

CHROM. 8959

THE PROPERTIES OF BINARY STATIONARY PHASES IN GAS-LIQUID PARTITION CHROMATOGRAPHY

COMPLEX ASSOCIATION SYSTEMS

TERESA CZAJKOWSKA and ANDRZEJ WAKSMUNDZKI

Department of Physical Chemistry, M. Curie-Skłodowska University, Lublin (Poland)

(First received October 2nd, 1975; revised manuscript received December 3rd, 1975)

SUMMARY

The application of gas chromatography to measurements of the association constants of organic molecular complexes is described. The way in which these measurements can be used to determine the effective concentration of a polar stationary phase in systems of mixed stationary phase-solid support and the analyzed substance is discussed.

INTRODUCTION

In most chromatographic systems, the properties of the adsorptive support affect the retention data, especially at low coverages of the support by the stationary phase. These effects have been studied by many workers and several methods are known for the quantitative determination of adsorptive effects in gas-liquid partition chromatography (GLPC)¹⁻⁴.

The equation of Conder *et al.*⁵ for the retention volume has been extended to include both adsorption on the solid support and adsorption at the gas-liquid interface. The recent modification of this equation by Waksmundzki and co-workers^{3,4,6} permits the quantitative determination of these adsorptive effects on the overall retention volume.

It has been observed that the properties of the adsorptive support have an effect mainly in systems with non-polar stationary phases, or when the solute is more polar than the stationary phase and is able to form hydrogen bonds or π -bonds with the support surface or to interact with the support via dipole-dipole interactions.

Scholtz and Brandt⁷ have shown that adsorptive properties do not play an important role in systems with polar stationary phases. Some functional groups of such stationary phases interact strongly with active sites on the support, causing their deactivation. The solute can then be adsorbed on these sites, which, for geometric reasons, are not occupied by functional groups of the stationary phase. These suggestions of Scholtz and Brandt have been confirmed by the recent investigations by Waksmundzki *et al.*⁸, who investigated the effective surface area of Polsorb C^{9,10}

covered with dilauryl phthalate. According to their results for some average support coverages, the effective surface area of the support decreases 10^3 -fold.

In addition to direct support-stationary phase interactions, there may also occur some perturbations due to mutual interactions of the molecules in the stationary phase^{7,11} on the support surface. These perturbations may change the properties of liquid films on the support, in comparison with bulk liquid properties. In this way, the non-ideality of support-stationary phase systems increases: the effective concentration of liquid becomes different from that calculated on the basis of the amount of stationary phase. As a result, the theoretically calculated retention volumes are very different from those measured experimentally.

Chromatographic systems with mixed stationary phases seem to be the most convenient for studying the influence of the effective concentration of a polar component on the retention data. In particular, systems in which complex-forming interactions between functional groups of liquid and polar solutes may occur show the most evident influence of the support surface, as the retention volume in this instance is a function of the concentration of the complex-forming groups in the stationary phase.

For this reason, in determining the effective concentration of polar stationary phases, we used chromatographically measured association constants of the complexes formed by polar solutes and the functional groups of the liquid phase. The measurements were made for the system *n*-octadecane (OD)-tetradecylamine (TDA)-Polsorb C (a support of the firebrick type). Methanol and chloroform were used as complex-forming substances.

THEORETICAL

In our measurements of association constants of the complex formed between chloroform and the amine groups of TDA we used the method of Purnell¹² and Cadogan and Purnell^{13,14}. According to their results, the partition coefficient, K_R , of a solute between a mixed stationary phase, in which the concentration of the active component (A) is C_A , and the gas phase is given by the equation

$$K_R = K_R^0 (1 + K_1 C_A) \quad (1)$$

where K_1 is the equilibrium constant of the reaction $A + B \rightarrow AB$, and K_R^0 is the partition coefficient of the solute (B) between the non-polar component (S) of the mixed stationary phase and the gas phase.

When the solute forms more than one complex with the stationary phase, for instance according to the reaction $A + B \rightarrow A_2B$, then

$$K_R = K_R^0 (1 + K_1 C_A + K_1 K_2 C_A^2) \quad (2)$$

where K_2 denotes the equilibrium constant of the reaction between the complex AB and the active component A. For non-ideal solutions where both K_R and the activity coefficient, γ_A , of the active component (A) depend on its concentration, C_A , eqn. 1 can then be written^{14,15} as

$$K_R = K_R^0 [1 + (\alpha_1 + K_1) C_A] \quad (3)$$

In eqn. 3, α_1 is a function of the molar volume of the solute (V_B) and of the molar volumes V_A and V_S of components A and S:

$$\alpha_1 = V_A \left[\frac{\exp(V_B/V_A)}{\exp(V_B/V_S)} - 1 \right] \quad (4)$$

In gas chromatographic measurements, the molar volumes of the components of the stationary phase are usually much greater than those of the solutes. Hsueh-Liang Liao *et al.*¹⁵ pointed out that in this case α_1 is well approximated by the equation

$$\alpha_1 \approx V_B \left[1 - \frac{V_A}{V_S} \right] \quad (5)$$

The function α_1 is similar to the ψ function developed by Eon and co-workers^{16,17}, who used it for the correction of complex constants measured chromatographically. When the molar volumes of the components of the liquid phase are identical or only slightly different, then $\alpha_1 = 0$ and eqn. 3 reduces to eqn. 1. Usually the values of α_1 are about of 0.01–0.1 l/mole, so that α_1 influences the constants of rather weak complexes only.

EXPERIMENTAL

Measurements were made at 60° with a Perkin-Elmer Model 116 E instrument equipped with a katharometer. Nitrogen was used as the carrier gas at a flow-rate of 50 ml/min; the flow-rate was measured with a bubble flow meter. The inlet pressure was measured with a mercury manometer.

Polsorb C, used as the support, had a particle size of 0.12–0.315 mm, its specific surface area was about 3.5 m²/g. Before covering it with liquid, the support was washed with methanol and dried at 200°.

Three mixtures of tetradecylamine and octadecane (3:1, 1:1 and 1:3) were investigated. Each mixture was introduced on to the support as solutions in methanol or diethyl ether. In this way, three coverages were obtained, containing 4, 6 and 10% of the stationary phase. The columns were then stabilized at 60° for 20 h. The amount of liquid covering the support was controlled carefully by extraction of liquid from the column packing using a diethyl ether–methanol mixture.

Different amounts of solute were used and the retention volumes were extrapolated to zero sample size. The densities of octadecane and tetradecylamine at 60° were measured with a pycnometer and were found to be 0.7545 and 0.7830 g/ml, respectively. These densities were used to calculate the volume of the mixed stationary phase and the molar volumes of the components.

RESULTS AND DISCUSSION

In Figs. 1 and 2, the K_R/K_R^0 ratios for chloroform and methanol, respectively, are shown as a function of tetradecylamine concentration. Curves No. 4 in both figures were constructed by using the values of K_L found by extrapolation of the function $V_N/V_L = f(1/V_L)$ to the limit $V_L \rightarrow \infty$ (Conder *et al.*⁵) (V_N is the absolute retention value, V_L is the volume of the liquid phase, and K_L is the bulk partition coefficient).

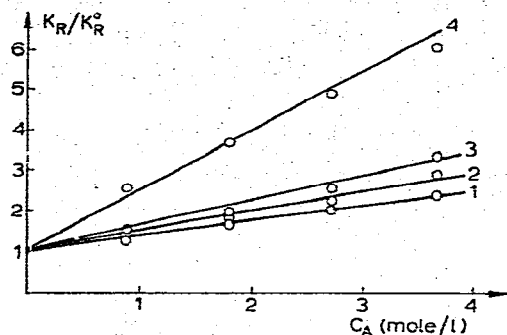


Fig. 1. Variation of K_R/K_R^0 with concentration of tetradecylamine in octadecane (mole/l) at 60° for chloroform. 1, For 4% coverage; 2, for 6% coverage; 3, for 10% coverage; 4, from K_L values.

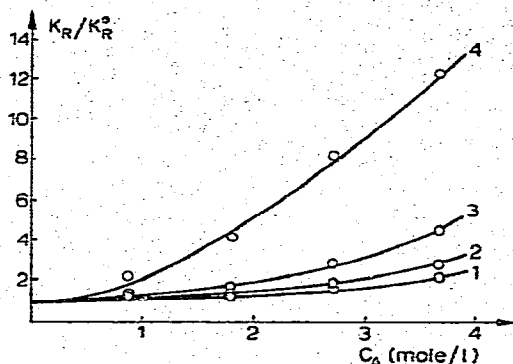


Fig. 2. Variation of K_R/K_R^0 with concentration (mole/l) of tetradecylamine in octadecane at 60° for methanol. Curves as in Fig. 1.

On the basis of curve No. 4 in Fig. 1, the association constant K_1 was calculated for the 1:1 complex of chloroform and tetradecylamine. According to eqn. 1, this association constant is equal to the tangent of this curve and is 1.48. According to eqn. 3, the tangent is $(\alpha_1 + K_1)$, so that $K_1 = 1.46$ as $\alpha_1 = 0.02$.

For methanol, the dependence of K_R/K_R^0 on the tetradecylamine concentration has a parabolic shape, which seems to be evidence for the formation of 1:2 complexes. The association constants for both 1:1 and 1:2 complexes has been calculated from the following linear form of eqn. 2:

$$\frac{K_R/K_R^0 - 1}{C_A} = K_1 + K_1 K_2 C_A \quad (6)$$

The function

$$\frac{K_R/K_R^0 - 1}{C_A} = \underline{f}(C_A)$$

is shown in Fig. 3. The association constants calculated in this way are $K_1 = 0.46$ and $K_2 = 1.61$ for the 1:1 and 1:2 complex, respectively. For the system octadecane-tetradecylamine-methanol, $\alpha_1 = 0.01$ so that $K_1 = 0.45$ and $K_2 = 1.64$.

In Figs. 1 and 2, curves No. 1, 2 and 3 were constructed by using the retention data for coverages of 4, 6 and 10%, respectively. With chloroform the tangents of these curves increase with increase in the amount of liquid phase. With methanol (Fig. 2), the curve relating to the coverage 4% is almost linear, which indicates the formation of a 1:1 complex only. At higher coverages, the tangent increases as the value of the argument increases, which suggests the formation of 1:2 complex. All of these observations suggest that at the coverages of 4, 6 and 10% the effective concentration of tetradecylamine is less than that calculated on the basis of the amount of liquid introduced.

Using the association constants K_1 and K_2 found from the bulk partition coefficients, the effective concentrations of tetradecylamine (C_{eff}) were calculated

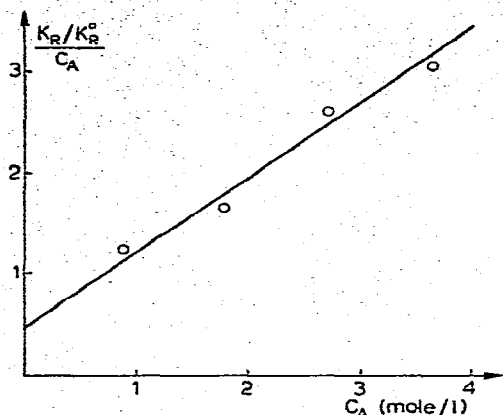


Fig. 3. Variation of $(K_R/K_R^0 - 1)/C_A$ with concentration (mole/l) of tetradecylamine in octadecane at 60° . Values obtained by introducing a correction for adsorption effects.

from eqns. 1 and 2 corresponding to coverages of 4, 6 and 10%. These effective concentrations for all composition of the liquid and for all surface coverages are reported in Table I.

It is shown in Fig. 4 that the K_R/K_R^0 plotted as a function of the calculated effective concentrations of liquid are almost identical with the functions corresponding to pure bulk solution (curves No. 4 in Figs. 1 and 2).

In the Table I, the ratios of the effective concentrations to the concentrations introduced are also reported. These ratios may be treated as activity coefficients of tetradecylamine for the systems support-stationary phase. Even considering some disagreement in the values of C_{eff} evaluated from K coefficients for methanol and

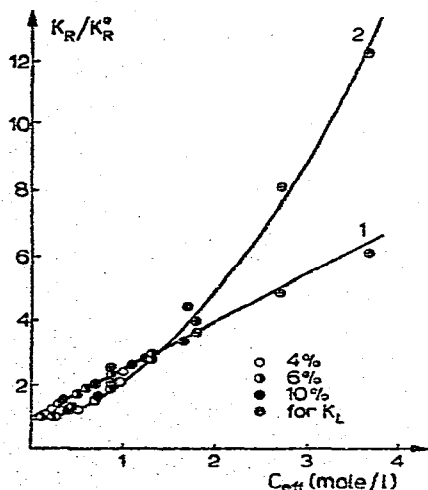


Fig. 4. Variation of K_R/K_R^0 with effective concentration (C_{eff} , mole/l) of tetradecylamine in octadecane at 60° for chloroform (curve 1) and methanol (curve 2) at different coverages of the support with liquid.

TABLE I
EFFECTIVE CONCENTRATIONS OF TETRADECYLAMINE AND RATIOS OF EFFECTIVE TO INTRODUCED CONCENTRATIONS OF
TETRADECYLAMINE IN THE SYSTEMS TETRADECYLAMINE-OCTADECANE-POLSORB C-CHLOROFORM AND TETRADECYL-
AMINE-OCTADECANE-POLSORB C-METHANOL FOR DIFFERENT COVERAGES OF THE SUPPORT WITH LIQUID

C_{inr} (mole/l)	C_{eff}/C_{inr}															
	C_{eff} (mole/l)				4%				6%				10%			
	$CHCl_3$	CH_3OH	$CHCl_3$	CH_3OH	$CHCl_3$	CH_3OH	$CHCl_3$	CH_3OH	$CHCl_3$	CH_3OH	$CHCl_3$	CH_3OH	$CHCl_3$	CH_3OH		
3.669	0.971	0.974	1.317	1.289	1.641	1.880	0.264	0.265	0.358	0.350	0.447	0.510	0.470			
2.726	0.705	0.740	0.912	0.850	1.099	1.271	0.260	0.270	0.334	0.310	0.403	0.470	0.405			
1.800	0.482	0.405	0.594	0.460	0.694	0.724	0.311	0.225	0.330	0.255	0.385	0.405	0.405			
0.892	0.219	0.126	0.298	0.110	0.369	0.387	0.245	0.141	0.334	0.123	0.413	0.434	0.434			

chloroform, it seems that both C_{eff} and $C_{\text{eff}}/C_{\text{intr}}$ should be treated as parameters that characterize the systems support-mixed stationary phase-solute.

It can be seen from Table I that at a coverage of 4% the effective concentration of the polar component is about four times lower than that introduced, while at a coverage of 10% the effective concentration is twice as low as that introduced.

The amount of polar liquid that does not take part in the complex-forming mechanism greatly exceeds that which corresponds to a monomolecular layer, even at a coverage of 4%. For Polsorb C (3.5 m²/g), the monolayer was determined for coverages of 0.2–0.6% due to the size of adsorbed functional groups of liquids.

However, the properties of the boundary layers of some polar organic liquids are different from the bulk liquid properties. It has been shown by Derjaguin¹⁸ that the contact of the liquid with a solid phase leads to a change in the physical properties of the adjacent liquid and also influences the structure of this layer, making it resemble liquid crystals. According to Derjaguin's results, the thickness of the boundary layer with specific properties is about 1000 Å, which means that many layers of spreading liquid differ from the bulk liquid.

In addition, the mixed stationary phase: octadecane-tetradecylamine forms a non-ideal solution. We have found¹⁹ that a considerable excess free enthalpy is observed when these two components are mixed.

Hence the disproportion found between the values of C_{eff} and C_{intr} (Table I) cannot be explained only in terms of the simple interaction of the polar groups of the liquid with the surface of the support.

We feel that the experimental data reported here are not adequate for conclusions to be drawn about the behaviour of γ (activity coefficient) considered as a function of the concentration of the complexing component. One can determine only approximately the contribution of the polar component in the complex-forming mechanism. Similarly, the quantitative determination of the effect of the surface area on the effective liquid concentration requires more experimental data.

The method used here for the determination of the activity of the polar component is evidently a simplification of the real chromatographic process. From the results reported, it follows that in addition to the bulk solution and to the support surface adsorption, many other effects influence the retention data. These effects arise from the form of the thin liquid film that covers the support. For instance, the properties of films must, of course, be different from the bulk properties. As mentioned above, this thin film is influenced directly, and perturbed indirectly, by the presence of solid.

REFERENCES

- 1 P. Urone and J. E. Parcher, *Advan. Chromatogr.*, 6 (1968) 229.
- 2 D. E. Martire, in J. H. Purnell (Editor), *Progress in Gas Chromatography*, Vol. 6, Interscience, New York, 1968, p. 93.
- 3 A. Waksmundzki, W. Rudziński, Z. Suprynowicz and J. Rayss, *J. Chromatogr.*, 74 (1972) 3.
- 4 Z. Suprynowicz, A. Waksmundzki, W. Rudziński and J. Rayss, *J. Chromatogr.*, 91 (1974) 67.
- 5 J. C. Conder, D. C. Locke and J. H. Purnell, *J. Phys. Chem.*, 37 (1969) 700.
- 6 Z. Suprynowicz, A. Waksmundzki and W. Rudziński, *J. Chromatogr.*, 67 (1972) 21.
- 7 R. G. Scholtz and W. W. Brandt, in N. Brenner, J. E. Callen and M. D. Weiss (Editors), *Gas Chromatography*, Academic Press, New York, 1962, p. 7.

- 8 A. Waksmundzki, J. Rayss, W. Rudziński and Z. Suprynowicz, *Chem. Anal. (Warsaw)*, 18 (1973) 695.
- 9 A. Waksmundzki, Z. Suprynowicz and T. Pietrusińska, *Chem. Anal. (Warsaw)*, 9 (1964) 721.
- 10 A. Waksmundzki, I. Miedziak, T. Czajkowska and J. Gawdzik, *Chem. Anal. (Warsaw)*, 18 (1973) 763.
- 11 O. Sinanoglu and K. S. Pitzer, *J. Chem. Phys.*, 32 (1960) 1279.
- 12 J. H. Purnell, in A. B. Littlewood (Editor), *Gas Chromatography 1966*, Institute of Petroleum, London, 1967, p. 3.
- 13 D. F. Cadogan and J. H. Purnell, *J. Chem. Soc., A*, (1968) 2133.
- 14 D. E. Cadogan and J. H. Purnell, *J. Phys. Chem.*, 73 (1969) 4389.
- 15 Hsueh-Liang Liao, D. E. Martire and J. P. Sheridan, *Anal. Chem.*, 45 (1973) 2087.
- 16 C. Eon, C. Pommier and G. Guiochon, *Chromatographia*, 4 (1971) 235.
- 17 C. Eon and B. L. Karger, *J. Chromatogr. Sci.*, 10 (1972) 140.
- 18 B. V. Derjaguin, *Discuss. Faraday Soc.*, 42 (1966) 109.
- 19 A. Waksmundzki and T. Czajkowska, *Ann. Soc. Chim. Pol.*, 47 (1973) 1909.