PHYSICAL REVIEW E **91**, 032306 (2015)

Brownian motion of single glycerol molecules in an aqueous solution as studied by dynamic light scattering

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(Received 7 November 2014; published 9 March 2015)

Aqueous solutions of glycerol are investigated by dynamic light scattering (DLS) over the whole concentration range (10–98 wt.% water) and in the temperature range 283–303 K. The measurements reveal one slow relaxation process in the geometry of polarized light scattering. This process is present in the whole concentration range, although it is very weak at the highest and lowest water concentrations and is considerably slower than the structural α relaxation, which is too fast to be observed on the experimental time scale in the measured temperature range. The relaxation time of the observed process exhibits a $1/q^2$ dependence, proving that it is due to long-range translational diffusion. The Stokes-Einstein relation is used to estimate the hydrodynamic radius of the diffusing particles and from these calculations it is evident that the observed relaxation process is due to the Brownian motion of single or a few glycerol molecules. The fact that it is possible to study the self-diffusion of such small molecules may stimulate a broadening of the research field used to be covered by the DLS technique.

DOI: 10.1103/PhysRevE.91.032306

PACS number(s): 66.10.−x, 05.40.−a

I. INTRODUCTION

The relaxation dynamics of liquids has been studied for several decades. The results have revealed a variety of relaxation processes, which span an enormous range of time scales. The most studied and established of these relaxation processes is the viscosity-related structural α relaxation, which is caused by density fluctuations on a length scale up to typically 2–3 nm near the glass transition temperature T_g [1,2]. However, it is also evident that liquids in general and mixtures of liquids, i.e., solutions, in particular may exhibit at least one relaxation process on a time scale much slower than the α relaxation. Such an ultraslow relaxation process has been observed by a wide range of different experimental techniques, such as dynamic light scattering (DLS) [3–7], dielectric spectroscopy [8–12], and Brillouin ultraviolet scattering [13]. Generally, it is acknowledged to be caused by long-range density fluctuations on a length-scale of 100–300 nm [14] or concentration fluctuations in the case of solutions [15], since its relaxation time usually exhibits a $1/q^2$ dependence (where q is the momentum transfer of the scattering event), as typical for long-range diffusion. However, despite the fact that this ultraslow relaxation process has been investigated in detail, its physical origin and possible universality are still not fully established.

In the case of aqueous sugar solutions of glucose, maltose, and sucrose the ultraslow relaxation process has been studied in detail by polarized dynamic light scattering measurements [5]. In this study Sidebottom and Tran attributed the ultraslow process to the diffusion of sugar clusters in the solutions. By applying the Stokes-Einstein relation with the viscosity of water as the Brownian medium, the hydrodynamic radius of the sugar clusters was estimated. The results showed that the size of the sugar clusters rapidly increased with increasing sugar concentration from single sugar molecules at low sugar concentrations to an infinitely large cluster at a weight fraction of about 83 wt.% sugar [5]. In contrast to these findings, our recent study on xylitol-water mixtures by using DLS and small-angle neutron scattering (SANS) experiments [7] revealed that the slow process, as observed by DLS, is due to the diffusion of single or a few xylitol molecules over the whole concentration range from 20 to 80 wt.% xylitol. This interpretation was reached by the fact that there was no indication of any preference for cluster formations or substantial concentration fluctuations from the SANS data, and when the hydrodynamic radius of the diffusing particles was estimated a size similar to the molecular size of xylitol was obtained. Hence, this study, in combination with the other previous studies, suggests that the origin of an ultraslow relaxation process can vary substantially between different solutions. Whether clustering occurs or not probably depends on the nature of the molecular interactions between different solute molecules as well as between solute and water molecules. Hence, the structural and dynamic behavior of a solution is governed by the exact details of the molecular interactions and only small differences may give rise to large effects.

In this paper we perform a similar study on glycerol-water solutions, using dynamic light scattering and broadband dielectric spectroscopy. There are several aims of this study. First, we want to elucidate whether the results for the xylitol-water solutions are unique or are also observed for similar systems, such as the glycerol-water solutions investigated here. Second, if the glycerol-water system is found to behave similarly to the xylitol-water system, we aim to verify the correctness of the interpretations made in Refs. [5,7] and establish that it is possible to study the self-diffusion of small molecules such as glycerol by DLS. The latter aim is reasonable since, despite the previous findings in Refs. [5,7], it is commonly believed to be too experimentally difficult to observe the Brownian motion of single molecules as small as glycerol. There is also a difficulty with this since the scattering power of a molecule decreases to the power of 6 with its decreasing size. This implies that the scattering power decreases 10^6 times when the weight of the molecule is reduced by a factor 10, e.g., from 10 000 to 1000 u. To further ensure that the Stokes-Einstein relation is valid and that the viscosity of water can be used as the viscosity of the Brownian medium we also extend our investigation to a very diluted solution of only 2 wt.% glycerol. The results are similar to what we observed for the xylitol-water system [7] and confirm that we are able to use DLS to study the Brownian motion of single or a few glycerol molecules in an aqueous solution. With this experimental observation we also aim to stimulate to new types of scientific investigations with the DLS technique.

II. SAMPLE PREPARATIONS AND EXPERIMENTAL METHODS

A. Dynamic light scattering

We have investigated mixtures of glycerol ($C_3H_8O_3$) ($\geqslant$99.5% purity, purchased from Sigma-Aldrich, CAS No. 56-81-5) and double-distilled water (Milli-Q water) over a broad concentration range from 10 up to 98 wt.% water. The solutions were prepared by choosing the exact amounts of glycerol and distilled water to directly give the desired composition of each solution. Before the DLS measurements the solutions were ultrasonicated for several minutes to obtain homogenous mixtures of the liquids. Thereafter, the solutions were placed in sample cells and filtered to remove any dust particles.

Dynamic light scattering measurements were performed in the temperature range 280–303 K on the light scattering instrument ALV/CGS-8F. This instrument is equipped with a laser source of a 150-mW 532-nm focused laser beam from a compact diode-pumped solid-state Oxxius single-mode source. Eight photomultiplier detectors, working in normal autocorrelation mode, were placed at different scattering angles to obtain a momentum transfer q dependence of the dynamics. All measurements were performed in a polarized scattering geometry. The sample environment was constituted by the usual index-matching vat filled with toluene, whose temperature was controlled by means of a thermal bath, to reduce spurious scattering from the walls of the sample vial.

The instrument used hardware ALV-7400/FAST Multiple Tau digital correlators, providing up to 288 correlation channels with an initial lag time of 25 ns. The output of the correlator is the normalized count rate (intensity) autocorrelation function $g_2(t) = \langle I(0)I(t)\rangle/\langle I\rangle^2$, which in the present case of homodyne detection is related to the normalized electric-field autocorrelation function $g_1(t)$ through $g_2(t) = 1 + a g_1^2(t)$, where $a \leqslant 1$ is an instrumental coherence factor [16]. This coherence factor a is related to the number of simultaneously detected coherence areas [16] and, in the case of single-mode fiber light collection, is expected to be about 1. In our case a was found to be 0.994 ± 0.001 from a measurement of a polystyrene latex standard. For each measurement data were collected for 2 h and at least 30 min was used to reach thermal equilibrium at each temperature.

III. EXPERIMENTAL RESULTS

Intensity-intensity autocorrelation functions $g_2(t) - 1$ are shown in Fig. 1. In Fig. 1(a) the angular dependence of the autocorrelation function is shown for a glycerol-water solution containing 30 wt.% water at $T = 293$ K. As evident from the figure, the relaxation process becomes faster with increasing scattering angle, i.e., increasing q value. An exponential relaxation process has been used to describe the experimental data and except for some deviations due to experimental errors, at short times, it is evident that this description of the data is correct. The inset of Fig. 1(a) shows the same type of data and exponential fit for a solution with 60 wt.% water, at temperatures in the range 283–303 K and a scattering angle of 90°. Here it is seen that the relaxation process speeds up with increasing temperature. Finally, in Fig. 1(b) data are shown for glycerol-water solutions of different water concentrations, at 293 K, and a scattering angle of 22°. As evident directly from these intensity-intensity autocorrelation functions, the amplitude of $g_2(t) - 1$ changes dramatically with the concentration of water in the solution. This is more quantitatively shown in the inset of Fig. 1(b), which shows a pronounced nonmonotonic concentration dependence of the

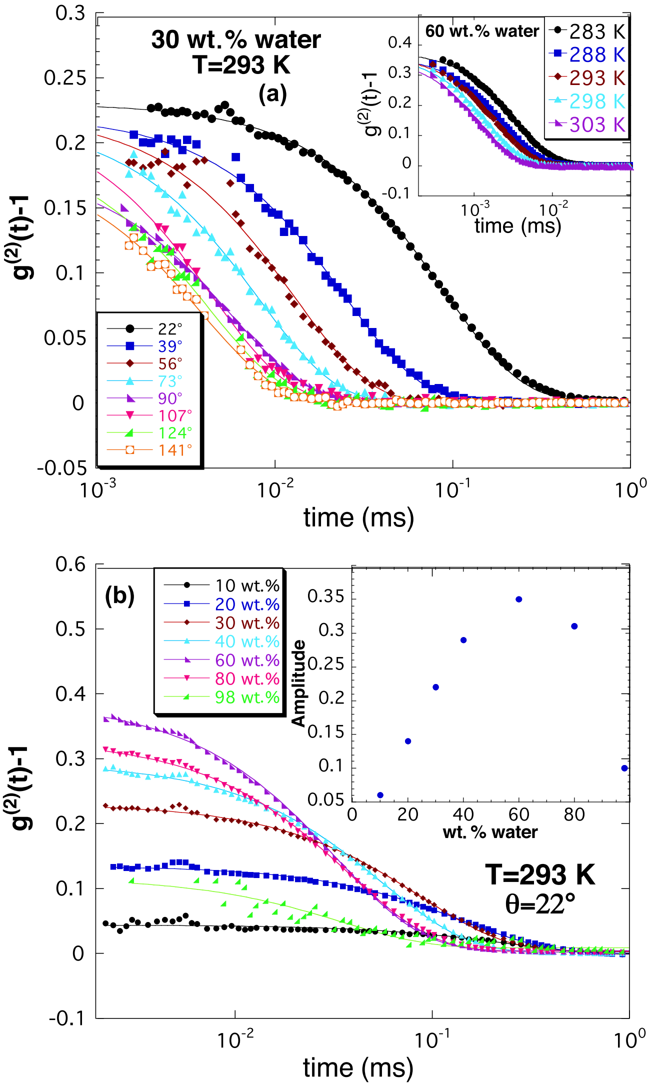

FIG. 1. (Color online) Intensity-intensity autocorrelation function $g_2(t) - 1$ for (a) a glycerol-water solution with 30 wt.% water at different scattering angles θ and $T = 293$ K and (b) glycerol-water solutions of different water concentrations at 293 K and at a scattering angle of 22°. The data have been fitted by single exponential relaxation functions, given by solid lines. In the inset of (a) $g_2(t) - 1$ is shown for a glycerol-water solution with 60 wt.% water in the temperature range 283–303 K and at a scattering angle of 90° and in the inset of (b) the amplitude of $g_2(t) - 1$ is shown as a function of the water content in the solution.

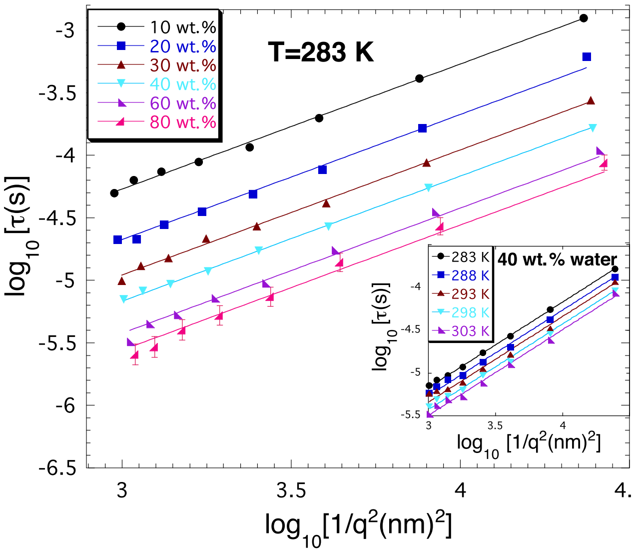

FIG. 2. (Color online) Relaxation times for glycerol-water solutions at $T = 283$ K, as obtained in Fig. 1 from exponential fits to the experimental $g_2(t) - 1$ data, as a function of $1/q^2$. The inset shows data for different temperatures for a solution containing 40 wt.% water. The lines have a slope of one in the given log-log representation, showing that the relaxation time is proportional to $1/q^2$. The symbols correspond to solutions with the water contents given in the figure.

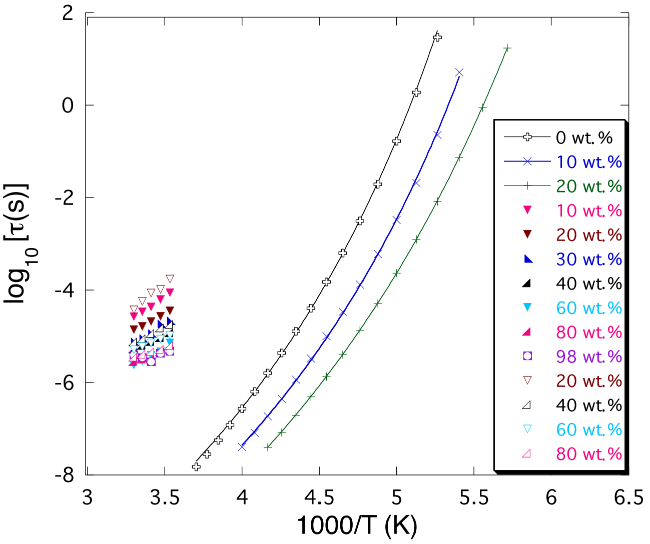

FIG. 3. (Color online) Temperature dependences of relaxation times for glycerol-water solutions (closed symbols) obtained from exponential fits to the experimental $g_2(t) - 1$ data taken at a 90° scattering angle. Previously obtained [7] DLS relaxation times for xylitol-water solutions (open symbols) and dielectric relaxation times (different types of crosses) for the structural α relaxation of glycerol-water solutions [17] are also shown for comparison.

scattering amplitude, with a maximum at about 60 wt.% water. The reason for this behavior will be discussed below.

From the exponential fits to the experimental data shown in Fig. 1 we obtain relaxation times τ of the observed process. In Fig. 2 these relaxation times are shown as a function of $1/q^2$ for different compositions at $T = 283$ K and in the inset different temperatures are shown for the solution with 40 wt.% water. These plots provide information about the physical nature of the relaxation process and make it possible to distinguish between, for instance, the structural α relaxation, which should be q independent in the measured q range, and long-range translational diffusion processes, which should exhibit a $1/q^2$-dependent relaxation time. As can be seen for the log-log representation shown in Fig. 2, a slope of one is obtained for all samples and temperatures, proving a linear relation between τ and $1/q^2$. This observation establishes that the relaxation process must be due to long-range translational diffusion.

In Fig. 3 the relaxation times obtained from the fitting shown in Fig. 1 are compared with previously obtained [17] dielectric relaxation times for the α process of glycerol-water solutions. We also compare the present DLS data with corresponding relaxation times for the xylitol-water system [7]. The relaxation times from the DLS measurements were obtained for a scattering angle of 90°, corresponding to a q value of about 0.025 nm^{-1}. From the figure it is clear that the diffusion process observed by DLS is considerably slower than the dielectric α relaxation, at least at this low-q value and the temperature range of the DLS measurements. However, the weaker temperature dependence of the DLS relaxation indicates that the difference in τ decreases with decreasing temperature. Figure 3 shows also that the relaxation times from DLS are very similar for the glycerol-water and xylitol-water solutions. It is only at low water concentrations, where the viscosities of the xylitol-water solutions are considerably higher, that the relaxation times of the xylitol-water system are substantially longer.

IV. DISCUSSION

Let us first discuss the nonmonotonic concentration dependence of the scattering amplitude, shown in Fig. 1(b). From the figure it is clear that the amplitude of $g_2(t) - 1$ goes from almost zero at low water contents to about 0.35 at 60 wt.% water and thereafter decreases again to about 0.09 at 98 wt.% water. This concentration behavior can be explained by a competitive balance between the number of particles scattering the light and multiple-scattering effects. At very low concentrations of glycerol there are few particles to cause the scattering and the scattering intensity becomes low. Thereafter, the scattering intensity increases with increasing number of particles (i.e., increasing glycerol content) until multiple-scattering effects are seriously affecting the scattering intensity. These multiple-scattering effects are detrimental for the intensity-intensity autocorrelation function and therefore its amplitude decreases at high glycerol contents. Also the relaxation time of the observed process may be affected by multiple-scattering effects. However, since the shape of the relaxation process does not deviate from exponential, as shown in Fig. 1(a), it is unlikely that the shape and relaxation time of the observed process are seriously affected by multiple-scattering effects.

From the $1/q^2$ dependence of the relaxation time, shown in Fig. 2, it is clear that the dynamical process is due to some kind of long-range translational diffusion. The same type of q dependence has previously been observed for other binary liquids [18–20]. In all these studies, the relaxation process has been interpreted as caused by long-range concentration fluctuations. However, our recent study of xylitol-water solutions [7] revealed that no substantial density fluctuations were present on a length scale from 2 to 100 nm, suggesting that the slow DLS relaxation has a different physical origin [7]. Since the glycerol-water system studied here shows a similar behavior (i.e., almost the same relaxation time with a $1/q^2$ dependence), it is natural to assume that the physical origin of this process is the same in both systems, i.e., due to Brownian motion of single or a few sugar alcohol molecules [7]. To elucidate whether this is the case we have also for this system used the Stokes-Einstein relation to estimate the hydrodynamic radius R_H of the self-diffusing particles

$$D = \frac{k_B T}{6\pi R_H \eta_B}, \qquad (1)$$

where D is the diffusion constant of the particles undergoing Brownian motions, η_B is the viscosity of the Brownian medium, and R_H is the hydrodynamic radius of the diffusing particles. The values of R_H so obtained are shown in Fig. 4 for the glycerol-water solutions studied here, as well as the previously studied xylitol-water mixtures [7], for comparison. Since it is far from obvious, except for the glycerol-water solution containing 98 wt.% water, which viscosity value we should use for the Brownian medium, i.e., the relevant microscopic viscosity the diffusing particles experience, we have used two approaches: In (a) the viscosity of bulk water was used as the viscosity of the Brownian medium and in (b) the macroscopic viscosity of each solution was used for the calculation. The same approach was used in our previous study of xylitol-water solutions since it was evident that neither the viscosity of bulk water nor the bulk viscosity of the actual solution gave realistic values of R_H.

The results shown in Fig. 4(b) confirm that the use of the macroscopic viscosity gives rise to unrealistically small values of R_H, at least at low water concentrations, where values less than 0.1 nm are obtained, i.e., values smaller than the radius of a water molecule. To estimate what the lower limit of a realistic value of R_H should be we calculate the approximate radius of a glycerol molecule from its bulk density by the following equation:

$$V = \frac{4}{3}\pi R^3 = \frac{M_W}{N_A \rho}, \qquad (2)$$

where M_W is molecular weight, N_A is Avogadro number, ρ is the density, V is the volume a glycerol molecule occupies, and R is the radius of this volume, assuming spherical geometry. This simple calculation gives a value of 0.31 nm for the radius of a glycerol molecule (and 0.34 nm for a xylitol molecule), which, therefore, should be the lower limit of a realistic value of R_H. For the solution containing 98 wt.% water the viscosity of the Brownian medium can be established to be the viscosity of bulk water. With this established value of the relevant viscosity it is possible to make an accurate estimation of R_H to about 0.35 nm, as shown in Fig. 4(a). The agreement is remarkable considering that the molecular interactions between glycerol and water molecules have been ignored. If such interactions had been taken into account the agreement would have been even better since molecular

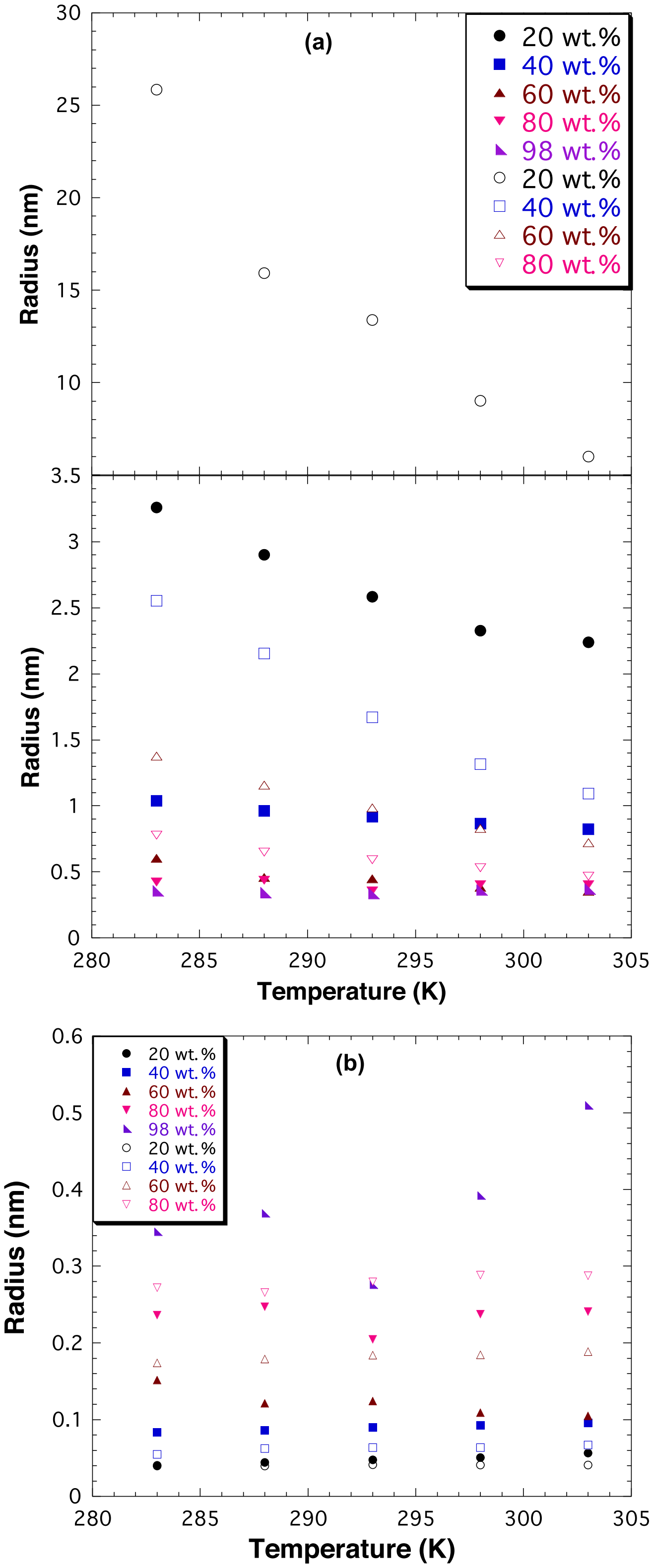

FIG. 4. (Color online) Hydrodynamic radii of diffusing particles have been estimated from measured diffusion constants of glycerol-water solutions containing 20, 40, 60, 80, and 98 wt.% water (closed symbols) by using the Stokes-Einstein relation. Previously obtained [7] values for xylitol-water solutions (open symbols) are also shown for comparison. In (a) the viscosity of bulk water was used as the viscosity of the Brownian medium, and in (b) the macroscopic viscosity of each bulk solution was used for the calculation.

interactions lead to an overestimation of the hydrodynamic radius [21]. This further implies that the observed long-range diffusion process is due to the Brownian motion of single glycerol molecules, possibly with one or two attached water molecules on a time average. Similar findings were observed at high water concentrations for the sugar solutions studied in Ref. [5] as well as for the solutions of xylitol [7], confirming the correctness of the interpretations made in Refs. [5,7]. In fact, the DLS technique is probably one of the most accurate methods to estimate the hydrodynamic radius of diffusing particles. For instance, the value of 0.35 nm obtained here for glycerol can be compared with previous estimations by viscometry [22] and ^{1}H NMR [23] measurements, which gave R_H values of 0.26 and 0.14 nm, respectively. Thus, the value we obtained should be at least as accurate as the value from the viscometry measurement and considerably more accurate than the value obtained by ^{1}H NMR.

It is, of course, not evident that the diffusing particles remain to be single glycerol molecules at higher glycerol contents. However, at least for our previously studied xylitol-water solutions it was evident from the SANS data that even at the highest concentration of xylitol, i.e., the sample with only 20 wt.% water, the radius of the diffusing particles was less than 2 nm [7]. Furthermore, if the bulk viscosity of that solution is used as the viscosity of the Brownian medium, an R_H value of less than 0.05 nm is obtained, as shown in Fig. 4(b). Although, this unrealistically low value mainly shows that the relevant microscopic viscosity the diffusing particles are experiencing must be considerably lower than the bulk viscosity; it also indicates that there is no significant growth in size of the diffusing particles with increasing xylitol concentration. In fact, even if the bulk viscosity of water is used as the viscosity of the Brownian medium it is only at the lower water concentrations and/or lower temperatures that the particles become substantially larger than the size of a xylitol molecule, despite the fact that the relevant microscopic viscosity must be considerably larger than the viscosity of water in the present case when no preferred clustering of xylitol molecules can be observed. Thus, with a more realistic value of the viscosity of the Brownian medium it is likely that no significant growth in size of the diffusing particles would occur with increasing xylitol concentration and/or decreasing temperature. Qualitatively, the same concentration and temperature dependences of the particle size occur for the glycerol-water solutions (see Fig. 4), although the dependences are now even weaker due to the lower viscosity of glycerol compared to xylitol. Thus, the tendency of growing particle size with increasing solute concentration is even weaker for glycerol than for xylitol. This further implies that also for the glycerol-water solutions it is unlikely that the R_H value of 0.35 nm, as obtained for the solution containing 98 wt.% water, should increase substantially provided that a correct value of the viscosity of the Brownian medium could have been obtained. In fact, even if the viscosity of water is used, which should be a too low viscosity giving an overestimation of R_H, the R_H value is less than 1 nm at room temperature for solute concentrations up to 60 wt.%. Thus, as for the xylitol-water solutions [7], there is no clear sign that motions of glycerol clusters can be detected, although we cannot exclude that small clusters of a few glycerol molecules are moving as single particles at high glycerol concentrations. In fact, clusters of glycerol must be formed at sufficiently high glycerol contents, such as 80 wt.%, even if there is no tendency to form glycerol clusters, by the simple fact that there is only about one water molecule per glycerol molecule at that concentration, which requires extensive glycerol-glycerol interactions. However, such networks of hydrogen-bonded glycerol molecules are, according to the data presented in Fig. 4, unlikely to be sufficiently stable (i.e., stable on the experimental time scale) to move as large particles. Hence, glycerol molecules completely surrounded by other glycerol molecules may still diffuse individually as single molecules, although this scenario cannot be fully proved by the data presented in Fig. 4. Furthermore, by comparing the results shown in Figs. 4(a) and 4(b), it is evident that the correct value of the relevant microscopic viscosity the diffusing particles experience should be between the bulk viscosities of water and the actual solution, with a value somewhat closer to the viscosity of water at high and intermediate water concentrations and a value closer to the bulk viscosity of the solution at low water concentrations, as must be the case when the concentration approaches bulk glycerol.

Finally, the Stokes-Einstein relation has been used for several decades to determine the hydrodynamic radius of diffusing particles, such as polymers and colloids, in dilute solutions. However, at least in the case of DLS measurements, it is generally assumed that the Stokes-Einstein relation cannot be used to study the diffusion of particles with a size comparable to the solvent molecules or at such high solute concentrations as studied here. To some extent, this study verifies that highly concentrated solutions cause difficulties, but not because the relation is not valid at high solute concentrations. The reason why it is difficult to apply the Stokes-Einstein relation to DLS data at high solute concentrations is rather the difficulty of knowing the correct value of the viscosity of the Brownian medium. This study clearly shows that the bulk viscosity overestimates the microscopic viscosity the diffusing particles experience. However, provided that the relevant microscopic viscosity can be estimated, the Stokes-Einstein relation should be valid (at least if multiple-scattering effects are ignored and intermolecular interactions are sufficiently weak [21]) for calculations of hydrodynamic radii, even at high solute concentrations.

The finding in this and some previous DLS studies [5,7] that it is possible to elucidate the Brownian motion of solute molecules only a few times larger than the solvent molecules is important to note since it indicates the possibility of using the DLS technique to study the microscopic mechanism of diffusion in low-molecular-weight solutions. Hence, we hope that this finding should stimulate a broadening of the research field used to be covered by the DLS technique.

V. CONCLUSION

In this study of glycerol-water solutions we have investigated the physical origin of a slow relaxation process observed by dynamic light scattering. The relaxation time of the observed process shows a $1/q^2$ dependence, proving that it is due to long-range translational diffusion. By using the Stokes-Einstein relation we were able to estimate the hydrodynamic radius of the diffusing particles and for a high water content of 98 wt.%, for which it is obvious that the viscosity of water can be used as the viscosity of the Brownian medium, a hydrodynamic radius of 0.35 nm was obtained. This value is in reasonable agreement with the molecular radius of a glycerol molecule, which can be approximated to about 0.31 nm, and therefore it is evident that the diffusing particles are essentially single glycerol molecules, particularly if we consider that the molecular interactions between glycerol and water molecules have been ignored, since molecular interactions result in an overestimation of the hydrodynamic radius [21]. At higher glycerol concentrations it is more difficult to estimate the size of the diffusing particles due to the problem of knowing the microscopic viscosity of relevance for the diffusing particles. However, by applying the two different approaches of using either the viscosity of water or the viscosity of the given bulk solution as the microscopic viscosity of the Brownian medium, we were able to conclude that the size of the diffusing particles cannot grow substantially with increasing glycerol concentration. For instance, at 60 wt.% glycerol the hydrodynamic radius becomes about 0.1 nm if the bulk viscosity of the solution is used as the viscosity of the Brownian medium and less than 1 nm if the bulk viscosity of water is used instead. These values suggest that the real hydrodynamic radius should be rather close to that of a single glycerol molecule, provided a correct viscosity of the Brownian medium is used in the calculation.

ACKNOWLEDGMENTS

This work was financially supported by the Swedish Research Council and the Swedish Energy Agency.

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