Scaling Equation for Viscosity of Polymer Mixtures in Solutions with Application to Diffusion of Molecular Probes

Agnieszka Wisniewska, Krzysztof Sozanski, Tomasz Kalwarczyk, Karolina Kedra-Krolik, and Robert Holyst*

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

E-mail: rholyst@ichf.edu.pl

Abstract

We measured macroscopic viscosity as well as nanoviscosity experienced by molecular probes diffusing in solutions containing two polymer species vastly differing in the molecular weight. On this basis we postulated a scaling equation for viscosity of complex liquids characterized by two distinct length-scales. As an experimental model, we used aqueous solutions of low-polydispersity poly(ethylene glycol) and poly(ethylene oxide) with molecular weight ranging from 6 to 1000 kg/mol, polymer concentrations from 0.25% up to 50%, and viscosity up to 500 mPa·s. The proposed model distinguishes between the contributions to the total viscosity stemming from the mesoscopic structure of the complex liquid and from the magnitude of interactions dictated by the chemical nature of its constituents. It allows to predict diffusion rates of nanoscaled probes in polymer solution mixtures and can be adapted to various multi-length-scale complex systems.

Introduction

Diffusion coefficient D of a probe suspended in a fluid is given by the Stokes-Sutherland-Einstein (SSE) equation

$$D = \frac{k_\mathrm{B}T}{6\pi\eta r_\mathrm{p}} \tag{1}$$

where: k_B – Boltzmann constant, T – absolute temperature, η – viscosity of the fluid, and r_p – hydrodynamic radius of the probe. Yet, it has been shown that this fundamental dependence is severely violated in complex liquids such as polymer solutions and melts, with D values exceeding the SSE-based predictions even by orders of magnitude.[1–6] The apparent breach of the SSE equation is observed when the probe size falls below the characteristic length-scale of the liquid: in case of polymer solutions, this means $r_\mathrm{p} \lessapprox R_\mathrm{g}$,[5–7] where R_g denotes the gyration radius of polymer coils. However, applicability of the SSE paradigm is retained in complex liquids across the whole range of probe sizes when the viscosity scaling approach is applied,[2,8] wherein viscosity experienced by the probe is treated as a function of its size.[6,9] In the large probe limit ($r_\mathrm{p} \gg R_\mathrm{g}$), $\eta(r_\mathrm{p})$ converges to the value of macroscopic viscosity.[10] In the small probe limit ($r_\mathrm{p} \ll R_\mathrm{g}$), $\eta(r_\mathrm{p})$ approaches the pure solvent viscosity, η_0. In the course of detailed experimental studies of polymer solution we have recently shown[6,9,11] that $\eta(r_\mathrm{p})$ is universally described over the whole r_p range by

$$\eta(r_\mathrm{p}) = \eta_0 \exp\left[\left(\frac{\gamma}{RT}\right)\left(\frac{R_\mathrm{eff}}{\xi}\right)^a\right], \tag{2}$$

where a is a scaling parameter of the order of unity. R_eff is the effective radius, embracing in its definition both the probe radius r_p and the hydrodynamic radius of the polymer R_h:[9,11]

$$R_\mathrm{eff}^{-2} = R_\mathrm{h}^{-2} + r_\mathrm{p}^{-2}. \tag{3}$$

The crucial length-scale appearing in Equation 2 is in fact the length-scale of the flow induced by diffusive motion of the probe. Therefore, its limiting case is macroscopic flow of the liquid (i.e. the traditionally understood dynamic viscosity of the solution is reproduced). Then, the term related to the probe radius in Equation 3 is omitted (since $r_\mathrm{p} \to \infty$) and R_eff is simply equal to R_h. Applicability of such approach to macroscopic viscosity of various complex liquids has been shown experimentally.[6,11,12]

γ is a parameter expressed in terms of energy and equal to 4.0±0.4 kJ/mol for poly(ethylene glycol) (PEG)/poly(ethylene oxide) (PEO)[*] aqueous solutions at the macroscale.[13] γ is temperature-independent and does not vary between dilute and entangled concentration regimes. It is related to the magnitude of polymer-polymer and polymer-solvent interactions (as well as polymer-probe interactions in case of probe diffusion). Therefore, it is expected to vary between different polymer/solvent systems, but it does not depend on the molecular weight of the polymer.

ξ is the correlation length and constitutes a crucial length-scale in complex liquids. In semi-dilute polymer solutions, it is described as distance over which local fluctuations of monomer concentration persist, which is equivalent to the average distance between points of entanglement between chains.[14–16] ξ also corresponds to the size of a single blob within the blob theory of de Gennes.[14,15] Its value can be estimated experimentally using light scattering methods.[15,17,18] It has also been shown that ξ in non-ideal polymer systems is equivalent to the distance over which hydrodynamic interactions are screened.[11,19,20] These observations allow to extend the applicability of some scaling laws based on correlation length and derived from studies of polymer solutions to other systems, such as hard-sphere, micelle, or protein solutions, as well as cellular cytoplasm.[9,11,12] For semi-dilute polymer solutions, ξ is defined as

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

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[*] Chemically, both PEG and PEO are the same linear polymer: $\mathrm{H{-}[O{-}CH_2{-}CH_2]_n{-}OH}$. The distinction between the two is only historically justified and based on molecular weight: PEG denotes polymers of $M_\mathrm{w} \leq 20$ kg/mol, PEO – polymers of $M_\mathrm{w} > 20$ kg/mol.

where c is the polymer concentration and β is a scaling exponent given by[14,21,22]

$$\beta = -\nu(1-3\nu)^{-1}. \tag{5}$$

The ν parameter accounts for repulsive excluded volume interactions within the mean-field approach. According to Flory,[23] ν should be equal to 3/5 for a three-dimensional polymer coil in a good solvent, which gives $\beta = 3/4$. c^* is the overlap concentration, described as

$$c^* = \frac{M_\mathrm{w}}{4/3\pi R_\mathrm{g}^3 N_\mathrm{A}}, \tag{6}$$

where M_w is the polymer molecular weight.

Transport properties of polymer solutions heavily depend on the polymer concentration. A qualitative change is observed between the dilute regime, where coils are separated from each other and behave similar to hard spheres, and the semi-dilute regime, when they start to interpenetrate each other. The border between these two regimes is usually defined as $c = c^*$. However, our recent findings imply that an abrupt change in solution properties is rather observed upon the onset of chain entanglement, i.e. at such polymer concentration that $R_\mathrm{h} = \xi$.[24] This is a point of topological change in the system:[25] at higher concentrations, entangled chains constitute parts of a polymer meshwork rather than independent entities. Equation 2 remains valid over both regimes, although the scaling exponent a changes at $R_\mathrm{h} = \xi$. The interpretation of parameter a is that it accounts for the internal structure of the complex liquid – hence its change upon crossing between entangled and non-entangled regimes. A recently suggested quantitative approximation is $a \approx R_\mathrm{h} R_\mathrm{g}^{-1} \beta^{-1}$.[9,24] The value of a established for entangled PEG/PEO aqueous solutions is 0.78.[24]

All the considerations presented above relate to the simple case of a solution of a single, monodisperse polymer. The goal of the current paper is to extend the viscosity scaling paradigm to liquid mixtures with multiple characteristic length-scales. Until now, various ways of predicting viscosity of liquid mixtures have been proposed, mainly for industrial purposes (for a review and comparison see Ref.[26]), which however provide no insight into the underlying physics. Models developed specifically for mixtures containing polymers[27–29] are rather scarce and require a number of empirical parameters, yet do not consider the mesoscopic structure of the complex liquid. This also means that there are no methods available that would allow for quantification and prediction of diffusion coefficients of (macro)molecular probes in systems containing more than a single type of crowding agent.

In this paper, we propose a model for description of the length-scale dependent viscosity in solutions containing two polymer species. To provide an easy to interpret reference, we use aqueous solutions of PEG/PEO, whose single-component solutions are already well described in terms of viscosity scaling.[24] We focus on double-entangled systems, where there are two polymers featuring two distinct characteristic length-scales, and concentrations of both of them fall within the entangled regime. To facilitate the elucidation of the contributions of the two components, we investigate systems containing two PEG/PEO species differing in their molecular weights strongly (by at least an order of magnitude). We analyze viscosity of such systems at the macro- and nanoscale (using rotational rheometry and measuring molecular probe diffusion by fluorescence correlation spectroscopy). On this basis, we provide a single equation describing viscosity of binary mixtures of polymer solutions across all length-scales. The suggested approach can be expanded to accommodate more than two system components. We provide a physical justification of all the parameters appearing in the proposed equations. This opens a perspective of their application to various complex liquids featuring multiple length-scales, including cellular cytoplasm.

Materials and Methods

Polymer Systems

We studied binary mixtures of aqueous solutions of PEG and PEO, where various distinct length-scales are observed, related to the hydrodynamic radii of the two polymers as well as the correlation length of the system. All experiments were conducted on molecular weight standard polymers with polydispersity close to one, obtained from Polymer Standards Service GmbH, Mainz, Germany (designated according to their approximate molecular weights in g/mol: PEG 6k, 12k, 18k, and PEO 500k, 1M – see Supporting Information for exact M_w and polydispersity index values). Such aqueous PEG/PEO solutions are commonly used as model complex liquids; binary mixtures of such polymer solutions have also been investigated previously,[30,31] although not within the viscosity scaling paradigm. The concentrations of polymers in the samples used in our experiments ranged from 5 to 50% (by weight) for short-chain PEGs and from 0.25 to 2.5% for long-chain PEOs. Such broad range of concentrations is experimentally available due to the very good solubility of these polymers in water at room temperature. All solutions were prepared in deionized water, except for protein diffusion experiments, where PBS (phosphate buffer saline, pH 7.4) was used instead. Samples were prepared at least 24 hours prior to the experiments and stirred gently during that time to assure full dissolution and equilibration of the polymers in the samples. All measurements were performed at 298 K. We estimated hydrodynamic and gyration radii, needed for further calculations, according to the previously established formulae for PEG/PEO coils in water in the dilute regime:[32,33]

$$R_\mathrm{g} = 0.0215 M_\mathrm{w}^{0.583\pm0.031} \qquad R_\mathrm{h} = 0.0145 M_\mathrm{w}^{0.571\pm0.009}. \tag{7}$$

Since some measurements were performed at relatively high polymer concentrations, we also included in the data analysis the weak dependence of the polymer radius on its concentration appearing in the semi-dilute regime:[15]

$$R_\mathrm{h} \propto (c/c^*)^{-1/8}. \tag{8}$$

According to de Gennes' original formulation,[14,15] correlation length ξ in polymer systems should depend on the total concentration of the polymer, but not on its molecular weight.

Indeed, if we combine Equations 4 and 6 with the empirical formula for R_{g} (Equation 7), we reach an expression where the M_{w}-dependence can be neglected: the remaining term of $M_{\mathrm{w}}^{0.021}$ falls within the error margin of estimation of the scaling exponent in the purely experimental Equation 7, and also is of the order of unity in all cases. Thus, a simple scaling approximation of ξ, expressed in nm, is obtained:

$$\xi = 0.341 c^{-3/4}, \tag{9}$$

which is valid for PEG/PEO aqueous solutions. c stands for the total polymer concentration of the solution, expressed in grams of polymer per cm^3 of solvent.[†] Such simplified, M_{w}-independent definition of ξ is particularly useful for the case of polymer solution mixtures, since it allows to define a single value of correlation length for a given system, solely based on the total concentration of PEG/PEO.

Methods

Rheometry

All viscosity measurements were performed using a Malvern Kinexus rotational rheometer. The geometry of choice was the cone-plate system and the experiments were performed in the controlled shear stress mode. The range of shear stress was from 0.01 Pa to 10 Pa. Assuming direct proportionality between shear stress and shear rate, characteristic for Newtonian fluids, we extrapolated the results to obtain the values of viscosity at zero shear rate. All macroviscosity results are given as such.

Fluorescence Correlation Spectroscopy

Fluorescence correlation spectroscopy (FCS) experiments were performed using a Nikon C1 confocal microscope with a water immersion objective (Nikon 60x, NA=1.20), time-correlated

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[†] Such concentration definition is justified theoretically on the basis of the simple model for viscosity of a hard-sphere solution when c/c^* scaling is used; it has also been shown to be applicable to description of experimental data.[12]

single-photon counting LSM upgrade kit by PicoQuant (Berlin, Germany) and temperature control of the sample (298 ± 0.2 K in all cases). A 488 nm pulsed diode laser was used as the excitation source to enable background removal based on fluorescence lifetime filtering. Two avalanche photodiode detectors were used in parallel for photon detection. As diffusing probes, we used rhodamine 110 (Sigma-Aldrich; applied as received) and a globular protein apotransferrin (Sigma-Aldrich) labeled with Atto 488 (NHS protein-reactive derivative obtained from Atto-Tec GmbH; labeling performed using the protocol supplied by the manufacturer; purification on size-exclusion column conducted immediately before the experiments). For each sample, a number of FCS curves was recorded, with at least 300 s of total data acquisition time. Global fitting procedure based on the least square method was performed to analyze the obtained autocorrelation curves (see Supporting Information for exemplary experimental and fitted curves). The model used for autocorrelation analysis was the simplest physically relevant one, i.e. single-component, three-dimensional free diffusion.[34] For rhodamine, a contribution of triplet states was also included in the model. Since Atto 488 featured low triplet fraction ($< 5\%$) at the applied laser power ($\sim 5\ \mu$W), the triplet term was disregarded for experiments utilizing labeled apotransferrin. System calibration was performed daily on rhodamine 110 diffusing in water (assumed diffusion coefficient at 298 K equal to 470 μm^2/s).[35] The value of the structure parameter of the detection volume established during calibration was fixed during subsequent data analysis (and fell within a range of 5.0 – 5.5).

FCS was applied to validate the applicability of the proposed scaling to molecular mobility. The results could be easily compared with the macroviscosity data, since within the paradigm of length-scale dependent viscosity the inverse proportionality of D and η is conserved across all length-scales and therefore[9]

$$\frac{D}{D_0} = \frac{\eta_0}{\eta}. \tag{10}$$

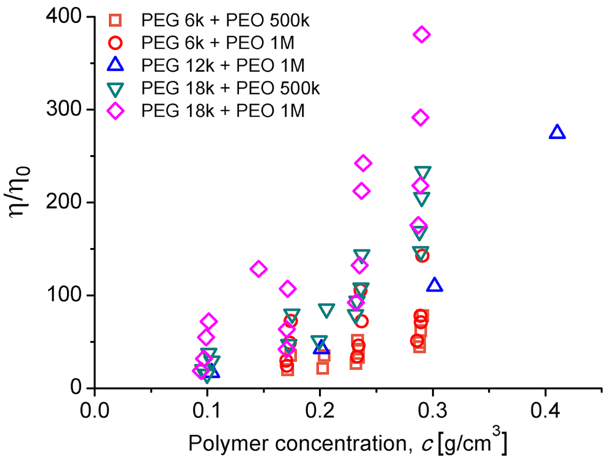

Figure 1: Selected results of viscosity measurements for mixtures of aqueous solutions of PEG/PEO. Measured dynamic viscosity η scaled by the solvent viscosity η_0 is plotted against polymer concentration c, calculated as a sum of concentrations of both polymers in the mixture. Vast scattering of the datapoints over the plot suggests that such simplistic approach cannot provide a reasonable description of two-component polymer systems.

D stands for diffusion coefficient in solution, D_0 is diffusion coefficient in pure solvent, η_0 is dynamic viscosity of pure solvent, and η is the effective viscosity experienced by the diffusing probe.

Results and Discussion

We performed the viscosity measurements for polymer solution mixtures of concentrations falling within the double-entangled regime. This means that both polymers constituting the mixture fulfilled the entanglement condition: $R_{\mathrm{h}}/\xi > 1$.[24] Each sample contained a short-chain (PEG) and a long-chain (PEO) component. In Figure 1 relative viscosity (η/η_0) is plotted against total polymer concentration c, simply calculated as sum of concentrations of both polymers. Clearly and expectedly, no direct and universal dependence is observed.

To empirically determine an adequate formula describing the viscosity scaling in polymer mixture solutions, a number of physically acceptable options was tested. In this manuscript we present only the obtained optimum result.

Viscosity of mixtures at the macroscale

The starting point for description of viscosity of polymer mixtures was the previously established formula for single-polymer solution, i.e. Equation 2.[24] A general, physically reasonable modification of Equation 2 that would allow to accommodate more than one polymeric crowder should take a form of

$$\eta = \eta_0 \exp\left[\sum_i f\left(M_{\mathrm{w}i}, c_i\right)\right] \tag{11}$$

where $M_{\mathrm{w}i}$ is the weight-average molecular weight of i-th polymer species in the solution and c_i is its concentration. $f(M_\mathrm{w}, c)$ is some function describing the contribution of a given polymer species to the overall crowding of the system. The sum of terms under the exponent stand for a sum of separate contributions of the different polymers. The formula needs to include the crucial length-scale of the system, i.e. the correlation length, defined by the total concentration of all the polymers. Also, the form of $f(M_\mathrm{w})$ must be such that in the limit where concentration of all but one of the polymers goes to zero, Equation 11 is reduced to the single-polymer case of Equation 2. To satisfy these conditions, we propose to put $f(M_{\mathrm{w}i}, c_i) = \gamma(RT)^{-1}x_i(R_{\mathrm{h}i}/\xi)^a$. x_i is the fraction of i-th component in the total amount of polymer in the solution. It is calculated with respect to the volume V_i occupied by monomers belonging to the i-th polymer species. In case of a mixture of polymers differing only in the degree of polymerization, x_i is congruent with the mass m_i of the i-th component divided by the total mass of polymers in the system:

$$x_i = \frac{V_i}{\sum_i V_i} = \frac{m_i}{\sum_i m_i}. \tag{12}$$

$R_{\mathrm{h}i}$ depends on $M_{\mathrm{w}i}$ and also, weakly, on c_i (via Equation 8). The single value of ξ, calculated from Equation 9, embraces all the polymers in the solution. For mixtures containing two species of chemically same polymer differing in M_w – such as the ones studied experimentally

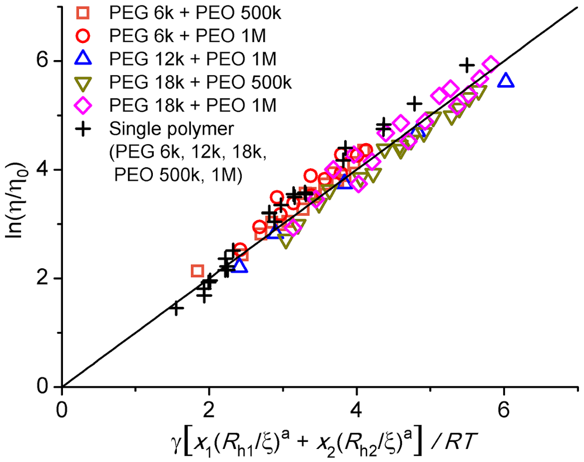

Figure 2: Results of the viscosity measurements for double-entangled aqueous PEG/PEO solution mixtures (including all data shown in Figure 1), plotted according to Equation 13 (solid line). No parameters were fitted; the applied values of γ=4.0 kJ/mol and a=0.78 were established previously for analogous systems containing a single polymer species.[24] A range of concentrations of up to 50% (w/w) for PEGs and up to 1.15% for PEOs is covered (see Supporting Information for a full list of samples and measured values of dynamic viscosity). Data for a limiting case of a solution containing a single polymer (black crosses)[24] are plotted as a reference.

in this work – we can therefore write:

$$\ln\left(\frac{\eta}{\eta_0}\right) = \frac{\gamma}{RT}\left[x_1\left(\frac{R_{\mathrm{h1}}}{\xi}\right)^a + x_2\left(\frac{R_{\mathrm{h2}}}{\xi}\right)^a\right]. \tag{13}$$

We applied Equation 13 to the experimental data on dynamic viscosities of PEG/PEO aqueous solution mixtures. Importantly, no parameters were fitted – we directly applied the values of γ=4.0 kJ/mol and a=0.78 established previously for analogous systems containing a single polymer species.[24] This is in line with the implied physical interpretation of these parameters (related to the polymer-polymer/polymer-solvent interaction balance and mesoscopic system topology, respectively). The result is plotted in Figure 2. The plot also includes data for a limiting case of a single polymer.[24] A complete table listing all the samples with their compositions and the measured viscosity values is available in the Supporting Information. Bearing in mind the simplicity of the proposed model as well as assumptions and approximations included in the definitions of ξ, c^*, and R_h, we find the conformity of the model with the experimental data observed in Figure 2 highly satisfactory.

Viscosity of mixtures at the nanoscale

The length-scale dependent viscosity approach was originally developed to describe both macroscopic flow as well as probe diffusion in complex liquids.[6,9,13] Therefore, by analogy to Equation 2, the description proposed here for macroviscosity of binary polymer solution mixtures is rewritten to embrace the case of molecular length-scale of flow as

$$\ln\left(\frac{\eta}{\eta_0}\right) = \frac{\gamma}{RT}\left[x_1\left(\frac{R_{\mathrm{eff1}}}{\xi}\right)^a + x_2\left(\frac{R_{\mathrm{eff2}}}{\xi}\right)^a\right]. \tag{14}$$

The values of R_{eff1} and R_{eff2} are calculated according to Equation 3, including a given probe size r_{p} as well as hydrodynamic radii of the polymers R_{h1} and R_{h2}. Since parameter a stems from the structure of the complex liquid itself, we expect it to remain in the nanoscale same as for macroviscosity, i.e. a=0.78. However, in case of probe diffusion, the interaction-related parameter γ must include not only the polymer-polymer and polymer-solvent interaction balance, but also the probe-polymer interactions. Therefore, we expect it to remain constant over systems containing PEG/PEO of various molecular weights and concentrations, but vary between different probes. Due to the complexity of the system and vast abundance of various contributions to the total magnitude of such interactions, we are yet unable to model or predict the values of γ. Therefore, we performed a range of FCS measurements for solutions containing only a single PEG or PEO (M_{w} range: 6k to 500k) and one of the selected molecular probes: rhodamine 110 (r_{p}=0.52nm) or apotransferrin labeled with Atto 488 (r_{p}=4.24nm). The results, plotted according to Equation 2, are given in Figure 3 (for raw experimental results see Supporting Information). From the slopes of the lines we obtain γ=7.4kJ/mol for rhodamine 110 and γ=3.7kJ/mol for apotransferrin in aqueous PEG/PEO solutions. These values are similar to those obtained previously for rhodamine dyes and proteins (respectively) in single-component PEG solutions.[13] For both probes, a

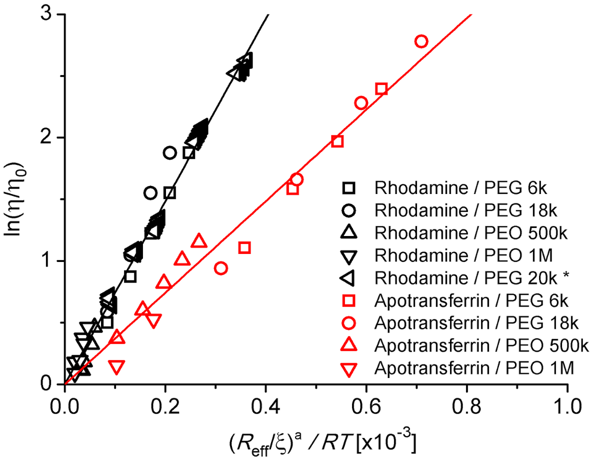

Figure 3: Results of fluorescence correlation spectroscopy measurements performed in solutions containing a single polymer. A range of samples differing in polymer molecular weight and concentration was investigated; motion of two probes – rhodamine 110 and apotransferrin labeled with Atto 488 – was observed. Data are plotted according to Equation 2 in terms of relative, effective viscosity experienced by the probes. Data on diffusion of rhodamine in PEG 20k (left triangles; marked with a star in the key) are taken from Ref.[13] The values of the interaction-dependent parameter γ, obtained as slopes of the linear plots, are 7.4 kJ/mol for rhodamine 110 and 3.7 kJ/mol for apotransferrin.

single γ value allows to describe the data across solutions of polymers of different M_w. This implies that the length-scale dependence is embraced by the $(R_\mathrm{eff}/\xi)^a$ term, while γ indeed relies solely on the chemical composition of the system.

Having established the γ values, we performed FCS experiments on the same molecular probes (rhodamine 110 and apotransferrin) in solutions containing PEG/PEO mixtures. Concentrations of the polymers ranged from 5 to 40% for PEGs and 0.5 to 2.5% for PEOs (for a full table of investigated solutions and measured data see Supporting Information). The results, plotted according to Equation 14, are summarized in Figure 4. Satisfactory conformity between the model and the experimental results is observed for both probes and all PEG/PEO mixtures.

Importantly, the formula describing macroscopic flow (Equation 13) is in fact a special case of Equation 14, where the probe size tends to infinity. Therefore, Equation 14 constitutes a universal and continuous approach, valid throughout all length-scales.

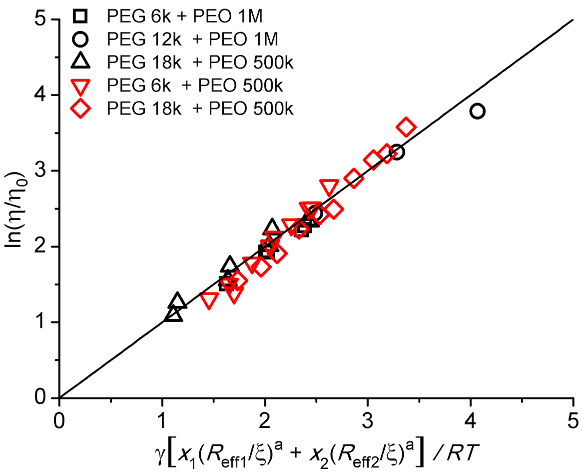

Figure 4: Results of fluorescence correlation spectroscopy measurements for double-entangled aqueous PEG/PEO solution mixtures. Diffusion of two probes – rhodamine 110 (black symbols) and apotransferrin labeled with Atto 488 (red symbols) – was observed. A range of concentrations up to 40% (w/w) for PEGs and up to 2.5% for PEOs is covered (see Supporting Information for a full sample and data table). Data are plotted in terms of relative, effective viscosity experienced by the probes according to Equation 14, which corresponds to the solid line. No parameters were fitted; the applied values of both γ and a were independently established in solutions containing a single polymer species (see Figure 3 and Ref. 24, respectively).

Probe diffusion in various multi-length-scale systems

The core significance of Equation 14 applied to molecular diffusion is that it connects the effective viscosity experienced by the probe to the relation between the probe's size and the key length-scales of the system. For a solution containing two chemically identical polymers (differing in molecular weight) dissolved in a good solvent, these length-scales are: hydrodynamic radii of the two polymers and effective correlation length of the system. Since monomers belonging to the short- and long-chained polymers are not distinguishable, the blob size only depends on the total polymer concentration, not on the particular contributions of polymers of given M_{w}. However, both polymer species have their particular impact on the length-scale dependent viscosity of the solution due to their different hydrodynamic radii. A full expected viscosity scaling curve for an exemplary system of this kind – PEG 6k 15% (w/w) + PEO 1M 1% aqueous solution – is plotted in Figure 5. The interaction

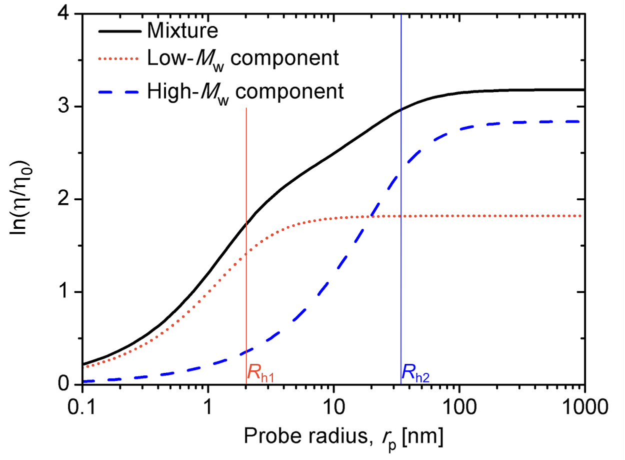

Figure 5: Illustration of the viscosity scaling equation for a binary mixture of polymer solutions (Equation 14; black line) – effective viscosity experienced by the probe as a function of the probe size r_{p}. The curve corresponds to an exemplary aqueous solution of PEG 6k and PEO 1M at concentrations of 15 and 1% (by weight), respectively. The dotted curve corresponds to the contribution of PEG 6k to the overall viscosity of the system; the dashed curve corresponds to the contribution of PEO 1M. The vertical lines mark the hydrodynamic radii of the two polymers.

parameter γ is fixed to the value obtained for the protein apotransferrin, so that the probe radius is the only variable. Effective viscosity experienced in such system by a small molecule ($r_{\mathrm{p}} \simeq 0.1$ nm) is lower than the macroviscosity of the solution by a factor of around 20. With increasing probe radius the effective viscosity also continuously increases, with points where r_{p} reaches the critical length-scales of R_{h1} and R_{h2} clearly separated. The contributions of each of the mixture constituents to the effective viscosity experienced by a probe of a given r_{p} are given in Figure 5 as curves drawn individually for each of the two polymers according to Equation 2.

The situation becomes qualitatively different when the two crowders differ not only in the physical dimensions, but also in their chemical composition. In such case it is no longer possible to arbitrarily define a single correlation length for the system. Moreover, interactions between the probe and the crowders would be different for each crowder type, rendering it impossible to establish a single γ value. Therefore, a more accurate description of effective viscosity experienced by a probe in a system containing i different types of crowders would rather read

$$\eta = \eta_0 \exp\left[\sum_i \frac{\gamma_i}{RT}\left(\frac{R_{\mathrm{eff}i}}{\xi_i}\right)^{a_i}\right], \tag{15}$$

with all scaling parameters defined independently for each of the constituents of the system. The shortcoming of such formulation is that it assumes no interactions between the various crowder populations, which would further increase the effective viscosity. Therefore, such approach could not be applied to e.g. PEG/PEO mixtures discussed hereby (where a synergistic, non-ideal effect is observed: total viscosity of the mixture is higher than the sum of the contributions of its components – this effect is accounted for in the definition of the effective correlation length of the mixture). Equation 15 may however prove useful in situations where the length-scales defined by the various crowders are well separated and their chemical nature does not promote entanglements or specific interactions between them. An important example is the cellular cytosol, where the key length-scales are roughly defined by average protein size (nm-scale) and cytoskeletal structure and compartmentalization (μm-scale). From the perspective of an organelle-sized object, the protein solution can be in fact treated as a continuous solvent, as if the presence of small crowders simply shifted the η_0 value. Therefore, the viscosity scaling curve for such system is expected to feature two distinct regions related to the two length-scales (similarly to the curve in Figure 5). However, at the moment we are only able to formulate qualitative predictions regarding such systems, opening a vast area for further experimental studies.

Conclusions

We examined viscosity of mixtures of aqueous solutions of various PEGs/PEOs at both macro- and nanoscopic length-scales. On this basis, we proposed a new scaling formula (Equation 14) for viscosity of binary polymer mixtures, where both short- and long-chain polymers are in the entangled regime. In the limiting case, the proposed equation reproduced the model developed previously for systems containing a single type of polymer. The empirical scaling parameters appearing in the model remained unchanged. We distinguished the term originating from the mesoscopic structure and topology of the system from the multiplicative term γ related to the magnitude and balance of interactions in the system, depending on its chemical composition. Thus, the proposed equation may prove useful not only for studies of transport properties of complex liquids, but also for investigations of interactions in such systems. We experimentally demonstrated the applicability of the scaling approach to probe diffusion in solutions containing two various polymers.

Quantitative description of transport properties of complex fluids within the paradigm of length-scale dependent viscosity is based on simple physical parameters characterizing the system. The discussed approach is therefore generalizable to systems containing more than two crowders, to other polymer/solvent/probe systems, and even to complex liquids other than polymer solutions. A particularly interesting application would be intracellular environment, where two key length-scales should be distinguished, corresponding to single proteins and the cytoskeletal structure. However, adaptation of the proposed general framework to transport properties of biological systems remains at the moment an open field for further investigations.

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Supporting Information Available

Supporting Information Available: technical details on rheometric experiments, data tables for viscosity and FCS measurements, exact M_w and polydispersity for the polymers used. This material is available free of charge via the Internet at http://pubs.acs.org.

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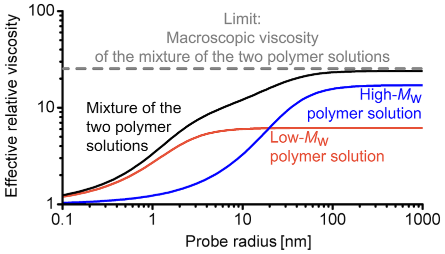

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