

CHROM. 6518

THE THEORY OF GAS-LIQUID CHROMATOGRAPHY

THE INFLUENCE OF THE THICKNESS OF THE STATIONARY LIQUID FILM

B. G. BELENKY, A. I. RUSANOV and L. D. TURKOVA

Institute of Macromolecular Compounds, Academy of Sciences of the U.S.S.R., Leningrad State University, Leningrad (U.S.S.R.)

(First received June 19th, 1972; revised manuscript received November 15th, 1972)

SUMMARY

The thermodynamic theory of gas-liquid chromatography has been developed, taking into account specific properties of thin films of the liquid phase expressed in terms of the "disjoining pressure". Equations were derived to describe the dependence of the retention volume on the thickness of the stationary phase over the whole range of thickness. The results are in good agreement with experimental values.

A chromatographic method for determining the constants of disjoining pressure is suggested.

INTRODUCTION

In gas-liquid chromatography (GLC), the retention volume of the maximum of a chromatographic peak is related to the distribution of the substance undergoing chromatography (the solute) between the mobile and the stationary phases by the following equation:

$$V_R^0 = \frac{m_1^{(f)}}{c_1^{(\beta)}} \quad (1)$$

where V_R^0 is the reduced specific retention volume (without the volume of the gas phase calculated per millilitre volume of the column), m_1 is the number of moles of the solute in the liquid film (f) and c_1 is the volume concentration of the solute in the gas phase (β). GLC is associated with the distribution of the substance in the multiphase system gas-liquid-solid support. It has been shown theoretically¹ and experimentally² that with a solid silica support, the liquid itself exists in two states: as a thin film covering the silica surface and as drops condensed in relatively narrow pores. It should be noted that when a support with a surface area of 5 m²/g (Chromosorb P) is used, the liquid phase present in an amount of less than 1% exists only as a film.

These circumstances permit consideration of the theory of GLC on the basis of the drop and film model. If the amount of stationary liquid is sufficiently high

and a homogeneous region exists inside it, eqn. 1 can be expanded in the usual manner.

We shall introduce interfaces that satisfy the condition $\Gamma_2 = 0$, where Γ_2 is the absolute adsorption of the stationary liquid component, and express $m_1^{(t)}$ as:

$$m_1^{(t)} = c_1^{(\gamma)} V^{(\gamma)} + \Gamma_{1(2)}^{(\alpha\gamma)} A^{(\alpha\gamma)} + \Gamma_{1(2)}^{(\beta\gamma)} A^{(\beta\gamma)} \quad (2)$$

where $\Gamma_{1(2)}$ is the relative adsorption of the solute, V is the volume of liquid between the interfaces, A is the surface area of the interface and superscripts α , β and γ indicate solid, gas and liquid phases, respectively, double superscripts referring to the corresponding interfaces. Substitution of eqn. 2 into eqn. 1 gives

$$V_R^0 = \frac{c_1^{(\gamma)}}{c_1^{(\beta)}} \left(V^{(\gamma)} + \frac{\Gamma_{1(2)}^{(\alpha\gamma)}}{c_1^{(\gamma)}} A^{(\alpha\gamma)} + \frac{\Gamma_{1(2)}^{(\beta\gamma)}}{c_1^{(\gamma)}} A^{(\beta\gamma)} \right) \quad (3)$$

The more usual form of eqn. 3 can be written with distribution constants:

$$V_R^0 = K_d(V^{(\gamma)} + K_a^{(\alpha\gamma)} A^{(\alpha\gamma)} + K_a^{(\beta\gamma)} A^{(\beta\gamma)}) \quad (4)$$

where $K_d = c_1^{(\gamma)}/c_1^{(\beta)}$ is the distribution coefficient for volume phases and $K_a^{(\alpha\gamma)} = \Gamma_{1(2)}^{(\alpha\gamma)}/c_1^{(\gamma)}$ and $K_a^{(\beta\gamma)} = \Gamma_{1(2)}^{(\beta\gamma)}/c_1^{(\gamma)}$ are the adsorption coefficients for the interfaces $\alpha\gamma$ and $\beta\gamma$, respectively.

Eqn. 4, which contains one volume distributing term and two adsorption terms, is a further development of the well known equations of JAMES AND MARTIN³, KELLER AND STUART⁴ and MARTIN⁵. Equations of this type for GLC were derived for the first time by BELENKII *et al.*⁶. Problems of the adsorption interactions in GLC have been investigated by several workers⁶⁻¹⁰, and it has been shown that a three-term equation similar to eqn. 4, with linear dependence of V_R^0 on V and A , satisfactorily describes experimental results obtained by GLC on columns with a stationary liquid in an amount greater than 2%. Nevertheless, as shown for the first time by BELENKII *et al.*⁶, when the liquid phase amounts to less than 1-2%, the dependence of V_R^0 on volume passes through a minimum. This effect cannot be explained on the basis of eqn. 4 even taking into account a possible change in the gas-liquid interface with varying volume of the liquid phase. Hence it is evident that the existing GLC theory is unable to distinguish between usual columns and columns that contain only small amounts of liquid phase.

One of the reasons is that the GLC theory does not take into account the specific properties of thin films, which are a form of liquid phase that exists when the amount of stationary liquid is small. This induced us to propose, on the basis of the modern theory of thin films, a universal GLC theory suitable for describing the chromatographic process on stationary liquid films of any thickness.

THEORETICAL

One of the paths for developing GLC theory, taking into consideration the specific properties of thin films, is as follows. Eqn. 3 is also applicable to thin (inhomogeneous) films. In this case, the superscript γ refers to the volume liquid phase, which consists of the same components as the film and may be in equilibrium with it (which means that the chemical potentials in phase γ and in the film are identical).

This phase is conceived as a hypothetical phase that can be used as a reference. However, this phase may be thought to exist in a real experiment in which it adjoins the film from the edge sides. This view is obviously consistent with the drop and film model of GLC. It is important, however, that with thin film the pressures in phases β and γ are different. The difference in pressures,

$$P^{(\beta)} - P^{(\gamma)} \equiv \Pi \quad (5)$$

is called the "disjoining pressure" and is an important characteristic of the thin film. When the thickness increases without limit then in the course of transition from a thin to a thick film, this difference (eqn. 5) tends to zero and the disjoining pressure disappears.

For a thin film at given $c_1^{(\beta)}$, the value of $c_1^{(\gamma)}$ depends on the film thickness. Hence the distribution coefficient, $c_1^{(\gamma)}/c_1^{(\beta)}$, is not constant even at low $c_1^{(\gamma)}$ and $c_1^{(\beta)}$ but is a function of the disjoining pressure and film thickness. This function can now be determined. For simplicity we shall consider the case of low concentrations of distributed components when all of the activity coefficients can be assumed to be unity. The following are expressions for chemical potentials in the ideal gas and in the infinitely diluted solution:

$$\mu_1^{(\beta)} = \mu_1(T) + kT \ln c_1^{(\beta)} \quad (6)$$

$$\mu_1^{(\gamma)} = \mu_1(T) + kT \ln c_1^{(\gamma)} + kT \ln \gamma_1^0 \quad (7)$$

where μ_1 is the chemical potential of the distributed component, γ_1^0 is the activity coefficient which acts as the conversion coefficient in passing from the standard state of the ideal gas to the standard state of an infinitely diluted solution, $\mu_1(T)$ refers to the standard state of the ideal gas, k is Boltzmann's constant and T is the absolute temperature.

From eqns. 6 and 7 and the equilibrium condition $\mu_1^{(\gamma)} = \mu_1^{(\beta)}$,

$$\frac{c_1^{(\gamma)}}{c_1^{(\beta)}} = \frac{1}{\gamma_1^0} \quad (8)$$

According to definition, the value of γ_1^0 does not depend on concentration but is a function of pressure in phase γ , and hence owing to the disjoining pressure, it will depend on the film thickness. The dependence of γ_1^0 on pressure is represented by the relationship obtained by RUSANOV¹³ with the aid of statistical mechanics:

$$kT \frac{\partial \ln \gamma_1^0}{\partial P} = - \frac{\Delta N_2^{(\gamma)}}{c_2^{(\gamma)}} \quad (9)$$

where $\Delta N_2^{(\gamma)}$ is the change in the number of molecules of the solvent in a given volume when one molecule of the dissolved substance is introduced into it. By using the well known thermodynamic equality

$$\left(\frac{\partial \mu_1}{\partial P} \right)_{T, x_1} = v_1^{(\gamma)} \quad (10)$$

where v_1 and x_1 are the partial molar volume and mole fraction of the first component, respectively, the following relationship is also obtained from eqn. 7:

$$kT \frac{\partial \ln \gamma_1^0}{\partial P} = v_1 - kT\chi^{(\gamma)} \quad (11)$$

where χ is the isothermal compressibility. Eqn. 11 is equivalent to eqn. 9.

Assuming that the right-hand side of eqn. 9 or 11 is constant over the range from $P^{(\gamma)}$ to $P^{(\beta)}$, and is designated δ , and integrating both parts of the equation taking eqn. 5 into account, we obtain

$$\gamma_1^0(P^{(\gamma)}) = \gamma_1^0(P^{(\beta)}) e^{-\delta\pi/kT} \quad (12)$$

Substituting eqn. 12 into eqn. 8, we have

$$\frac{c_1^{(\gamma)}}{c_1^{(\beta)}} = \frac{1}{\gamma_1^0(P^{(\beta)})} e^{\delta\pi/kT} \quad (13)$$

It is well known from statistical mechanics (see, e.g., HILL's work¹⁴) that the quantity $1/\gamma_1^0$ represents the distribution constant for two volume phases. When the thickness of the film increases, Π tends to zero and only the distribution constant remains in the right-hand side of eqn. 13, as expected.

Substitution of eqn. 13 into eqn. 3 gives

$$V_R^0 = K_d e^{\delta\pi/kT} \left(V^{(\gamma)} + \frac{\Gamma_{1(2)}^{(\alpha\gamma)}}{c_1^{(\gamma)}} A^{(\alpha\gamma)} + \frac{\Gamma_{1(2)}^{(\beta\gamma)}}{c_1^{(\gamma)}} A^{(\beta\gamma)} \right) \quad (14)$$

Eqn. 14 is valid for a stationary phase with an arbitrary form and thickness.

For a plane-parallel film, $A^{(\alpha\gamma)} = A^{(\beta\gamma)} \equiv A$ and $V^{(\gamma)} = \tau A$, where τ is the film thickness, and eqn. 14 becomes

$$V_R^0 = AK_d e^{\delta\pi/kT} \left(\tau + \frac{\Gamma_{1(2)}^{(\alpha\gamma)} + \Gamma_{1(2)}^{(\beta\gamma)}}{c_1^{(\gamma)}} \right) \quad (15)$$

or

$$V_R^0 = AK_d e^{\delta\pi/kT} (\tau + K_n) \quad (16)$$

where $K_n \equiv (\Gamma_{1(2)}^{(\alpha\gamma)} + \Gamma_{1(2)}^{(\beta\gamma)})/c_1^{(\gamma)}$ is the adsorption coefficient.

It is assumed that the dependence of K_n on the film thickness is negligible in comparison with τ (when $\tau \rightarrow \infty$, the equality $K_n = \text{constant}$ is strictly fulfilled).

We shall substitute for Π in eqn. 16 for the constant of the molecular disjoining pressure, B , and the film thickness, τ : $\Pi = B/\tau^3$ (refs. 15-17):

$$V_R^0 = AK_d e^{\delta B/kT\tau^3} (\tau + K_n) \quad (17)$$

This expression is the desired equation. It shows clearly that at small film thickness, V_R^0 should increase with decrease in τ , owing to the presence of the exponential factor. At high τ , the exponent becomes zero and a linear dependence of V_R^0 on τ should be observed.

This eqn. 17 theoretically predicts the dependence of V_R^0 on τ with the presence of a minimum, which is consistent with experiment.

The compressibility of the stationary phase can be neglected without introducing excessive error ($v_1 \gg kT\chi^{(\gamma)}$), so that $\delta = v_1$, and eqn. 17 can be transformed into

$$V_R^0 = AK_d e^{v_1 B/kT\tau^3} (\tau + K_a) \quad (18)$$

Eqn. 18 relates simply $v_1 B/kT \equiv b$ with the minimum coordinate on the curve of V_R^0 against τ . It permits the determination of b from the minimum condition

$$1 - \frac{3b}{\tau^4} (\tau + K_a) = 0 \quad (19)$$

Thus the GLC method is useful in determining the disjoining pressure of thin films.

EXPERIMENTAL

Instruments

We used a Pye gas chromatograph with an argon ionization detector (Model 12001).

Chromatographic column

Glass chromatographic columns, 125 cm in length and 4 mm I.D. were used and the diatomite support INZ-600 (U.S.S.R.), surface area 7.9 m²/g, was used as packing impregnated with the stationary liquid phase 1,2,3-Tris(2-cyanoethoxy) propane (Reakhim, U.S.S.R.). It was applied as a chloroform solution, the solvent being removed under vacuum, and the packing was dried at 150 °C.

Determination of the surface area of the stationary phase

The specific surface of the film of liquid phase was determined by a gas chromatographic variant of the B.E.T. method¹⁸.

Solutes

Chromatographically pure cyclic oxides obtained by the method described by GELLER *et al.*¹⁹ were used.

Calculation procedures

The thickness of the film of liquid phase, τ , was determined from the ratio of the specific volume of the liquid phase (per gram of packing) to its specific surface area. V_R^0 was determined by reducing the specific retention volume to normal pressure and temperature ($P = 760$ mm Hg, $T = 273$ °K) and subtracting from this value the specific volume of the gas phase in the column, as recommended by DALNOGARE AND JOUVET²⁰.

RESULTS AND DISCUSSION

Fig. 1 shows the dependence of the specific surface of the packing (surface area of the liquid phase film determined by the B.E.T. method) on the film thickness. It is clear that when the film becomes thinner, its surface area increases because the liquid is removed from the micropores of the solid support. Evidently, simultaneously with the increase in the film surface area $A^{(\beta\gamma)}$, the term $\Gamma_{1(2)}^{(\beta\gamma)} A^{(\beta\gamma)} / c_1^{(\gamma)}$ in eqn. 14 will increase.

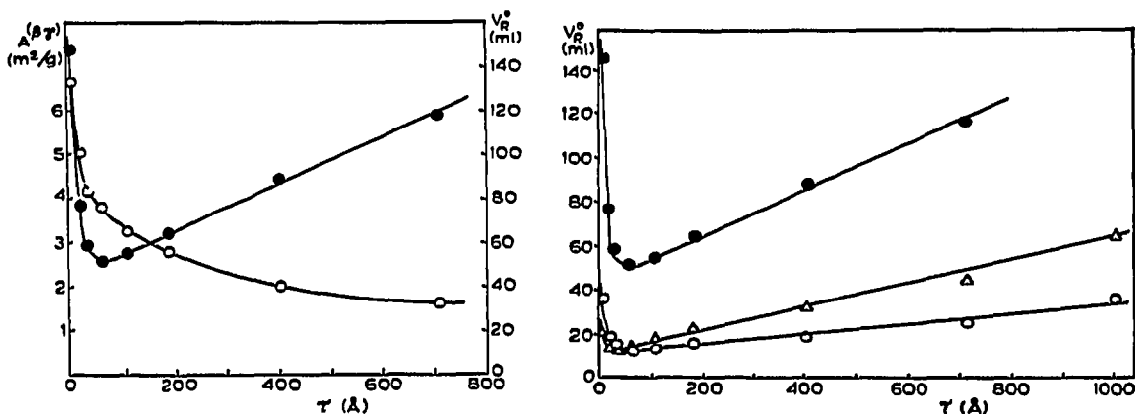


Fig. 1. Surface area of liquid film, $A(\beta\gamma)$, of 1,2,3-Tris(2-cyanoethoxy)propane versus its thickness, τ (○), and V_R^0 versus τ for bismethylmethoxyoxacyclobutane obtained by GLC (●).

Fig. 2. V_R^0 for 3-methyl-3-methylmethoxyoxacyclobutane (○), 3-methyl-3-chloromethyloxa-cyclobutane (Δ) and bismethylmethoxyoxacyclobutane (●) versus thickness, τ , of the film of 1,2,3-Tris(2-cyanoethoxy)propane.

It is possible to ensure that this factor is not associated with the appearance of a minimum in the dependence of V_R^0 on τ . For this purpose we have shown in Fig. 1 the dependence of $A(\beta\gamma)$ on τ for one of the investigated cyclic oxides. It can be seen that the beginning of this curve does not coincide with the minimum in the curve of V_R^0 against τ and, hence, is not the cause of the appearance of the minimum.

Fig. 2 shows the dependence of V_R^0 on τ for three cyclic oxides. The positions of the minima of the curves permit the calculation of the constant of the disjoining pressure, B , according to eqn. 19. For these oxides at 100 °C, B is $2 \cdot 10^{-12}$, $3 \cdot 10^{-13}$ and $9 \cdot 10^{-13}$ erg, respectively. These results are in good agreement with the theoretical value of the constant B calculated by GAMAKER²¹, 10^{-12} – 10^{-13} erg. The results are also in good agreement with the results of direct measurements of disjoining pressure²². Hence the evaluations that we have carried out indicate that the theory is in quantitative agreement with experimental data.

REFERENCES

- 1 J. C. GIDDINGS, *Anal. Chem.*, **34** (1962) 458.
- 2 J. SERPINET, *J. Chromatogr.*, **68** (1972) 9.
- 3 A. T. JAMES AND A. J. P. MARTIN, *Biochem. J.*, **50** (1952) 679.
- 4 R. A. KELLER AND G. H. STEWART, *J. Chromatogr.*, **9** (1962) 1.
- 5 R. L. MARTIN, *Anal. Chem.*, **33** (1961) 347.
- 6 B. G. BELENKII, A. E. VITTENBERG, L. D. TURKOVA AND N. N. TCHERNISHKOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1967) 269.
- 7 V. G. BEREZKIN, V. P. PACHOMOV, A. S. TATARINSKII AND V. M. FATEEVA, *Dokl. Akad. Nauk SSSR*, **180** (1968) 1135.
- 8 V. G. BEREZKIN, *Uspekhi Khromatografii*, Nauka, Moscow, 1972, p. 215.
- 9 B. G. BELENKII, L. D. TURKOVA, N. M. GELLER AND V. A. KROPACHEV, *Osnovnie Problemi Teorii Fizicheskoi Adsorbtsii*, Nauka, Moscow, 1970, p. 474.
- 10 V. G. BEREZKIN AND V. M. FATEEVA, *J. Chromatogr.*, **58** (1971) 73.
- 11 B. V. DERYAGIN, *Kolloid. Zh.*, **17** (1955) 207.
- 12 A. I. RUSANOV, *Fazovie Ravnovesiya i Poverkhnostnyie Yavleniya*, Khimiya, Leningrad, 1967.

- 13 A. I. RUSANOV, *Zh. Fiz. Khim.*, 46 (1972) 750.
- 14 T. L. HILL, *Statistical Mechanics*, McGraw-Hill, New York, 1956.
- 15 I. E. DZIALOCHINSKY, E. M. LIFSHIZ AND A. P. PISHOEVSKY, *Zh. Eksp. Teor. Fiz.*, 37 (1959) 229.
- 16 A. I. RUSANOV AND F. M. KUNI, *Issledovaniya v Oblasti Poverkhnostnikh Sil*, Nauka, Moscow, 1967, p. 129.
- 17 F. M. KUNI, A. I. RUSANOV AND E. N. BRODSKAYA, *Kolloid. Zh.*, 31 (1969) 860.
- 18 F. M. NELSON AND F. T. EGGERTSEN, *Anal. Chem.*, 30 (1958) 1387.
- 19 N. M. GELLER, V. A. KROPACHEV AND B. A. DOLGOPLOSK, *Vysokomol. Soedin.*, A-9, (1967) 575.
- 20 S. DALNOGARE AND R. N. JOUVET, *Gas-Liquid Chromatography*, Interscience, New York, 1962.
- 21 H. C. HAMAKER, *Physica*, 4 (1937) 1058.
- 22 B. V. DERYAGIN AND U. U. KUSAKOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1937) 1119.