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THIN-LAYER CHROMATOGRAPHY OF OLIGOMERS

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SUMMARY

The mechanism of the thin-layer chromatography of oligomers based on the different adsorption activities of the end groups and the central units, characterized by adsorption energies $-\varepsilon_e$ and $-\varepsilon_c$, is discussed. It is shown that the application of the concept of the critical adsorption energy, $-\varepsilon^\circ$, to the central oligomer units makes it possible to distinguish three cases of the molecular weight dependence of R_F values: at $-\varepsilon^\circ > -\varepsilon_c$ and $-\varepsilon^\circ < -\varepsilon_c$ we have a negative and positive molecular weight dependence of R_F values, respectively, while at $-\varepsilon^\circ = -\varepsilon_c$ the R_F values do not depend on molecular weight. In the last instance, thin-layer chromatography can be used for the separation of oligomers on the basis of functional groups and degree of branching independent of their molecular weights. For the separation of oligomers on the basis of molecular weight thin-layer chromatography, hydroxyl end groups should be blocked in the case of poor adsorption activity of the central units. In this instance the second type of molecular weight dependence of R_F values is observed. A quantitative method for the determination of low-functionality impurities monools and poly(propylene oxide)diols in oligomers based on the chromatographic spot length is suggested.

INTRODUCTION

The thin-layer chromatography of oligomers is of great interest both analytically (for the analysis of this most significant class of polymers) and in view of the specific features of the adsorption chromatography of polyfunctional compounds that have chemically different structures of the end and central units in a macromolecular chain. The thin-layer chromatography of many classes of oligomer has been described, including polyols[1–11], polyethers and polyesters [12–16], polyolefins[17] and polyamides[18]. Most of these papers indicated the possibility of separating oligomers that differ in the number and structure of the end groups. Some workers[6,7,10,11,14] showed that the chromatographic behaviour of oligomers is independent of their molecular weight when only the amount of functional groups present in the oligomers determines the difference in their R_F values. This enables one to carry out the highly important

analysis of the functionality of oligomers[19], which is responsible for the quality of oligomer-based high polymers such as polyurethanes.

On the other hand, it is possible to separate substituted poly(ethylene oxides) on the basis of molecular size with the isolation of separate polymer homologues up to 12-mers to 15-mers[9]. It has been shown that the efficiency of the separation of polyols on the basis of molecular weight depends on the type of the substituent blocking the hydroxyl end unit. The more hydrophobic the substituent (in fact probably the larger the volume of the hydrocarbon radical of the substituent and hence the lower the adsorption of the end units), the more effective is the separation of the oligomer into separate polymer homologues.

Hence it is of interest to elucidate the mechanism of the thin-layer chromatography of oligomers in order to determine the molecular weights of oligomer and conditions for the separation on the basis of functional groups and to examine these regularities for different classes of oligomers.

MECHANISM OF THIN-LAYER CHROMATOGRAPHY OF OLIGOMERS

The peculiarities of the adsorption of oligomers are determined by their functional end groups. These end units usually have a larger adsorption activity than the central units and the free energy of the oligomers during the adsorption process changes primarily with the free energy of the end groups being adsorbed. It is clear that the greater the difference in adsorption activity between the central and end units in an oligomer, the lower is the contribution of the central units to the free energy change on adsorption and consequently the less evident the molecular weight dependence of the R_F value of the oligomer in adsorption thin-layer chromatography should be.

The regularities of the thin-layer chromatography of oligomers are considered in detail below.

The change in the free energy (ΔF) in the adsorption of macromolecules (adsorption coefficient $K_d = e^{-\Delta F/kT}$, where k is Boltzmann's constant and T is the absolute temperature) is related to an increase in enthalpy $-\Delta H = -\varepsilon N$ (where $-\varepsilon$ is the energy of interaction of a macromolecular unit with the adsorption surface and N is the number of units) and to a decrease in entropy $T\Delta S$. Di Marzio[20] introduced the concept of critical energy, $-\varepsilon = -\varepsilon^{\circ}$, at which the entropy losses of a polymer macromolecule are completely compensated for by an increase in its enthalpy ($\Delta H = T\Delta S$). In this instance the macromolecule is thermodynamically indifferent to the adsorption surface. The concept of the critical energy can be exteded to oligomers, assuming that changes in entropy are related to a decrease in the number of possible comformations in adsorption. If we designate the energies of interaction of the end and central units with the adsorption surface by $-\varepsilon_e$ and $-\varepsilon_c$, respectively, then the change in $-\Delta F$ on adsorption of the oligomer will be represented by the equation

$$-\Delta F = -\varepsilon_e\, n - \varepsilon_c\, (N-n) + T\Delta S \tag{1}$$

Depending on the relationship between $-\varepsilon_c$ and $-\varepsilon^{\circ}$ ($-\varepsilon_c$ is always lower than $-\varepsilon^{\circ}$), the following three cases of the dependence of $-\Delta F$ on the number of macromolecular units, N, are observed:

$$-\varepsilon_c < -\varepsilon^\circ: \quad -\Delta F = -(\varepsilon_e - \varepsilon^\circ)n - (\varepsilon_c - \varepsilon^\circ)(N-n) + T\Delta S \tag{2a}$$

$$-\varepsilon_c > -\varepsilon^\circ: \quad -\Delta F = -(\varepsilon_e - \varepsilon^\circ)n + (\varepsilon_c - \varepsilon^\circ)(N-n) + T\Delta S \tag{2b}$$

$$-\varepsilon_c = -\varepsilon^\circ: \quad -\Delta F = -(\varepsilon_e - \varepsilon^\circ)n + T\Delta S \tag{2c}$$

It is clear that in the first instance the dependence of K_d on N is positive, in the second it is negative and in the third it does not depend on N and is determined only by the number of functional groups in the oligomer, n. In accordance with these dependences, in the first instance the R_F value of the oligomer decreases with increasing molecular weight, in the second it increases and in the third it does not depend on molecular weight and is determined only by the functionality of the oligomer.

It should be mentioned that in the absence of functional groups ($n = 0$), only the first type of dependence is observed, because in the second type of dependence all of the oligomers will move with the solvent front.

Fig. 1 shows chromatograms of similar functionless polystyrene and poly-(α-methylstyrene) oligomers, which clearly exhibit the first type of molecular weight dependence.

The molecular weight dependence of the R_F values is revealed most strongly with functionless oligomers. For an oligomer with functional groups, there is a de-
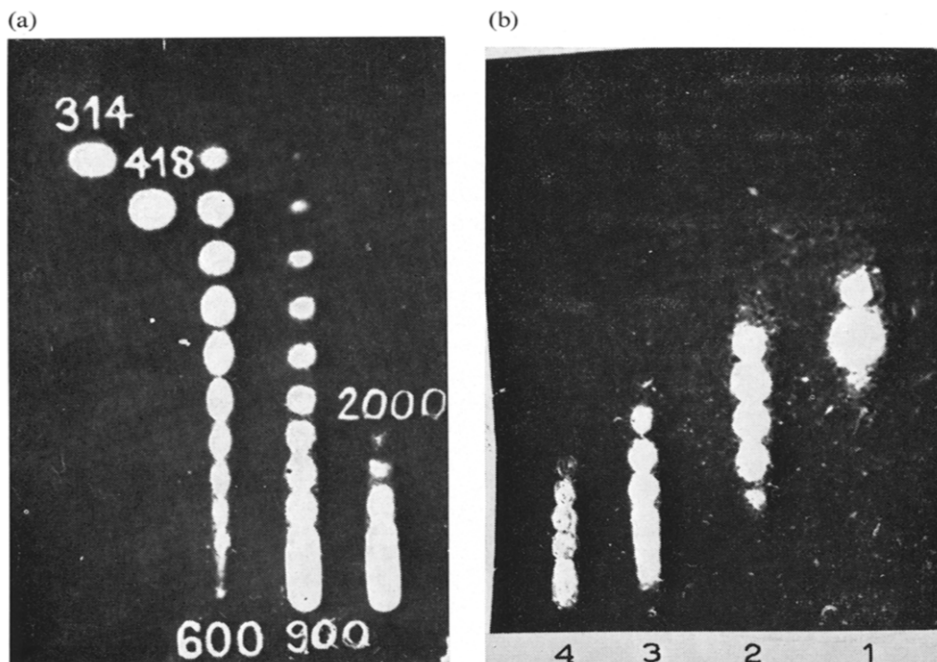
(a) (b)

Fig. 1. Thin-layer chromatograms of (a) polystyrenes with $M_n = 314$, 418, 600, 900 and 2000 in cyclohexane–benzene (14:3) system and (b) poly(α-methylstyrene) fractions (1, tetramer; 2, hexamer; 3, octamer; 4, decamer) in CCl_4–heptane (2:1) on KSK silica gel. Thin-layer chromatography was carried out on 6 × 10 cm plates, covered with 5–10 μm of adsorbent. Styrene trimer and tetramer are obtained on recirculation gel chromatography with 500, 250 and 100 A columns (Waters Assoc.) from polystyrene with $M_n = 600$.

crease in the molecular weight dependence of R_F values with an increase in the difference between $-\varepsilon_e$ and $-\varepsilon_c$.

The latter property becomes evident if we examine eqn. 1. In order to observe chromatographic differences between oligomers with different molecular weights, it is necessary to increase $-\varepsilon_e$ and $-\varepsilon_c$ so as to make the R_F values greater than zero. For $-\varepsilon_e \ll -\varepsilon_c$, $-\varepsilon_c$ becomes very small in absolute value, and consequently the value of $(N-n)$ in eqn. 1 becomes lower than at closer values of $-\varepsilon_e < \varepsilon_c$, when the R_F values of the oligomers are approximately equal. The above-mentioned three types of molecular weight dependence of R_F are worth obtaining experimentally for oligomers that have functional groups such as polyols.

Fig. 2 shows thin-layer chromatograms of poly(ethylene oxide) with M_n values of 300, 400 and 600 in chromatographic systems where the first, second and the third types of molecular weight dependence of R_F values are observed. As shown in Fig. 2a, the polymer homologues in poly(ethylene oxides) of different molecular weight have the same R_F value. It is interesting that the dependence of R_F on molecular weight for poly(ethylene oxide) shown in Fig. 2b is similar to the dependence characteristic of the molecular-sieve effect but the thin-layer chromatographic mechanism is different. In separate experiments it was established that these oligomers begin to be excluded from the pore space in silica gel and aluminium oxide when their molecular weight exceeds 10,000, *i.e.*, when it is much higher than the molecular weight of the poly-(ethylene oxide) being investigated.

The peculiar action of concentration effects on the adsorbability of polyols is manifested by the moon-shaped form of the chromatographic spots in thin-layer chromatography. The R_F value is known to increase with increase in concentration for a convex adsorption isotherm. Hence the R_F value of the side-wings of the chromatographic spot where the concentration of the substance is decreased will be less than the R_F value of the central part of the polymer zone. As a result, the chromatographic spot assumes an unusual shape with a clearly defined "nose", the R_F value of which
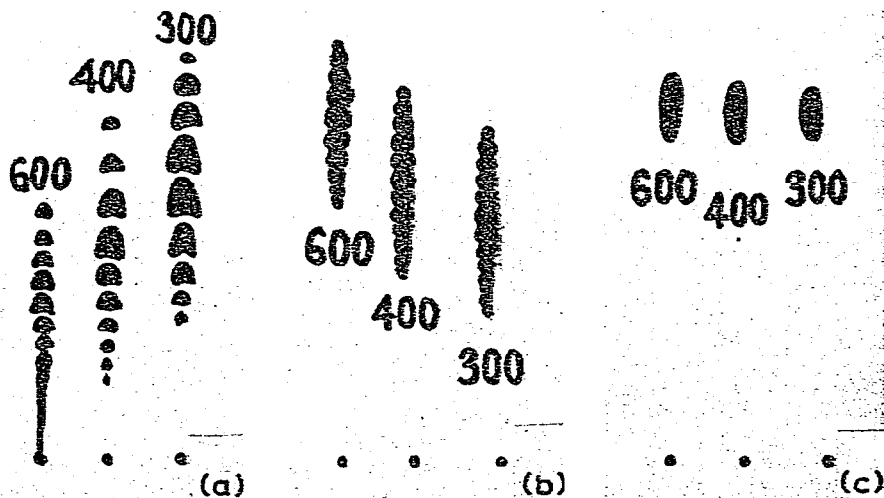

Fig. 2. Thin-layer chromatograms of poly(ethylene oxide) with $M_n = 300, 400$ and 600 on (a) KSK silica gel in pyridine–water (0.1:10), (b) aluminium oxide in chloroform–ethanol (10:1) and (c) KSK silica gel in chloroform–pyridine (5:7).

with respect to the R_F of the side-wings or the spot with a low polyol content is useful in quantitative analysis (it has been shown[11] that there is a linear dependence of the R_F value on the amount of substance in an oligomer spot).

It should be noted that the replacement of poly(ethylene oxide) end hydroxyl group with less adsorbable groups facilitates the generation of the positive molecular weight dependence of $-\Delta F$ adsorption (and consequently the negative dependence of R_F).

With oligomers that have poorly adsorbable central units, such as poly(dimethylsiloxane diols), their highly efficient molecular weight separation is not possible without blocking the end groups (Fig. 3). It is clear that having blocked the end hydroxyl groups, for example with dinitrobenzoic acid, only the second type of molecular weight dependence is easily realized when, on increasing the number of poorly adsorbable siloxane units in the oligomer, the R_F value increases.

The above results show that the peculiarities of the thin-layer chromatography of oligomers are related to the ratio of the adsorption activities of the end and central units. An appropriate choice of the separating systems that will change this ratio enables one to realize variants of thin-layer chromatography in the absence of a molecular weight dependence of R_F value with separation of oligomers on the basis
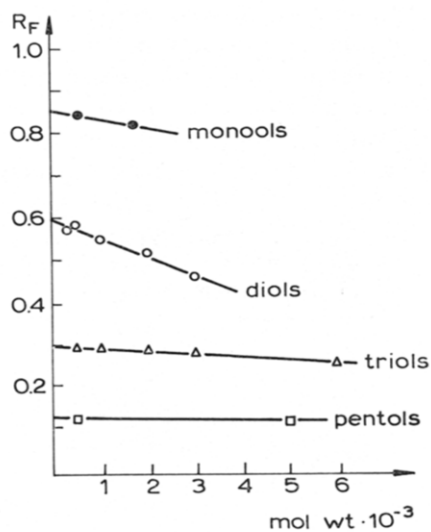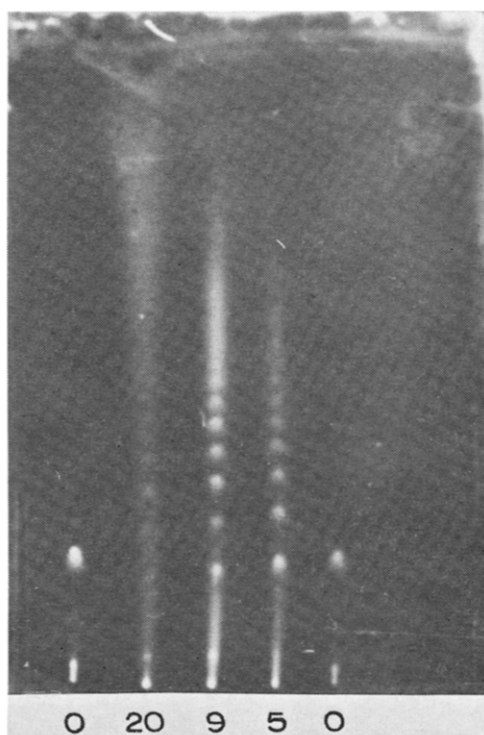

Fig. 3. Thin-layer chromatograms of 3,5-dinitrobenzoate poly(dimethylsiloxane) diols with $n = 0, 5,$ 9 and 20 on KSK silica gel, 0.07% of fluoresceine being introduced into the layer, in benzene–ethyl acetate (10:0.1). Thin-layer chromatography was performed twice (luminescent photography).

Fig. 4. Separation of poly(propylene oxide) polyols (PPOP) on KSK silica gel in ethyl acetate saturated with water containing 5–10% of methyl ethyl ketone.

of functional groups, and also with both positive and negative molecular weight dependences of R_F. The last two variants of thin-layer chromatography can be used for the determination of the molecular weights of oligomers.

SEPARATION OF OLIGOMERS ON THE BASIS OF FUNCTIONAL GROUPS

In the absence of a dependence of molecular weight on R_F value (the third type of molecular weight dependence), the separation of oligomers on the basis of functional groups is of great practical interest. The suitability of thin-layer chromatography for the determination of the functionality of oligomers can be illustrated with poly(propylene oxide) polyols (PPOP) as an example. As shown in Fig. 4, thin-layer chromatography of PPOP in ethyl acetate saturated with water and containing 5–10% of methyl ethyl ketone permits the separation of monools, diols, triols, pentols over a wide range of molecular weights. Here a slight molecular weight dependence (the first type) of the R_F value of PPOP, unaffected by the effect of functionality on the R_F value, is observed. It is interesting that the molecular weight dependence of the R_F value of PPOP can be suppressed or changed by decreasing the adsorption capacity of the silica gel. The chromatograms of monools and triols on standard KSK silica gel and on KSK with its specific adsorption capacity reduced by treatment with sodium hydroxide and sodium chloride are compared in Fig. 5[21]. In the latter case the R_F value increased with a polyol molecular weight that is specific to the second type of molecular weight dependence. However, even in this instance the chromatographic behaviour of the polyols with different functionalities remains different. Therefore, the thin-layer chromatographic conditions selected enable one to determine the PPOP functionality independent of molecular weight[19]. This approach to the determination of functionality permits the separation of linear and branched oligomers that differ in the number of functional end groups present. Thus, in benzene–ethanol (3:1), a complete separation of the linear and branched oligoester polyols with the same molecular weight is achieved (Fig. 6). In the above system, the molecular weight dependence of R_F values is very weak, and increases with decreasing ethanol content in the eluent (Fig. 7). The system benzene–tetrahydrofuran (1:1) was also found to be suitable for
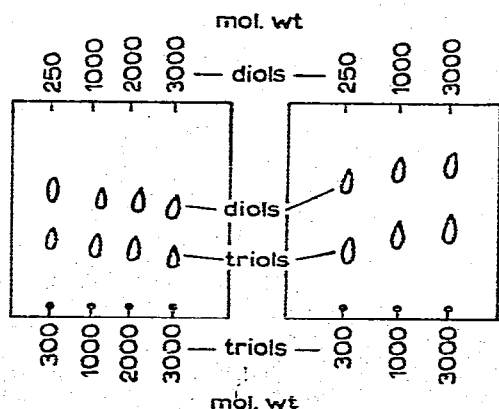

Fig. 5. Thin-layer chromatograms of PPOG with different molecular weights on (a) KSK silica gel and (b) KSK-2 silica gel treated with NaOH and NaCl.
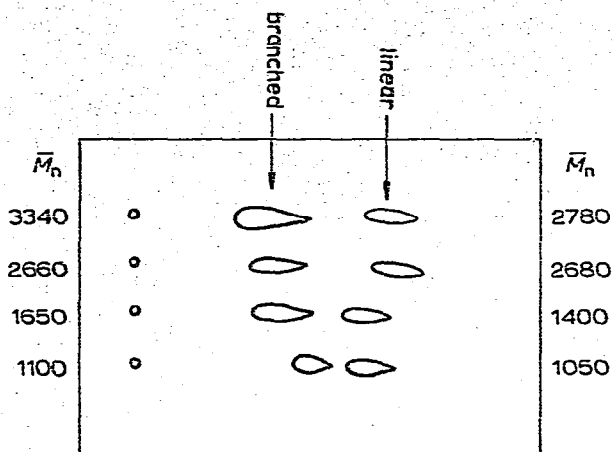
Fig. 6. Thin-layer chromatograms of linear [poly(propylene oxide) adipates, PPOA] and branched (polyglycerol adipates, PGA) of polyesters with similar molecular weights in benzene–ethanol (3:1) on KSK-2 silica gel.

the separation of linear and branched oligoester polyols, as shown in Fig. 8. This system permits the thin-layer chromatographic analysis of oligoester samples containing 10% of branched macromolecules together with the linear macromolecules (Fig. 9). The lower chromatographic mobility of the branched compared with the linear
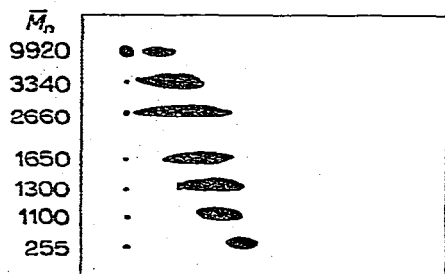

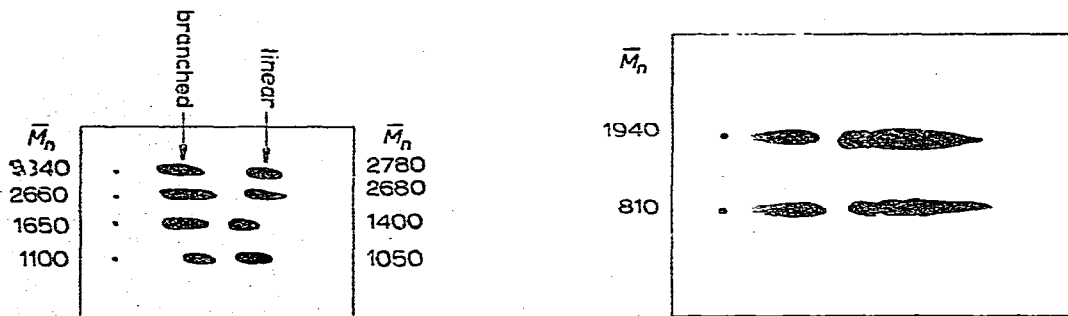Fig. 7. Separation of branched polyesters (PGA) on KSK-2 silica gel in benzene–ethanol (85:15).

Fig. 8. Thin-layer chromatograms of linear (PPOA) and branched (PGA) polyesters with similar molecular weights in benzene–tetrahydrofuran (1:1).

Fig. 9. Determination of content of branched component (PGA) in a polyester sample on KSK-2 silica gel in benzene–tetrahydrofuran (1:1).

oligoesters is related to an increase in the number of hydroxyl end groups present. It is of great analytical interest to reveal the difference in R_F values between linear and branched oligoesters with the same molecular weight because, as we have found[22], this difference is not revealed by gel permeation chromatography. Hence the molecular weights of oligoesters obtained by gel permeation chromatography can be substantially supplemented by the results of the molecular weight dependence of the branched polyfunctional oligomer distribution in a sample being analyzed.

QUANTITATIVE DETERMINATION OF LOW-FUNCTIONALITY IMPURITIES IN PPOP BY THIN-LAYER CHROMATOGRAPHY

A useful method for the determination of low-functionality species in PPOP is based on the dependence of the mobility of a chromatographic spot on the oligomer content. As illustrated in Fig. 10, the chromatographic spots of PPOP have a sharp central "nose" with a clearly defined front, while the rear front of the spot is blurred. As indicated above, this shape of the chromatographic zone is attributed to specific concentration effects during adsorption of the oligomer, giving a convex adsorption isotherm where the point corresponding to the maximum concentration is in the front part of the spot while the side zones corresponding to lower concentrations trail further behind. Hence it is natural to use the chromatographic mobility value for the "nose" of the spot, the R_F value of which can be measured exactly for the determination of its PPOP content[*]. The existence of such a dependence was shown experimentally. It is linear and remains constant over two orders of magnitude of concentration, its slope depending on the molecular weight of the PPOP and the length of the track of the substance on the plate (Fig. 11). This type of dependence is obtainable from a simplified model of the adsorption thin-layer chromatography of oligomers described below.
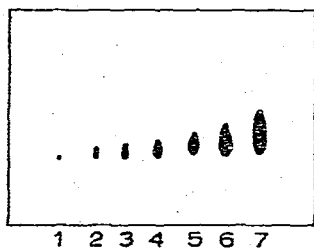

Fig. 10. Thin-layer chromatograms of poly(propylene oxide) diols (PPOD) with $M_n = 1000$. Amount of PPOD: (1) 6; (2) 20; (3) 30; (4) 35; (5) 50; (6) 65; (7) 100 μg.
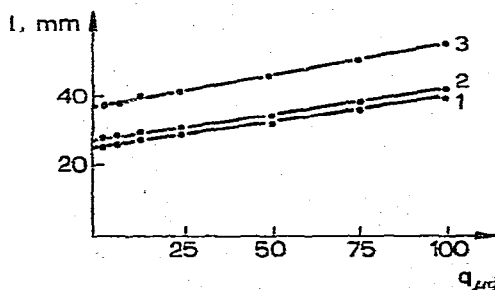
Fig. 11. Chromatographic spot length (*l*) obtained on KSK silica gel in ethyl acetate saturated with water containing 2% of methyl ethyl ketone *versus* the content of PPOD (*q*) with M_n values of (1) 1000, (2) 425 and (3) 1000 (40% of methyl ethyl ketone was added to the system).

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[*] The chromatographic homogeneity of the substance under investigation is an indispensable condition for using this method of quantitative analysis. Under our experimental conditions, the R_F values of oligomers do not depend on their molecular weights (third case)[2], and hence poly(oxyethylene) polyols of the same functionality are chromatographically homogeneous.

It is known that the R_F value for the point of maximum concentration of a spot containing an amount q of a substance, R_{Fq}, is related to the concentration of the substance in the spotmaximum by the relationship

$$R_{Fq} = \frac{l_q}{l_s} = \frac{1}{1 + \dfrac{m_c}{c}} \qquad (3)$$

where l_q and l_c are the lengths of the tracks of the chromatographic spot maximum and the solvent front on the plate, respectively, and c and m_c are the concentrations of the substance in the spot maximum for the mobile and stationary phases, respectively (based on the overall thickness of the chromatographic layer).

The m_c/c ratio can be defined from the Freundlich equation, which is suitable for describing the adsorption of polymers in many instances[23]:

$$m_c = \alpha c^\beta \qquad (4)$$

where α and β are constants ($\beta < 1$).

The concentration of the polymer in the mobile phase, c, can be related to the amount of the substance in the spot, q, by the equation

$$c = kR_Fq \qquad (5)$$

where k is a constant ($k \ll 1$). Substitution of eqns. 4 and 5 into eqn. 3 gives

$$R_{Fq} = \frac{1}{1 + \alpha(kR_Fq)^{\beta-1}} \qquad (6)$$

Thus, for $R_{Fq} = l_q/l_c$ in the case of an extremely small but still detectable amount q_0, we have

$$R_{Fq_0} = \frac{1}{1 + \alpha(kR_{Fq_0}q_0)^{\beta-1}} \qquad (7)$$

After some simple transformations, assuming that $kR_{Fq}q$ and $kR_{Fq_0}q_0 \ll 1$, we obtain the desired dependence

$$\Delta l = \gamma q \qquad (8)$$

where $\Delta l = l_q - l_{q_0}$ and $\gamma = \alpha(1-\beta)^2 klq_0R_{Fq_0}/(1-\alpha)$

Eqn. 8 implies that there is a linear dependence between Δl and q, which was also derived experimentally. It can also be seen from eqn. 8 that the sensitivity of a quantitative analysis based on the measurement of the chromatographic spot length, Δl, is higher the lower is the adsorbability of the polymer, that is, the lower is β and the higher is R_{Fq_0}. The slope of the dependence $\Delta l/q = \gamma$ is also increased.

This approach to the quantitative analysis of thin-layer chromatograms, which combines extreme simplicity and a satisfactory precision ($\sigma_q/q = 2-3\%$), can be recommended for practical use. This method has been applied successfully to the determination of monool and diol impurities in PPOP samples with the above precision, the content of the impurities being 1–2%.

ACKNOWLEDGEMENTS

REFERENCES

1 K. Bürger, *Z. Anal. Chem.*, 196 (1963) 259.
2 I. A. Vakhtina, P. A. Okunev and O. G. Tarakanov, *Zh. Anal. Khim.*, 21 (1966) 630.
3 K. Bürger, *Z. Anal. Chem.*, 224 (1967) 421.
4 L. Favretto, G. Pertoldi Marletta and L. Favretto Gabrielli, *J. Chromatogr.*, 46 (1970) 255.
5 T. Salvage, *Analyst (London)*, 95 (1970) 363.
6 I. A. Vakhtina, R. I. Khrenova and O. G. Tarakanov, *Zh. Anal. Khim.*, 28 (1973) 1625.
7 I. A. Vakhtina, O. G. Tarakanov and R. I. Khrenova, *Vysokomol. Soedin.*, A16 (1974) 2598.
8 M. S. J. Dallas and M. F. Stewart, *Analyst (London)*, 92 (1967) 634.
9 L. Favretto, L. Favretto Gabrielli and G. Pertoldi Marletta, *J. Chromatogr.*, 66 (1972) 167.
10 W. A. Manenskii, *J. Appl. Polym. Sci.*, 14 (1970) 1189.
11 B. G. Belenky, I. A. Vakhtina and O. G. Tarakanov, *Vysokomol. Soedin.*, A17 (1975) 2116.
12 K. Koninshi and S. Yamaguchi, *Anal. Chem.*, 38 (1966) 1755.
13 S. Hayano, T. Nihongi and T. Asahara, *Tenside*, 5 (1968) 80.
14 K. Kondo. M. Miyazaki, M. Hori and M. Hattori, *Bunseki Kagaku (Jap. Anal.)*, 16 (1967) 419.
15 Th. Pye and U. Wuntue, *Plaste Kautsch.*, 15 (1963) 274.
16 V. A. Dorman-Smith, *J. Chromatogr.*, 29 (1967) 265.
17 M. T. Bryck, A. S. Shevlyakov and O. B. Krezub, *Vysokomol. Soedin.*, B10 (1968) 893.
18 Y. Kobayashi, *J. Chromatogr.*, 24 (1966) 447.
19 S. G. Entelis, V. V. Evreinov and A. P. Kuzaev, in *Progress in Polymer Chemistry and Physics*, Khimiya, Moscow, 1973, p. 201.
20 E. A. di Marzio and F. L. McCrakin, *J. Chem. Phys.*, 43 (1965) 539.
21 A. V. Kiselev and Ya .I. Yashin, in *Gas Chromatography for Physico-chemistry*, Khimiya, Moscow, 1973, p. 5.
22 B. G. Belenky, I. A. Vakhtina and O. G. Tarakanov, *Vysokomol. Soedin.*, B16 (1974) 507.
23 Yu. S. Lipatov and L. M. Sergeeva, *Kolloidn. Zh.*, 27 (1965) 217.