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CALCULATION PRINCIPLES OF MULTI-STAGE PREPARATIVE CHROMATOGRAPHY ON THE BASIS OF THE THEORY OF NON-LINEAR MULTI-COMPONENT CHROMATOGRAPHY

A. I. KALINITCHEV* and O. G. LARIONOV

Institute of Physical Chemistry, U.S.S.R. Academy of Sciences, Leninsky Prospekt 31, 117915 Moscow (U.S.S.R.)

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SUMMARY

A generalized theoretical analysis of multi-stage cyclic preparative chromatographic processes is presented. The mathematical model is based on the equilibrium theory of non-linear multi-component chromatography. This model is applied to the consideration of the principal characteristics of the chromatographic process including its optimization.

The results of the theoretical analysis are used for the elaboration of a mathematical model and calculations in preparative chromatography. The computer calculations permit moving and interfering concentration waves to be represented by lines (trajectories) on the physical (X,T) plane, where X is the distance coordinate and T is time. The minimal and optimal column lengths that are necessary for the separation of components can be easily calculated when the picture of the lines on the (X,T) plane is derived. The proposed model is used for the quantitative description of the separation of alkenes from alkene–alkane mixtures by preparative liquid chromatography.

INTRODUCTION

Non-linearity of sorption isotherms due to high concentrations of components should be taken into account when carrying out calculations for preparative chromatographic processes. The presence of many components in column makes it necessary to consider the interference of several concentration waves.

These peculiarities manifest themselves in the separation of alkene–alkane mixtures by preparative liquid chromatography. The subject may be considered on the basis of a model derived from the equilibrium theory of non-linear multi-component chromatography[1,2] where mass transfer effects in the chromatographic column have been neglected.

In addition, it is necessary to calculate the interference of concentration waves during the process. Theoretical bases for the calculations have been developed for multi-component systems for Langmuir sorption systems only[2] by the use of Riemann

invariants[3]. The separation factors of the components are constant in Langmuir multi-component systems. The separation factors are functions of the composition of the mixture for the system under consideration, and therefore the general case of the calculation of the interference ("crossover") of self-sharpening and widening concentration waves in a two-component system[4] has been used for the theoretical analysis of the process.

THEORETICAL

All alkene species separated from alkene–alkane mixtures are considered in this analysis as a component to which the number 2 is assigned. The number 4 is assigned to all alkane species contained in mixtures of components 2 and 4. For the regeneration treatment to which the column is subjected in the last stage of the process pentane is used, to which the number 3 is assigned. The number 1 is assigned to hexene, which is used in the process as a displacement substance. The separation of component 2 from a mixture of 2 and 4 is performed by preparative liquid chromatography on a column packed with NaX zeolite.

The components 1, 2, 3 and 4 form an affinity sequence according to their sorption affinities, where species 1 is the most preferred species. For the separation factor α_{kj}, it holds that $\alpha_{kj} > 1$ when the affinity of component k is higher than that of component j.

Experimental binary sorption isotherms, $f_{k/j}$, of components k and j in NaX zeolite are shown in Fig. 1 for a dimensionless concentration field $0 \leqslant C'/C_0$; $a'/a_0 \leqslant 1$. The total concentration is constant:

$$C_k + C_j = 1;\ a_k + a_j = 1;\ a_k = f_{k/j}(C_k);\ a_j = f_{j/k}(C_j);$$

$$C_k = C'_k/C_0;\ a_k = a'_k/a_0 \tag{1}$$

so the pair of isotherms $f_{k/j}$ and $f_{j/k}$ can be drawn by one line (Fig. 1). The isotherm $f_{k/j}$ is convex whereas $f_{j/k}$ is concave. These isotherms have been used for the calcu-
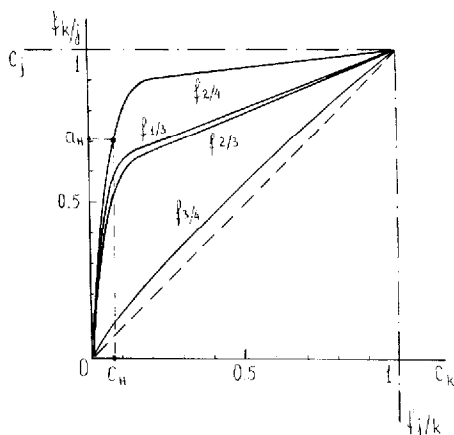

Fig. 1. Experimental binary sorption isotherms, $f_{k/j}$. C_{II}, a_{II} = concentration of component 2 in a mixture of components 2 and 4.

lation of the process. The curvature of the binary isotherm is the larger the greater is difference in the sorption affinities of the components. The separation factors α_{kj} are not constant for all the concentration field $0 < C'/C_0 < 1$.

The velocity $V_{j/k}$ at which a constant concentration C_j in a widening j/k wave travels through the column is given by[1,2]

$$V_{j/k} = (dX/dT)_{j/k} = 1/[C_0/a_0 + f_{j/k}(C_j)] \tag{2}$$

$$X = x/x_0 = x/ut_0; \quad T = utC_0/x_0a_0$$

where X and T are dimensionless distance and time, respectively, x_0 and t_0 are the characteristic length and time of the system, respectively, and u is the linear flow velocity.

The velocity $\sigma_{k/j}$ of the concentration discontinuity $(\Delta C_k, \Delta a_k)$ for a self-sharpening k/j wave is given by[1,2]

$$\sigma_{k/j} = (\Delta X/\Delta T)_{k/j} = 1/(C_0/a_0 + \Delta a_k/\Delta C_k) \tag{3}$$

The movement of concentration waves along the column can be visually (graphically) represented on a physical (X,T) plane[2,4,5] (Fig. 2). The movement of a self-sharpening k/j wave is represented by one line (σ, Fig. 2), the slope of which is determined by eqn. 3. The movement of a widening j/k wave is given by a pencil of rays (broken lines V, Fig. 2). Every broken line $V_{j/k}$ corresponds to the movement of concentration C_j and the slope of the line is determined by the wave velocity eqn. 2.

The column profiles can be predicted for different moments (T_s) when the physical plane (Fig. 2) is cut by the different vertical lines, $T_s = $ constant. An example of a set of column profiles is shown in Fig. 3 for the separation process under consideration.

Eqns. 2 and 3 have been applied to the calculation of the multi-stage preparative chromatography of hydrocarbon mixtures. One cycle of this process is divided into four stages (Fig. 3):

1st stage: sorption of a mixture of components 2 and 4: $0 < T \leqslant T_c$;
2nd stage: elution: $T_c < T \leqslant T_B$;
3rd stage: displacement: $T_B < T \leqslant T_E$;
4th stage: regeneration: $T_E < T \leqslant T_F$.

The calculation of the process is accomplished by the use of a physical plane (Fig. 2) where one cycle of the process is pictured. The coordinates X_M, T_M of any point of intersection (M) of two lines QM and RM are calculated by the triangulation method, i.e., using known coordinates of two points (Q, R) and the corresponding slopes of the two lines (QM and RM). In this calculation the velocities of widening $(V_{j/k})$ or sharpening $(\sigma_{k/j})$ waves are used as the slopes of the lines[2].

A computer program has been developed in which the described principles for the calculation of lines in a physical plane are realized for the process. The input data of the program are four tables representing isotherms $f_{1/3}$, $f_{2/3}$, $f_{2/4}$ and $f_{3/4}$ (Fig. 1),
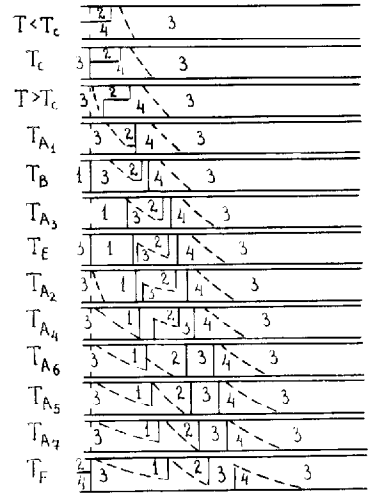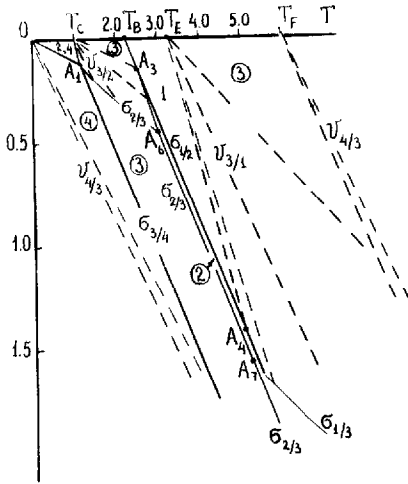
Fig. 2. Representation of the separation process on the physical (X, T) plane.

Fig. 3. Concentration distribution along the column for different moments in time.

the composition of the mixture of components 2 and 4 (C_H, a_H) (Fig. 1) and the values of T_c, T_B, T_E, T_F (Figs. 2 and 3).

Previous results[4] for the calculation of interferences of widening (3/1) and self-sharpening (1/2) waves (stage IV, Fig. 3) were used. Previously it was shown[4] that this interference may be calculated using individual isotherms $f_{1/3}$ and $f_{2/3}$ only when the mixture compositions on the left-hand side (3/1) and the right-hand side (3/2) of the interference zone (Fig. 3, moment T_{A_6}) are on the boundaries of the concentration space $\{C_1, C_2, C_3\}$.

EXPERIMENTAL

An experimental example is presented to show the use of the theoretical approach and including transformation from dimensionless X, T values to x, t values. The relationship between T and the input solution volume V_t is $T = V_t C_0 / \varepsilon S x_0 a_0$, where ε is porosity and S is the cross-section of the column. Let us choose the value of x_0 such that $T_c = 1$. Then x_0 can be easily calculated from

$$x_0 = V_c C_0 / \varepsilon S a_0 \qquad (4)$$

The parameters of the experimental column packed with NaX zeolite were $S = 2$ cm² and $\varepsilon = 0.5$. In sorption stage I $V_c = 250$ ml, so from eqn. 4 $x_0 = 250$ cm. The experimental values $T_B = 2.2$, $T_E = 3.2$ and $T_F = 6$ (Fig. 2) were calculated by use of this x_0 value.

The computer calculation of the lines on a physical plane (Fig. 2) allows x_{min} to be determined, where x_{min} is the minimal length of the column after which the separation of components 2 and 4 occurs (Fig. 3, moment T_{A_1}). This value was obtained from the calculated picture on the (X, T) plane (Fig. 2) and $X_{A_1} = 0.13$. The
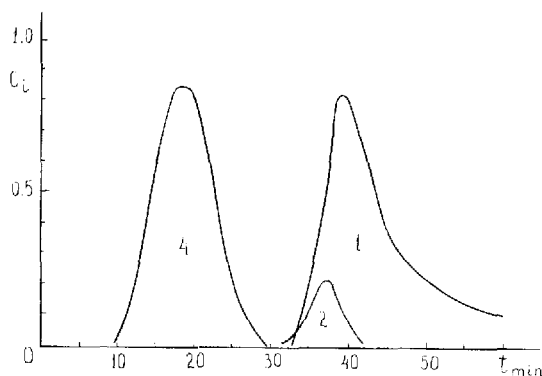
Fig. 4. Experimental output chromatogram. Length of column, 2 m; volume velocity, 25 cm³/min.

corresponding value $x_{min} = X_{A_1} \cdot x_0 = 32.5$ cm was obtained. This value is not optimal, however, as component 2 is not yet concentrated to the moment T_{A_1} (Fig. 3, T_{A_1}). It follows from the computer calculation that component 2 is concentrated (moments T_{A_2}, T_{A_4} and T_{A_6}, Fig. 3) in the region $0.5 < X_{opt} < 1.2$ (Fig. 2; region A_6–A_4), i.e., the optimal length of the column is in the range 1.25 m $< x_{opt} < 2.7$ m. A column length of 2 m was choosen for the experiment.

The retention times are 18, 37 and 39 min in the experimental output chromatogram for components 4, 2 and 1, respectively (Fig. 4). These values are 1.9, 3.7 and 4.1 in dimensionless form for a volume velocity $V = 25$ cm³/min and $x_0 = 250$ cm. The theoretical values 2, 3.8 and 4 are in good agreement with the experimental values.

The forms of the output peaks (Fig. 4) agree qualitatively with the calculation, i.e., peak 4 has an almost symmetric form as the isotherm $f_{3/4}$ is close to linear (Fig. 1); peak 2 has an almost symmetric form (Fig. 4) although the isotherm $f_{2/3}$ is strongly convex (Fig. 1). This is due to the displacement of the widening wave 3/2 by the self-sharpening wave 1/3 (Fig. 3, moments T_{A_3}–T_{A_4}).

The widths of the output peaks in Fig. 4 correspond to the theoretical values only approximately.

CONCLUSION

The theoretical and experimental results confirm the conclusion that the equilibrium theory of non-linear chromatography describes adequately the movement of centres of gravity of concentration waves and the principal features of the discussed separation process. The mass transfer effects lead to additional widening of chromatographic peaks. The application of the calculation principles for the movement of concentration waves[2] and for the interference of widening and self-sharpening concentration waves[4] allows one to calculate and optimize the discussed process of the separation of alkenes from alkene–alkane mixtures by preparative liquid chromatography.

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