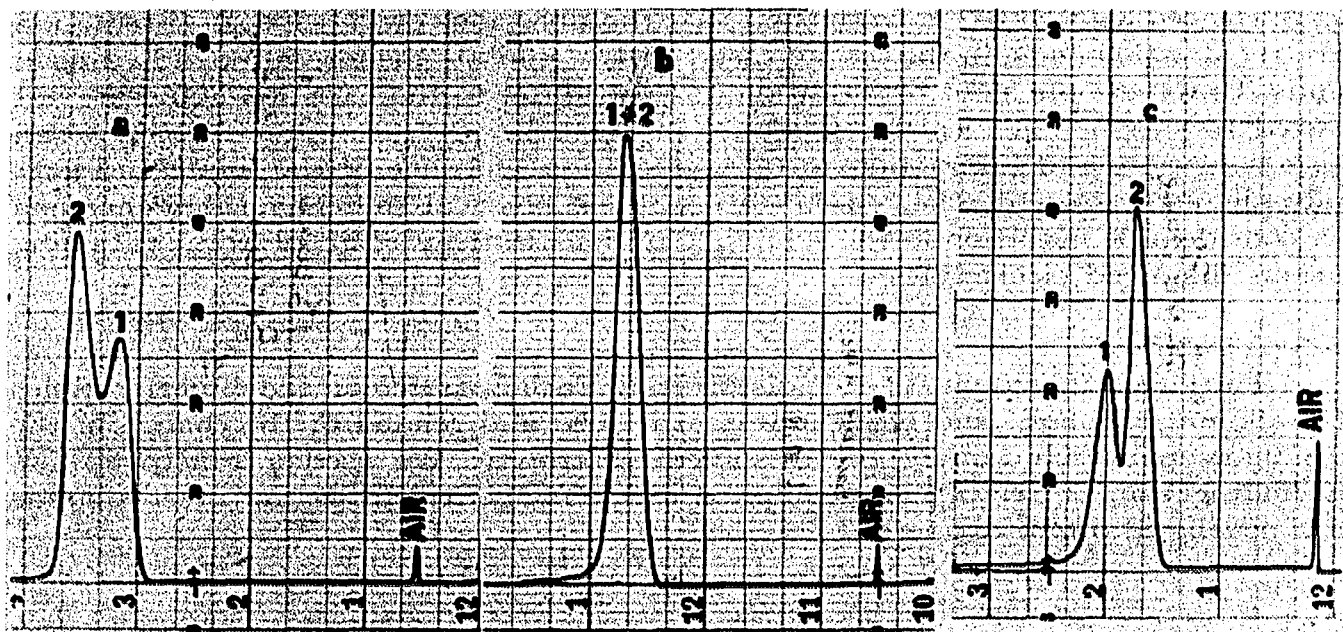


Fig. 1. Chromatograms of a mixture of benzene (1) and decane (2) at 78°. (a) Carbowax 400; (b) Carbowax 400 + LiCl (0.186 *M*); (c) Carbowax 400 + LiCl (0.766 *M*).

Fig. 1 shows chromatograms of the benzene–decane elution from Carbowax columns without electrolyte (a) and with LiCl at the two concentrations stated above (b,c). The ratio, 1.03, of the retention times at the lower salt concentration produces a virtually simultaneous elution of the two substances, while at the higher concentration (retention time ratio = 0.90) there is a clear separation again but with an inversion of the elution order, decane (b.p. = 174°) before benzene (b.p. = 80.1°). Alcohols show the opposite behavior in that they become more highly retained with increase of added salt; the increased ratio causes an increase in the retention volume when compared to the saltless phase.

There could be considerable use of this phenomenon since it provides the

research worker with a new parameter by which means the elution order of a variety of materials can be changed virtually at will.

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- 1 J. HERLING, J. SHABTAI AND E. GIL-AV, *J. Chromatog.*, 8 (1962) 349.
- 2 J. SHABTAI, J. HERLING AND E. GIL-AV, *J. Chromatog.*, 11 (1963) 32.
- 3 A. ZLATKIS, G. S. CHAO AND H. R. KAUFMAN, *Anal. Chem.*, 36 (1964) 2354.
- 4 C. BIGHI, G. LUCCI AND G. SAGLIETTO, *Ann. Univ. Ferrara*, 9 (1964) 107.
- 5 C. BIGHI AND G. SAGLIETTO, *J. Gas Chromatog.*, 4 (1966) 303.
- 6 C. BIGHI, A. BETTI AND G. SAGLIETTO, *Ann. Chim. (Rome)*, 57 (1967) 1142.
- 7 H. S. HARNED AND B. B. OWEN, *The Physical Chemistry of Electrolytic Solutions*, 2nd Ed., Reinhold, New York, 1950, p. 397.

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Gas chromatographic analysis of hydroxydichlorophenoxyacetic acids*

Recently, certain hydroxydichlorophenoxyacetic acids have been reported to be metabolites of 2,4-dichlorophenoxyacetic acid (2,4-D) in plants¹ and microorganisms² in a reaction which has been named the "NIH shift" by later workers³. We found higher diazoalkanes useful in the preparation of derivatives for gas chromatography of phenolic compounds because they have greater phenol-alkylation activity than diazomethane and their activity is further increased by boron trifluoride catalysis⁴. An important feature of the above procedure is that derivatives may be made from each of several diazoalkanes and that set chosen which gives the best resolution by GLC. The higher diazoalkanes, therefore, offer advantages over conventional procedures for phenolic acids in the GLC analysis of hydroxydichlorophenoxyacetic acids.

Experimental apparatus

An F & M gas chromatograph, Model 400, equipped with a flame ionization detector and a 2 m × 5 mm I.D. glass column, packed with SE-30 (15%, w/w) on Chromosorb W (60-80 mesh), was operated isothermally at 190°. The injection port and detector were maintained at 235° and 240°, respectively, and the helium carrier flow was 60 ml/min.

Materials

Diazoalkanes were prepared in ethyl ether without distillation⁴. The following acids were prepared: 6-hydroxy-2,4-dichlorophenoxyacetic acid (6-OH-2,4-D)⁵;

* Adapted from Ph. D. thesis of senior author.