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## SOLUTION OF THE INVERSE PROBLEM AND CALCULATION OF SORPTION ISOTHERMS IN CHROMATOGRAPHY

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### SUMMARY

The ideal conditions in chromatography and the limits of Huber's method are defined with a model based on a layer of equilibrium adsorption. New methods for solution of the inverse problem are proposed.

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### INTRODUCTION

The development of a phenomenological theory of elution chromatography is necessary for the estimation of the physicochemical properties of substances and the characteristics of sorbents and catalysts.

It has been noted<sup>1</sup> that in ideal chromatography the equilibrium between the particle and fluid is immediate, the mass transfer coefficient is infinitely high. In the theory of ideal chromatography, the correlation between the elution curve and the sorption isotherm is determined<sup>2</sup>. So far, no criteria have been found for the quantitative assessment of the ideal conditions within the framework of the existing theoretical models.

The theory of non-ideal non-linear (or real) chromatography has been inadequately developed<sup>3</sup>. This is apparently due to the impossibility of obtaining a satisfactory solution to the material balance and sorption kinetics equations for random isotherms. The methods of definition of the sorption isotherm in real chromatography<sup>4-6</sup> have a particular character.

The present report concerns the quantitative assessment of the ideal conditions in chromatography and the limits of Huber's method, and the development of new methods for solution of the inverse problem, when the sorption isotherm and effective kinetic constant are simultaneously defined.

### THEORETICAL

The layer-by-layer method developed in plate theory<sup>7</sup> applied to non-linear isotherms could be of great interest. Despite the fact that the effective kinetic constant is represented on a length scale in the analytic solution of plate theory for a linear isotherm and the diffusion-mass exchange theory<sup>1</sup> arrives at the same conclusion,

chromatographic constants determined by the ratio of the elementary volumes of the mobile phase and the sorbent have been used as the experimental kinetic constants in the layer method<sup>8-10</sup>, i.e., the two scales  $\Delta l$  and  $\Delta t$  have been used for characterization of sorption kinetics. Nevertheless, an additional introduction of the time scale,  $\Delta t$ , greatly complicates the description of real chromatography and belittles the approach suggested in plate theory.

A new variant of the layer method based on a model of an equilibrium adsorption layer ( $L_e$  in Fig. 1) has been proposed<sup>11</sup>. The original equation may be written in the form

$$\frac{d\bar{c}}{dt} + \frac{d\bar{a}}{dt} = \frac{v}{L_e} [c_B - c(\bar{a})] \quad (1)$$

where  $\bar{a}$  and  $\bar{c}$  are, respectively, the mean weight adsorbed and the concentration in the column volume with thickness  $L_e$ ,  $v$  is the superficial velocity of the mobile phase,  $c_B$  is the concentration entering the layer  $L_e$ ,  $c(\bar{a})$  is the concentration leaving this layer and also the analytical or numerical expression of a sorption isotherm and  $t$  is the time.

#### *Quantitative estimation of ideal conditions in chromatography and limits of Huber's method*

According to the model based on a layer of equilibrium adsorption<sup>12</sup> we have calculated the elution curves for isotherms  $a = kc^{1/n}$ , where  $n < 1$  and  $n > 1$ , at different thicknesses,  $L_e$ , of the layer of equilibrium adsorption column length,  $l$ , and sample sizes,  $q$ , introduced.

The leading edges of the elution curves (Fig. 2), which coincided at different  $q$  and were linear, were used to calculate the sorption isotherms according to the equation of ideal chromatography. The ideal-state coefficient,  $k_{id}$ , was defined as the

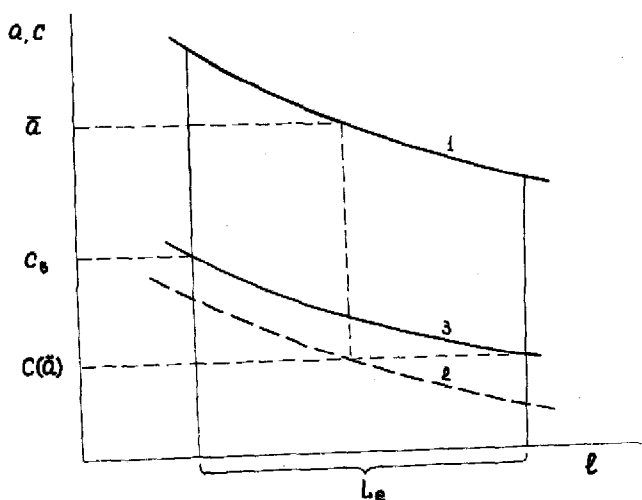


Fig. 1. Scheme of the layer of equilibrium adsorption. Curves: 1, adsorption; 2, concentration in ideal chromatography and 3, real concentration.

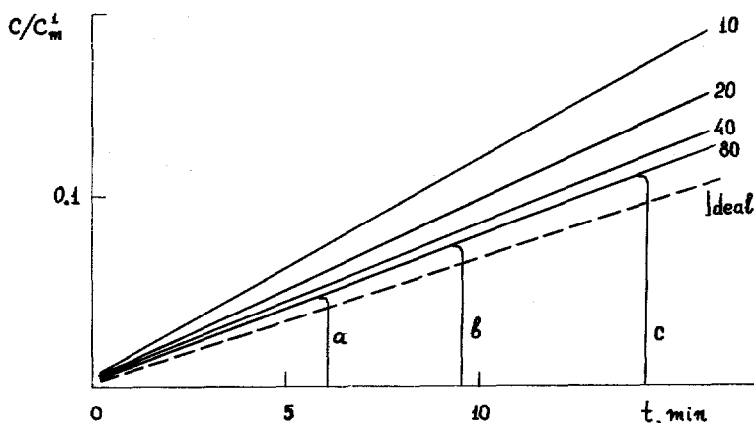


Fig. 2. Outlet elution curves for a concave sorption isotherm  $a = kc^2$ . Numbers on the curves denote the relative column length,  $l/L_e$ . Ideal = isolength line in ideal chromatography. Conditions:  $l = 5$  cm;  $v = 500$  cm/min;  $k = 1.41 \cdot 10^6$  cm<sup>3</sup>/mg. The amounts of substance introduced for  $l/L_e = 80$  are: a, 1.41; b, 2.82 and c, 6.79 mg. The starting concentration,  $C_m^1$ , was 5 mg/l.

ratio of the calculated sorption to that characteristic of ideal chromatography. It was found (Fig. 3) that  $k_{id}$  increased with increasing number of layers in the column and that it is independent of the absolute value of the effective kinetic constant,  $L_e$ . Thus, ideal conditions in chromatography are determined by the relative length of the column. At values of  $l/L_e > 100$ –250 the real processes in the column can be described with sufficient accuracy on the basis of the theory of ideal chromatography, and the sorption isotherm can be calculated by De Vault's method<sup>2</sup>.

The validity of this was confirmed by an analysis of the initial equation of the model, eqn. 1. In fact,  $L_e$  approaches  $dl$  when the ratio  $l/L_e$  is very large. Consequently,  $[c_B - c(\bar{a})] \approx dc$  and the model equation transforms to that for ideal chromatography.

The numerical calculation of the convex isotherm were performed according to the conditions and constants presented previously<sup>1,3</sup>. It follows from the results of

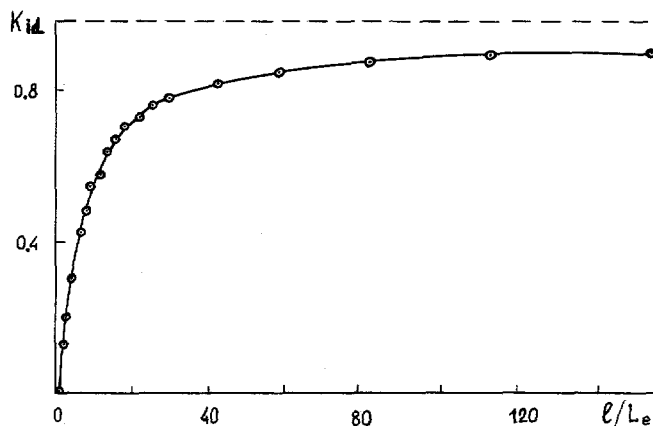


Fig. 3. Dependence of the ideal-state coefficient  $k_{id}$ , on the relative chromatographic column length.

these calculations (Fig. 4) that the peak maxima do not coincide with the isolength line in ideal chromatography in the case of short columns ( $l/L_e = 1, 2$  and  $4$ ). However, the peak maxima approximate to the isolength line with increasing value of  $l/L_e$ . The isolength line, calculated with the ideal chromatography equation, connects the peak maxima for different sample sizes only at a certain column length.

For example, for the adsorption of anisole on silica SCP under the given conditions, a calculation of the sorption isotherm by Huber's method becomes possible only for column lengths  $l/L_e > 8-10$ .

#### *New methods for solution of the inverse problem*

The solution of the inverse problem in the model based on a layer of equilibrium adsorption, when  $d\bar{c}/dt \ll d\bar{a}/dt$ , is concluded by integration of

$$\bar{a} = \frac{v}{L_e} \int_0^t [c_B - c(\bar{a})] dt \quad (2)$$

where the functions  $c(\bar{a})$  and  $c_B$  represent outlet curves for column lengths  $l_1$  and  $l_2$ , respectively, and  $(l_1 - l_2) = L_e$ .

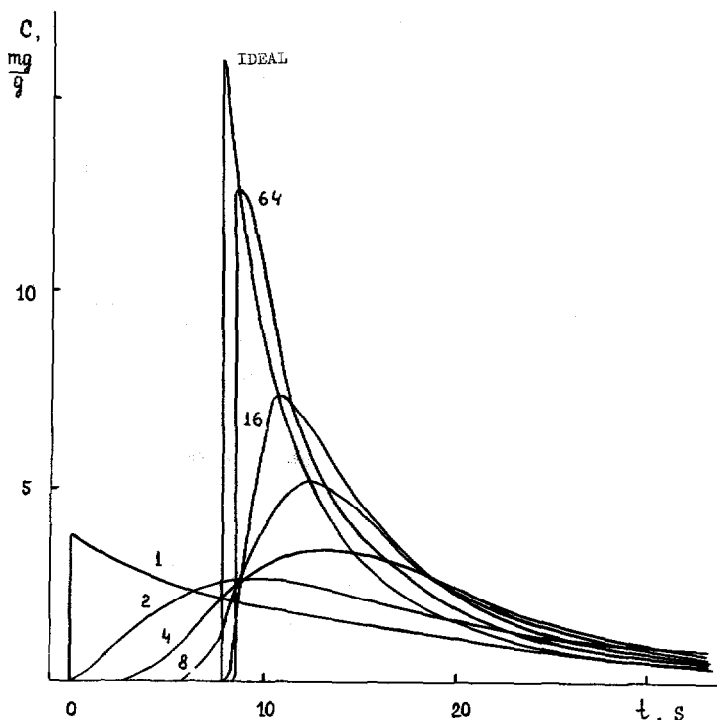


Fig. 4. Elution curves calculated for a convex sorption isotherm (anisole adsorption on silica SCP<sup>13</sup>). Numbers on the curves denote the relative column length,  $l/L_e$ . IDEAL = isolength line in ideal chromatography. Column sorbent mass = 0.96 g; sample size, 1 mg; volume velocity of the mobile phase,  $\omega = 0.68$  g/min.

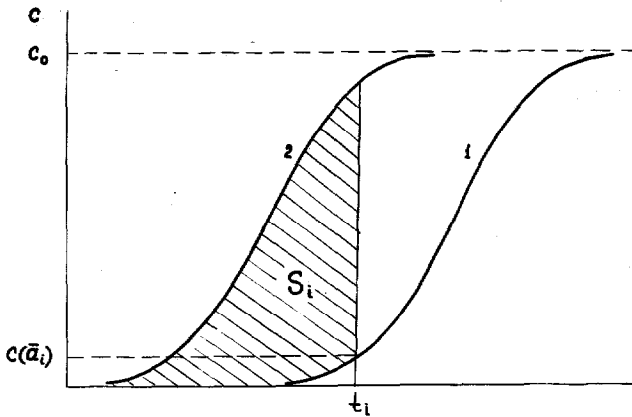


Fig. 5. Scheme for solution of the inverse problem on the basis of an exit curve measured in the stage of parallel transfer. Curves: 1 = measured,  $c(\bar{a}_i)$ ; 2 = constructed,  $c_B$ .

*Frontal chromatography*

(1) *Stage of the parallel transfer.* Solution of the inverse problem becomes possible on the basis of a single experimentally determined outlet curve. Parallel to the measured curve 1 (Fig. 5), curve 2 is plotted, nominally corresponding to the function  $c_B$  for the layer of equilibrium adsorption determined by the relationship

$$L_e = L \cdot \frac{t_1 - t_2}{t_1} \tag{3}$$

where  $L_e$  is the length of the layer in which the exit curve is measured, and  $t_1$  and  $t_2$  are the exit times of equal concentration for the measured and constructed curves, respectively.

The amounts of adsorption,  $\bar{a}_i$ , for the corresponding concentrations,  $c(\bar{a}_i)$ , are

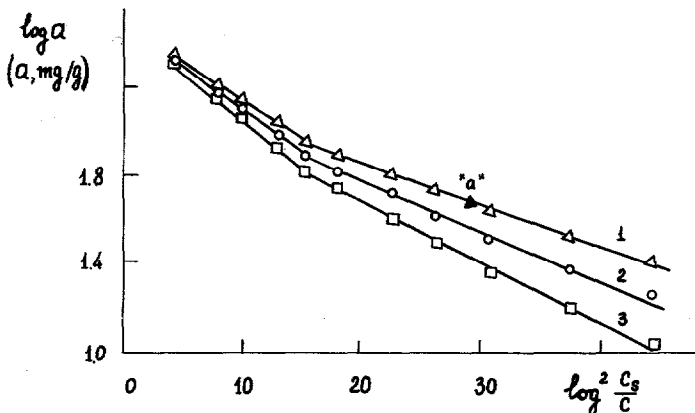


Fig. 6. Isotherms for cyclohexane adsorption on activated carbon, calculated according to the scheme in Fig. 5 with an experimental exit curve for different values of  $L_e$ : 1 = 1.0 cm; 2 = 0.9 cm and 3 = 0.8 cm. Point "a" was measured by another method. Concentration of saturated vapour,  $C_s$ , is 357 mg/l.

calculated with eqn. 2. The integral on the right-hand side is determined by the area,  $S_i$ , bounded by curves 1 and 2 and the vertical at time  $t_i$  corresponding to the appearance of the concentration  $c(\bar{a}_i)$ . The value of the length of the layer of equilibrium adsorption, with a given accuracy, is determined by matching the matrices of values of  $a_i$  and  $c_i$ , obtained with different values of  $L_e$ , to the adsorption isotherm fragments.

We will examine the results of such a calculation in the case of the adsorption of cyclohexane on activated carbon<sup>14</sup>. It was found (Fig. 6) that the best agreement with the isotherm fragment (point "a") is observed in the case of the isotherm calculated for a layer of equilibrium adsorption with  $L_e = 1$  cm, and this can also serve as a kinetic constant for the system consisting of cyclohexane and activated carbon.

(2) *Column length,  $l \approx L_e$ .* In frontal chromatography when the layer  $L_e$  is situated at the beginning of a column, the solution of the inverse problem is conducted according to the scheme in Fig. 7.

Let us examine the results of such a calculation in the case of the adsorption of carbon tetrachloride on activated carbon<sup>15</sup>. It was found (Fig. 8) that the best agreement with the measured<sup>16</sup> equilibrium adsorption isotherm is observed in the case of the isotherm calculated for a tube mass of 3.04 g or with  $L_e = 1.7$  cm.

#### *Elution chromatography*

In elution chromatography when the layer  $L_e$  is situated at the beginning of a column the expression

$$\bar{a} = \frac{v}{L_e} \int_t^{\infty} c(\bar{a}) dt \quad (4)$$

may be evaluated.

The scheme in Fig. 9 illustrates the calculation conducted according to eqn. 4. For each time  $t_i$  corresponding to the concentration  $c(\bar{a}_i)$ , the amount of the adsorp-

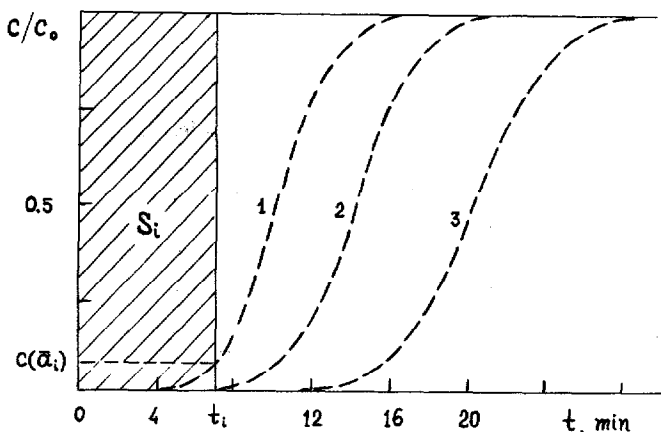


Fig. 7. Carbon tetrachloride penetration curves for carbon columns of various weights: 1 = 2.12; 2 = 3.04 and 3 = 4.29 g<sup>15</sup>. Scheme for solution of the inverse problem in frontal chromatography when  $l \approx L_e$ .

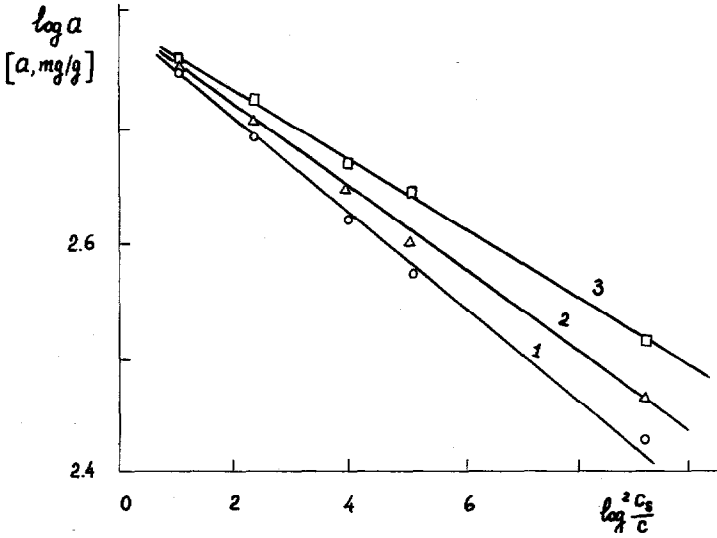


Fig. 8. Isotherms for adsorption of carbon tetrachloride on activated carbon, calculated according to the scheme in Fig. 7 for different carbon columns (see Fig. 7).

tion,  $\bar{a}_i$ , is determined. The integral in the right-hand part of eqn. 4 is calculated as the area  $S_i$ .

Fig. 10 shows the calculated elution curves, which are in a good agreement with the experimental data for  $l \approx L_c$ . Elution curves for the column length  $l = L_c$  are characterized by an appearance in the maxima with the velocity of the mobile phase, as noted previously<sup>17,18</sup>.

The solution of the inverse problem is conducted according to the scheme in Fig. 11, when the curves are measured for arbitrary column lengths. In this case, curve 1 (where  $l_1 < l_2$ ) intersects the maximum of curve 2.

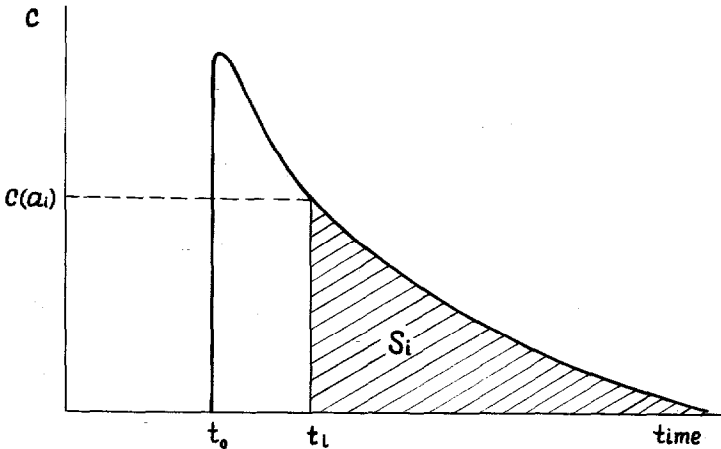


Fig. 9. Scheme for solution of the inverse problem in elution chromatography when  $l \approx L_c$ .

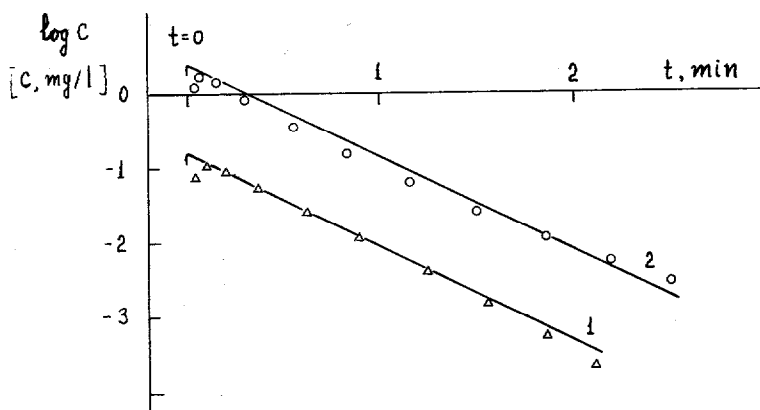


Fig. 10. Ethyl chloride outlet elution curves measured on activated carbon in air of a flow-rate of 700 cm/min at 423 K. Length of sorbent column: 0.7 cm. Amounts of substance introduced are: (1) 0.1 and (2) 1.0 mg. O,  $\Delta$ , Experimental data; —, theoretical calculation.

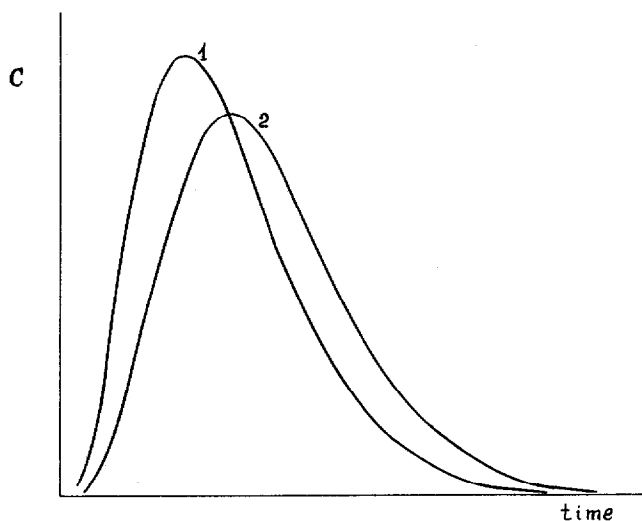


Fig. 11. Scheme for solution of the inverse problem in elution chromatography. Curve 1 crosses the maximum of curve 2 when  $l_2 - l_1 = L_e$  ( $l_2 > l_1$ ).

## CONCLUSIONS

On the basis of the model of the equilibrium adsorption layer it has been demonstrated that the shape of the outlet curve is defined by the relative length of the chromatographic column,  $l/L_e$ , and by the sorption isotherm. At  $l/L_e > 100-250$ , chromatographic systems with either concave and convex isotherms can be described by the equation for ideal chromatography and the sorption isotherms may be calculated by De Vault's method.



The isolength line, calculated with the ideal chromatography equation, connects the peak maxima for different sample sizes only at a certain length of the column. For example, a calculation of the sorption isotherm by Huber's method becomes possible only at  $l/L_e > 8-10$  (in the case of anisole adsorption on silica).

The examples that we have examined for solution of the inverse problem of chromatography by the model based on a layer of equilibrium adsorption have yielded simple algorithms for finding the effective kinetic constant from the outlet curves, measured in elution or frontal chromatography. The additional measurement of the sorption at small concentrations allows us to define the effective kinetic constant as well as the sorption isotherm from the outlet curves. In the cases of vapour adsorption on activated carbon there is good agreement between the calculated and experimental isotherms.

#### REFERENCES

- 1 J. J. van Deemter, F. J. Zuiderweg and A. Klinkenberg, *Chem. Eng. Sci.*, 5 (1956) 271.
- 2 D. de Vault, *J. Am. Chem. Soc.*, 65 (1943) 532.
- 3 P. P. Zolotarev, *Zh. Vses. Khim. Ova.*, 28 (1983) 7.
- 4 G. Schay, *Theoretische Grundlagen der Gas Chromatographie (DDR)*, V.E.B. Deutscher Verlag der Wissenschaften, Berlin, 1960.
- 5 O. G. Larionov and A. I. Kalinitchev, *Zh. Vses. Khim. Ova.*, 28 (1983) 53.
- 6 J. F. K. Huber and A. I. M. Keulemans, *Gas Chromatography*, Butterworths, London, 1962.
- 7 A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, 35 (1941) 1358.
- 8 E. Glueckauf, *Trans. Faraday Soc.*, 51 (1955) 34.
- 9 V. V. Rachinskii, *Dokl. Akad. Nauk SSSR*, 88 (1953) 701.
- 10 H. Vink, *J. Chromatogr.*, 15 (1964) 488.
- 11 A. V. Larin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1983) 236.
- 12 A. V. Larin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1984) 1212.
- 13 N. A. Chuduk and Yu. A. Eltekov, *J. Polym. Sci. Polym. Symp.*, 68 (1980) 135.
- 14 A. V. Larin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1983) 2668.
- 15 L. A. Jonas and W. J. Svirbely, *J. Catal.*, 24 (1972) 446.
- 16 P. J. Reucroft, W. H. Simpson and L. A. Jonas, *J. Phys. Chem.*, 75 (1971) 3526.
- 17 A. V. Larin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1983) 1235.
- 18 M. L. Gubkina, A. V. Larin and L. G. Shehovtsova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1985) 513.