Scaling of activation energy for macroscopic flow in poly(ethylene glycol) solutions: Entangled − Non-entangled crossover

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ABSTRACT

We postulate an empirical scaling equation, which accurately describes flow of polymer solutions, complimenting the paradigm of length-scale-dependent viscosity. We investigated poly(ethylene glycol) aqueous solutions and observed an exponential dependence of viscosity on the hydrodynamic radius of a single coil R_h divided by the correlation length ξ. Properties of the system changed abruptly with the onset of chain entanglement at concentration corresponding to $\xi = R_h$. We propose a single equation valid for all the investigated systems, analyze the physical meaning of parameters appearing therein and discuss the impact of chain entanglement. Viscous flow is treated as an activated process, following the Eyring rate theory. We show that the difference of activation energy for flow between pure solvent and polymer solution, ΔE_a, is a function of concentration, whose derivative has a discontinuity at the crossover concentration. For dilute PEG solutions ΔE_a takes values of up to several kJ/mol and is proportional to the intrinsic viscosity. We successfully apply the scaling approach to the diffusive motion of a protein (aldolase) in solutions of 25 kg/mol PEO (concentrations of 2−20%), investigated by fluorescence correlation spectroscopy (FCS). A significant difference in the influence of crowding on translational and rotational motion of the protein is revealed.

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1. Introduction

Transport properties of complex liquids are often determined not only by the chemical composition and molecular characteristics of their constituents, but also by the characteristic length scales of the system [1,2]. In polymer solutions, the key ones are the hydrodynamic and gyration radii of single coils (R_h and R_g, respectively) and the correlation length ξ. These parameters are the basis for estimation of the effective viscosity experienced by diffusing probes, which may be lower than the bulk viscosity by orders of magnitude [3,4]. The intrinsic microstructure of the solution depends heavily on the molecular weight and concentration of macromolecules: increasing congestion of coils leads to qualitative changes in the structure of the liquid, shifting the balance of predominant interactions and severely affecting the dynamics [5−9]. In this paper, we demonstrate a scaling approach allowing for

unified description of viscosity of polymer solutions at different concentration regimes, fully consistent with the paradigm of length-scale-dependent viscosity. We show that the intrinsic viscosity is a function of activation energy for viscous flow. We provide an explicit definition of this activation energy and quantitatively describe its changes upon the onset of entanglement of polymer chains, which marks the crossover between different concentration ranges.

Polymer handbooks define three main concentration regimes: dilute, semi-dilute, and concentrated [5,10]. In the dilute regime polymer coils are separated and behave similarly to hard spheres with respect to each other [11], while the dynamics of the system are well approximated by the Zimm model and predominated by the hydrodynamic interactions [2,12]. Various subdivisions of the dilute regime have been suggested, based on changes in the interactions between coils [13−16]. Although the implications of the existence of the extremely dilute regime are potentially important, this concentration range is in fact approaching the infinite dilution limit and is not accessible in most experimental setups nor practically exploited.

In the semi-dilute regime polymer coils start to overlap, gradually loosing their individuality to constitute a uniform mesh − a toy-model depicting the shifts occurring in the solution is presented in Fig. 1a. With further increase of the volume fraction of macromolecules, the solution approaches the polymer melt conditions, where chains are assumed to be ideal. This situation corresponds to the concentrated regime. The critical concentration separating dilute and semi-dilute regimes, c^*, is usually defined as the concentration at which the whole volume is occupied by polymer coils, so that they touch, but not interpenetrate each other significantly [5,10,17,18]. Therefore, it can be simply defined as

$$c^* = \frac{M_w}{4/3 \pi R_g^3 N_A},\tag{1}$$

where M_w is the polymer molecular weight, R_g is the polymer gyration radius and N_A is the Avogadro number. We shall use this definition further on, although it must be noted that it does not constitute a sharp boundary [6,19,20]. Several definitions of c^* other than Equation (1) have also been proposed [10,19,21] that give slightly different values. Moreover, even if we assume the polymer coils at c^* to be impenetrable spheres of radius R_g, including different theoretically possible sphere packing arrangements (Fig. 1) could shift the predicted overlap concentration value even by a factor of 2 from the value given by Equation (1). Another uncertainty to this definition comes from Refs. R_g, which usually is determined for very dilute solutions and may shift upon concentration changes [10,13,22]. The theoretical and experimental difficulties concerning the intermediate concentration range may conceal important changes occurring in the system. Graessley et al.19 proposed to divide the semi-dilute region into distinct subregimes: entangled and non-entangled [2]. It has been shown that the onset of entanglement between chains crucially influences the properties of the system − e.g. its rheology and elasticity [23], grafting efficiency [24], or fiber formation [25,26]. We shall use this notion further on to explain the changes in transport properties of polymer solutions.
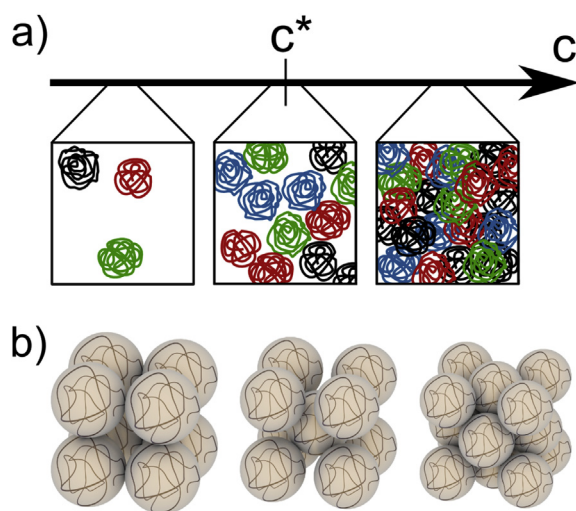

Fig. 1. a) Schematic changes of the internal structure of a polymer solution with increasing concentration. c^*, overlap concentration, is usually treated as the threshold separating dilute and semi-dilute regimes. b) Different possible packing models of polymer chains treated as impenetrable hard spheres at c^*. Real polymer coils are not that well defined in terms of shape, and the onset of overlap as well as entanglement is gradual. Therefore, strict determination of critical crossover concentration is somewhat dubious.

The dynamic, internal structure of complex liquids is of key importance for description of probe diffusion therein. Numerous experimental observations of unexpectedly high mobility of small probes in such systems [3,27–31] suggested a breakdown of the Stokes-Sutherland-Einstein relation ($D = k_B T / 6 \pi \eta r_p$, where: D − diffusion coefficient, η − viscosity, r_p − probe radius) for $r_p < R_g$ [31,32]. In our recent works on semi-dilute systems [3,4], we demonstrated that the application of de Gennes' scaling framework [5] to the description of size-dependent viscosity [33] allows to resolve this issue. In this approach, the notion of effective radius R_{eff} is introduced, where

$$R_{eff}^{-2} = R_h^{-2} + r_p^{-2}.\tag{2}$$

Viscosity experienced by the probe is then given by

$$\eta = \eta_0 \exp\left[b\left(\frac{R_{eff}}{\xi}\right)^a\right],\tag{3}$$

where: η_0 − solvent viscosity, a and b − parameters of the order of unity. ξ is the correlation length of local monomer concentration fluctuations, interpreted also as the mesh or blob size in entangled systems [5,10,18]. It is estimated as

$$\xi = R_g\left(\frac{c}{c^*}\right)^{-\beta},\tag{4}$$

where β is a scaling exponent given by Ref. $\beta = -\nu(1 - 3\nu)^{-1}$ [5,34,35]. The ν parameter relates the coil size to the M_w, accounting for repulsive excluded volume interactions within the mean-field approach. According to Flory [11], ν should be equal to 3/5 for a three-dimensional polymer coil in a good solvent, which gives $\beta = 3/4$.

Equation (3) is in line with the well established paradigm of stretch exponential dependence of effective solution viscosity on the polymer concentration [36–39]. It has been proven functional for different complex liquids, including systems other than flexible polymer solutions, e.g. suspensions of rigid micelles [4] or bacterial cytoplasm [40]. Recently [41], it was merged with Eyring's rate theory [42,43] to describe mass transport in complex systems as an activated process [44–50]. It was found that parameter b from Equation (3) is temperature-dependent, and the viscosity scaling can be written in terms of the Arrhenius equation as [41]

$$\eta = \eta_0 \exp\left(\frac{\Delta E_a}{RT}\right),\tag{5}$$

where

$$\Delta E_a = \gamma\left(\frac{R_{eff}}{\xi}\right)^a,\tag{6}$$

which is the excess activation energy for viscous flow over the one observed for pure solvent. γ is a system-dependent parameter expressed in terms of energy and equal 4.0 ± 0.4 kJ/mol for PEG (PEO) aqueous solutions [41]. It should be noted that in the large probe limit ($r_p \gg R_h$) the effective radius reduces to the polymer hydrodynamic radius and therefore both Equations (3) and (5) apply also to the macroscopic viscosity and viscous flow of the polymer solution.

However, most of the aforementioned scaling considerations refer to the case of heavily entangled systems. In this paper we attempt to extend this reasoning to dilute systems, investigating the experimentally observed changes of scaling parameters. We provide a simple, qualitative physical explanation of the observed changes and crossover between concentration regimes, along with