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Abstract

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ON THERMODIFFUSION FRACTIONATION OF POLYMER SOLUTIONS

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From the phenomenological theory of thermodiffusion separation of liquid binary mixtures of low-molecular-weight substances in vertical columns with chambers, it follows that at the initial stage the degree of separation is determined by the value of the separation coefficient γ, equal to

$$\gamma = ka^3 \frac{g\beta\rho}{\eta} \frac{D_T}{D} (\Delta T)^2 \tau, \tag{1}$$

where k is a coefficient depending on the dimensions of the column and the chambers; a is the distance between the hot and cold walls; g is the acceleration due to gravity; β, ρ, and η are the mean values of the thermal expansion coefficient, density, and viscosity; D_T and D are the coefficients of thermodiffusion and diffusion; ΔT is the temperature difference and τ is the time (^{1,2}). For small τ the following inequality must be satisfied:

$$\gamma \operatorname{cth} \left(252 \frac{\eta}{g\beta\rho} D_T \frac{h}{a^4} \right) \ll 1, \tag{2}$$

where h is the height of the column (^{2}). Subsequently this process slows down greatly, and the quantity γ will no longer be the only dimensionless parameter of separation. Since for solutions of high-molecular-weight substances $D_T/D \sim 1$ (^{3,4}), whereas for solutions of low-molecular-weight substances $D_T/D \sim 10^{-2}$, then, in accordance with (1), thermodiffusion separation in solutions of high-molecular-weight substances, other conditions being equal, should proceed much more rapidly than separation of low-molecular-weight substances. In addition to concentration separation, owing to the dependence of the quantity γ on molecular weight, separation of polymer solutions also occurs according to average molecular weight, which makes it possible to use thermodiffusion for fractionating polymer solutions and for obtaining molecular-weight distribution curves ($^{5-9}$).

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

In thermodiffusion fractionation of solutions of samples of light and heavy polyisobutylene (average molecular weights respectively $3 \cdot 10^4$ and $6 \cdot 10^5$) in heptane in a cylindrical column ($h = 30$ cm, $a = 0.05$ cm, $\Delta T = 40°$, the capacity of the upper and lower chambers being 10 cm^3 each), it was established that, in the case of heavy polyisobutylene ($6 \cdot 10^5$), the greater part of the polymer is not found in samples taken at different heights, but remains in the column and forms a thickened immobile layer on the cold wall. As a result of intense thermodiffusion separation, the polymer concentration in the solution near the cold wall increases sharply and, consequently, so does its viscosity. The increase in concentration, depending on the ratio D_T/D, and the corresponding increase in viscosity (exponentially dependent on concentration) occur the more abruptly, the higher the average molecular weight of the polymer. It is possible that near the cold wall a thin layer of structured gel is formed. A hydrodynamic calculation of the convective movi-

of the solution in the gap of the column shows that the dependence of viscosity on temperature and concentration leads to a slowing of the flow near the cold wall and to its acceleration near the hot one. The wall layer, whose viscosity increases as it approaches the cold wall, does not participate in the convective circulation that leads to separation along the height of the column. It was established experimentally that the use of thermodiffusion as a method for fractionating solutions of polydisperse polymers is ineffective if the average molecular weight of the polymer exceeds $5 \cdot 10^5$.

Fig. 1. Dependence of the concentration C of a solution of polyisobutylene in heptane on the duration of thermodiffusion separation. 1 —solution from the lower chamber; 2 —from the upper chamber

Fig. 2. Dependence of the intrinsic viscosity $[\eta]$ of a solution of polyisobutylene in heptane on the duration of thermodiffusion separation. 1 —solution from the lower chamber; 2 —from the upper chamber

Therefore, in our experiments a mixture of light and heavy polyisobutylenes in a ratio of 2 : 1 was used. A solution of this mixed polymer in heptane with a concentration of 0.68 g/100 cm^3 was subjected to separation.

Figure 1 shows the time dependence of the total concentration of polyisobutylene in the upper and lower chambers of the column. After 2 hours the maximum concentration separation is reached, and subsequently the efficiency of the process decreases, since a considerable fraction of the polymer is concentrated in

Fig. 3

Figure 3: Fig. 3

the wall layer. It was established that in this layer, after 5 h, up to 30% of the initial amount of polymer accumulates. The optimum separation time for solutions of high-molecular-weight substances does not exceed, and may even be less than, that for mixtures of low-molecular-weight substances ([10,11]).

Fig. 3. Differential distribution curve of mixed polyisobutylene by intrinsic viscosities in heptane, obtained after double thermodiffusion separation

The dependence of the intrinsic viscosity of these fractions on time (Fig. 2) shows that a higher-molecular-weight portion of the polymer is concentrated in the upper part of the column than in the lower. This result can also be explained by the wall effect, which hinders the transfer of the dissolved high-molecular-weight substance from the upper part of the column to the lower.

Figure 3 shows the molecular-weight distribution curve for the same mixture of two polyisobutylene samples, constructed from the data of double thermodiffusion fractionation. The initial solution was divided into 5 fractions, and the wall layer was washed off with heptane, forming a 6th fraction. Each of the 5 fractions was then divided again. The solution of the wall layer was not divided, since upon repeated separation a considerable part of it ···

part again precipitated on the cold wall of the column. The two principal maxima on the curve correspond, in characteristic viscosity, to the light and heavy polymers.

The data presented attest to the great influence of the wall effect (precipitation of the polymer on the cold wall) on the thermodiffusion fractionation of solutions of high-molecular-weight substances.

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Note: Figure translations are in progress. See original paper for figures.