PHYSICAL CHEMISTRY

1964

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

T. N. Khazanovich

ON THERMODIFFUSION IN DILUTE SOLUTIONS OF POLYMERS

(Presented by Academician V. N. Kondrat' ev, January 16, 1964)

Thermodiffusion in dilute solutions can be an effective means of fractionating polymers ([1],[2]). This determines the need for experimental and theoretical study of the dependence of the thermodiffusion constant on molecular weight. Moreover, if the theoretical dependence of the thermodiffusion coefficient on molecular parameters is known, the study of thermodiffusion will make it possible to obtain new information on the structure of the macromolecule and its interaction with the solvent.

At the present time four attempts are known to construct a molecular theory of thermodiffusion in polymer solutions ([3–6]). All these works have one common shortcoming: they did not take sufficient account of the flexibility of polymer chains. In the present work it will be shown that such an account substantially affects the results.

The thermodiffusion of absolutely rigid macromolecules is no different from the thermodiffusion of Brownian particles considered by Chapman ([7]), who found for the thermodiffusion coefficient in a dilute suspension the relation:

$$D_\tau = C\, dD/dT, \tag{1}$$

where C is the dimensionless concentration, T is the absolute temperature, and D is the coefficient of ordinary diffusion. (Here the thermodiffusion coefficient is defined so that the flux under the action of a temperature gradient has the form: $\mathbf{J} = -\rho D_\tau \nabla T$, where ρ is the density.) Relation (1) can be given a clear interpretation: the probability for a Brownian particle to leave a region where the temperature is lower and, consequently, the viscosity is greater, is less than the probability of leaving a region with a higher temperature. This difference in probabilities leads to the appearance of a flux of particles in the direction of the cold wall.

It follows from formula (1) that thermodiffusion is ineffective for fractionating rigid macromolecules, since the thermodiffusion constant

$$\alpha = D_\tau T/DC,$$

which basically determines the efficiency of separation, in this case does not depend on molecular weight.

To describe the motion of a flexible chain we shall use the well-known bead-and-spring model introduced by V. A. Kargin and G. L. Slonimskii ([8]). Assume, following Chapman ([7]), that the Brownian motion of the beads also in a temperature field is such a Markov process for which there exists the Einstein-Fokker-Planck equation (E.F.P.). The coefficients of the E.F.P. equation, as is known (see, for example, ([9])), are determined by the processes occurring in the immediate vicinity of the particle. Therefore, if the temperature gradients are small, the coefficients of the E.F.P. equation will be equal to the coefficients of the E.F.P. equation in a homogeneous medium with a temperature equal to the temperature of the point at which the particle is located. These arguments, which, of course, cannot be considered rigorous, are a paraphrase of Chapman' s reasoning ([7]), which led to formula (1). However, relation (1) can be obtained rigorously from certain simple models of Brownian motion and, as Chapman noted, is in qualitative agreement

with the results of an exact calculation of thermodiffusion in dilute gases. In accordance with what has been said, we shall write the Fokker-Planck equation for a chain consisting of n beads in the usual form (see, for example, (10)):

$$\begin{aligned}\frac{\partial W(\mathbf{r}_1,\dots,\mathbf{r}_n,t)}{\partial t} &= \frac{\partial}{\partial \mathbf{r}_1}\left[\sigma_1(\mathbf{r}_1-\mathbf{r}_2)W\right]- \\ &-\sum_{i=2}^{n-1}\frac{\partial}{\partial \mathbf{r}_i}\left[\sigma_i(\mathbf{r}_{i-1}-2\mathbf{r}_i+\mathbf{r}_{i+1})\right]- \\ &-\frac{\partial}{\partial \mathbf{r}_n}\left[\sigma_n(\mathbf{r}_{n+1}-\mathbf{r}_n)\right]+\sum_{i=1}^{n}\frac{\partial^2}{\partial \mathbf{r}_i^2}(\delta_i W),\end{aligned} \tag{2}$$

where $W(\mathbf{r}_1,\dots,\mathbf{r}_n,t)$ is the probability density in the configurational space of the chain; $\mathbf{r}_i$ and $\delta_i(\mathbf{r}_i)$ are, respectively, the radius vector and the diffusion coefficient of the i-th bead; $\sigma_i = 3\delta_i/b^2$; b^2 is the mean square length of a segment. For simplicity we do not take hydrodynamic interaction into account, i.e., we confine ourselves to the case of a freely draining macromolecule.

We shall be interested in the motion of the center of gravity of the chain

$$\mathbf{R} = \left(\sum_{i=1}^{n}\mathbf{r}_i\right)/n,$$

therefore equation (2) must be averaged over all variables except $\mathbf{R}$. As a result we obtain

$$\frac{\partial w(\mathbf{R},t)}{\partial t} = \frac{\partial}{\partial \mathbf{R}}\left[\frac{1}{n}\left\langle\sum_{i=1}^{n-1}(\sigma_i-\sigma_{i+1})(\mathbf{r}_i-\mathbf{r}_{i+1})\right\rangle w\right] + \\ + \frac{1}{n^2}\frac{\partial^2}{\partial \mathbf{R}^2}\left(\left\langle\sum_{i=1}^{n}\delta_i\right\rangle w\right), \tag{3}$$

where the angle brackets denote averaging over the internal coordinates. Assuming that the temperature gradient is small, we shall neglect terms of higher order of smallness. We write

$$\sigma_i - \sigma_{i+1} = \frac{3}{b^2}\frac{d\delta}{dT}\nabla T\cdot(\mathbf{r}_i-\mathbf{r}_{i+1}), \tag{4}$$

where

$$\delta = \left(\sum_{i=1}^{n}\delta_i\right)/n$$

is the mean diffusion coefficient of a segment. After averaging we obtain

$$\frac{\partial w(\mathbf{R},t)}{\partial t} = \left(3+\frac{1}{n}\right)\frac{d\delta}{dT}\nabla T\frac{\partial w(\mathbf{R},t)}{\partial \mathbf{R}} + \frac{\delta}{n}\frac{\partial^2 w}{\partial \mathbf{R}^2}. \tag{5}$$

It follows from (5) that for a flexible polymer chain

$$D_\tau = \left(3+\frac{1}{n}\right)C\frac{d\delta}{dT}. \tag{6}$$

Comparison of (1) with (6), and allowance for the fact that within the framework of the model under consideration the diffusion coefficient of the chain is $D = \delta/n$, shows that the flexibility of the polymer chain leads to a considerable increase in the thermodiffusion coefficient. This increase can be understood in the following way: a decrease in the mobility of those parts of the chain which are in the region of greater viscosity produces a force acting on the remaining parts of the chain and directed toward the cold wall.

Measurement of D_τ or α is a difficult experimental problem; therefore the available data are rather contradictory. The most reliable should be considered the measurements of Meyerhoff et al. [11–13], from which it follows that the values of D_τ for polystyrene in toluene depend neither on molecular weight nor on concentration (in the region of large dilutions). This conclusion agrees with relation (6).*

* The same conclusion follows from the work of Haase [6], although quantitatively his result differs from formula (6). Haase' s theory, however, is based on

very strange assumptions, some of which contradict the basic relations of the thermodynamics of irreversible processes.

As already mentioned, the proposed calculation did not take into account hydrodynamic interaction, although practically all flexible macromolecules are nondraining ([14]). Therefore one cannot expect quantitative agreement of formula (6) with experimental data. Taking account of hydrodynamic interaction in a temperature gradient is a very complicated problem, the solution of which was not attempted in the present work. As follows from (6), the thermodiffusion of a flexible chain is determined by the mobility of individual segments; therefore one may suppose that hydrodynamic interaction will have a less pronounced effect than in such transport processes as diffusion and viscosity, where the mobility of the macromolecule as a whole is important. In the present calculation, no account was also taken of the possible deviation of the temperature gradient inside the molecular coil from its value in the bulk of the solvent.

Another difficulty for quantitative comparison with experiment is connected with the fact that the segment size in the bead-and-spring model is, in a certain sense, a conditional quantity, whose determination by an independent method is difficult. For an order-of-magnitude estimate one may take

$$\delta = kT/6\pi\eta_0 r_0, \tag{7}$$

where η_0 is the viscosity coefficient of the solvent, r_0 is the effective hydrodynamic radius of a monomer unit, approximately equal to $b/2$ ([14,15]), and b is the effective segment length. It may be taken that in a good solvent $b \approx 10$ Å ([15]). Substitution of (7) into (6) gives

$$D_T \simeq \frac{3E\delta}{RT^2}\, C, \tag{8}$$

where E is the activation energy of the solvent viscosity. For toluene at 20° $\eta_0 = 0.585$ cP, $E/RT = 3.66$, which gives $D_T/C = 3 \cdot 10^{-7}$ cm^2/sec · deg. The experimental value is $1 \cdot 10^{-7}$ cm^2/sec · deg ([11–13]). At the present stage, of course, it is difficult to say what causes the discrepancy: the neglected hydrodynamic interaction or the crudeness of the model; but the closeness of the theoretical and experimental values confirms the supposition made above concerning the relative weakness of the influence of hydrodynamic interaction on the thermodiffusion of polymer chains.

The author expresses sincere gratitude to Prof. N. D. Sokolov for discussing the work.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
16 I 1964

CITED LITERATURE

[1] S. R. Rafikov, S. A. Pavlova, I. I. Tverdokhlebov. *Methods for Determining Molecular Weights and Polydispersity of High-Molecular Compounds*, Moscow, 1963.
[2] G. Langhammer, H. Pfenning, K. Quitzsch, Zs. Electrochem., **62**, No. 4, 458 (1958); I. Kössler, J. Kreisa, J. Polymer Sci., **57**, No. 165, 509 (1962); H. Seidel, G. Langhammer, Plaste u. Kautschuk, **9**, No. 12, 573 (1962).
[3] P. Debye, A. M. Bueche, *High Polymer Physics*, Brooklyn, 1948, p. 457.
[4] A. H. Emery jr., H. G. Drickamer, J. Chem. Phys., **23**, No. 12, 2252 (1955).
[5] K. F. Alexander, J. Chim. Phys., **54**, No. 11–12, 866 (1957).
[6] J. S. Ham, J. Appl. Phys., **31**, No. 11, 1853 (1960).
[7] S. C. Chapman, Proc. Roy. Soc. London, A119, 34 (1928).
[8] V. A. Kargin, G. L. Slonimsky, ZhFKh, **23**, No. 5, 563 (1949).
[9] M. A. Leontovich, *Statistical Physics*, Moscow–Leningrad, 1944.
[10] B. Zimm, J. Chem. Phys., **24**, No. 2, 269 (1956). Collected translations: *Physics of Polymers*, Moscow, 1960, p. 379.
[11] L. Nachtigal, G. Meyerhoff, Zs. phys. Chem. (B.R.D.), **30**, No. 1–2, 17, 35 (1961).
[12] G. Meyerhoff, K. Nachtigal, J. Polymer Sci., **57**, No. 165, 227 (1962).
[13] B. Rach, G. Meyerhoff, J. Phys. Chem., **67**, No. 4, 946 (1963).
[14] Yu. E. Eizner, O. B. Ptitsyn, A. G. Piliposyan, *High-Molecular Compounds*, **5**, No. 11, 1711 (1963).
[15] S. I. Klenin, O. B. Ptitsyn, *High-Molecular Compounds*, **3**, No. 9, 912 (1961).

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