SHORT COMMUNICATIONS

Theoretical Fundamentals of the Sedimentation Behaviour of a Semidilute Polymer Solution

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In a previous paper,¹ a theoretical model was presented to give a good description^{1,2} of the concentration dependence of sedimentation coefficient s

$$s = (\rho_s - \rho_1)(1 - \varepsilon)/(\mu\lambda^2)$$

where ρ_s and ρ_1 are the solute density and solvent density, respectively, $1 - \varepsilon$ is the solute volume fraction in the solution, μ is the solvent viscosity, and λ is the reciprocal square root of solution permeability. This model predicts an interdependence of three dimensionless parameters λR , PR , and δ^3

$$f(\lambda R, PR, \delta^3) = 0 \quad (1)$$

where R is the blob radius, P is the reciprocal square root of blob permeability, and δ^3 is the solution volume fraction occupied by blobs

$$\delta^3 = (1 - \varepsilon)/(1 - \varepsilon_{\text{blob}}) \quad (2)$$

$1 - \varepsilon_{\text{blob}}$ being the solute volume fraction in the blob.

It was assumed,¹ without any proof, that for a semidilute solution the dimensionless parameters λR , PR , and δ^3 corresponded to the inflection point of the $\ln \lambda R$ vs. $\ln \delta^3$ -model curve described by eq 1, at a PR -value such that

$$d \ln \lambda R / d \ln \delta^3 \big|_{PR = \text{constant}} = n \quad (3)$$

where n denoted the exponent in the well experimentally supported relation³

$$\lambda \sim (1 - \varepsilon)^n \quad (4)$$

This exponent is equal to 0.75 for a polymer-good solvent system and reaches 1 at the theta temperature.

From eq 4 one can derive the following relations

$$d \ln \lambda / d \ln (1 - \varepsilon) = n \quad (5)$$

$$d^2 \ln \lambda / d \{\ln (1 - \varepsilon)\}^2 = 0 \quad (6)$$

Fix any blob characteristics R and $1 - \varepsilon_{\text{blob}}$. Then

$$d \ln \lambda R / d \ln \delta^3 = d \ln \lambda / d \ln (1 - \varepsilon) \quad (7)$$

$$d^2 \ln \lambda R / d (\ln \delta^3)^2 = d^2 \ln \lambda / d \{\ln (1 - \varepsilon)\}^2 \quad (8)$$

According to eq 1, vanishing the second derivative of $\ln \lambda R$ with respect to $\ln \delta^3$ for constant blob characteristics determines the inflection point at a constant value of PR . This is for P being a unique function of $1 - \varepsilon_{\text{blob}}$ for a given polymer-solvent system, so PR is completely determined by blob characteristics. The slope n of eq 5 and 7, equal to that of eq 3, determines by eq 1 the values of λR , PR , and δ^3 at the inflection point. Although eq 7 and 8 are valid for any fixed blob characteristics, R and $1 - \varepsilon_{\text{blob}}$ must be chosen to fulfil the coor-

dinates of the inflection point. Consider a solution of the solute concentration $1-\varepsilon$ and reciprocal of square root of solution permeability λ . The λR -parameter at the inflection point and the λ -value determine the blob radius R . The δ^3 -parameter at the inflection point and the $1-\varepsilon$ -value determine the blob solute volume fraction $1-\varepsilon_{\text{blob}}$.

The above estimation of blob characteristics dealt with one point of the line described by eq 4. The procedure can be repeated for other

solution concentrations to get the variability of blob characteristics along this line, which is characteristic for a semidilute concentration range of a given polymer-solvent system. The rules are given in.¹

REFERENCES

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