# Resolving the Mystery of Aqueous Solutions of Tertiary Butyl Alcohol

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ABSTRACT: We have resolved a long-standing issue in the discussion on the origin of the mesoscale inhomogeneities observed in aqueous solutions of tertiary butyl alcohol (TBA). We have shown that the formation of stable mesoscale particles (of about 100 nm in size) can be triggered by the addition of trace amounts of propylene oxide (an impurity expected to be present in all commercial samples of TBA) to a solution, which was previously filtered at a low temperature to remove these inhomogeneities. We hypothesize that these particles are aggregates of mixed clathrate-hydrates that are formed through the stabilization of fluctuations of the intrinsic structure in TBA aqueous solutions by the clathrate-forming ability of propylene oxide.
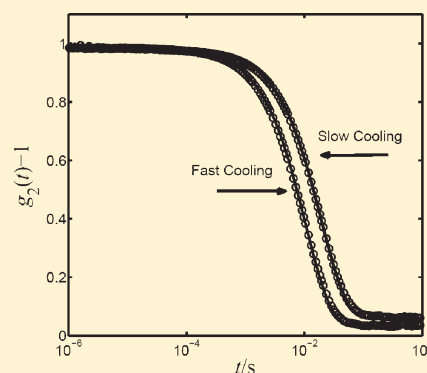
1. INTRODUCTION

The behavior of aqueous solutions of some ordinary organic substances, such as amines, alcohols, and ethers, has posed a mystery for a long time. Although considered homogeneous at the macroscopic scale, observations sometimes reveal the presence of mesoscopic inhomogeneities of the order of hundreds of nanometers in size. The observed phenomena have been discussed and their existence has been debated since the early 1970s, with explanations ranging from alleged artifacts to genuine equilibrium mesoscale structures, thus far without any consensus.

A few years ago, extensive static and dynamic light-scattering studies of around 100 different solute—solvent pairs were carried out by Sedlák.[1−3] Sedlák observed the presence of mesoscale inhomogeneities in all solutions studied (nonelectrolytes and electrolytes) and interpreted them as genuine equilibrium structures in aqueous solutions. Later, Jin et al. observed, by dynamic light scattering, a slow relaxation mode corresponding to inhomogeneities of about 100 nm in aqueous solutions of tetrahydrofuran, ethanol, urea, and α-cyclodextrin.[4,5] Jin et al. attributed this effect to the existence of gaseous nanobubbles stabilized by solute molecules adsorbed at the gas—water interface. The interpretations given by Sedlák and by Jin et al. raise serious questions. If, in accordance with Sedlák, the observed inhomogeneities are genuine equilibrium structures, why do they not reemerge after they have been removed by centrifugation? Regarding the existence of gaseous nanobubbles, to unambiguously confirm such an interpretation, one needs to quantitatively compare the initial inhomogeneities and those generated by gas injection.

Of all such cases, the story of mesoscale inhomogeneities in aqueous solution of tert-butyl alcohol (TBA) is the most bizarre and long-standing. In 1972, Vuks and Shurupova observed anomalous light scattering at about 0.03 mole fraction of TBA in water and attributed it to a "phase transition" between a clathrate-like structure and a less ordered molecular structure.[6] Indeed, some aqueous solutions that exhibit similar behavior, such as solutions of tert-butyl alcohol, 3-methylpyridine, tetrahydrofuran, and 2-butoxyethanol, can form either pure clathrate-hydrates or mixed clathrate-hydrates with another solute.[7−10] More detailed light-scattering experiments on TBA solutions were carried out by Beer and Jolly,[11] who reported that the observations, similar to those of Vuks and Shurupova, were dependent on the purity and the prehistory of the sample and thus could be attributed to the effect of the formation of droplets of insoluble impurities. Dynamic light-scattering experiments performed by Euliss and Sorensen[12] showed stable inhomogeneities of about 100 nm in radius below room temperature at a TBA concentration of about 0.07 mole fraction. Euliss and Sorensen speculated that the effect might be related to the formation of solid clathrates involving tert-butyl alcohol, water, and a trace amount of help gas.[12] However, subsequent light-scattering experiments, carried out by Bender and Pecora,[13] did not reveal any such inhomogeneities in TBA—water solutions, but did reveal mesoscale inhomogeneities in aqueous solutions of 2-butoxyethanol.[14]

Two relaxation modes in aqueous solutions of 3-methylpyridine and TBA, the "molecular-diffusion" mode and a slower "mesoscale-diffusion" mode, have recently been observed and studied by our research group for a broad range of concentrations and at various temperatures.[15] In both systems, the slow mode dominates below room temperature and is most pronounced at solute concentrations of about 0.07−0.08 mole fraction. It was

hypothesized that the emergence of mesoscale particles, associated with the slow mode, might be caused by the anomalous sensitivity of the intrinsic solution structure to small amounts of certain impurities. The main purpose of this paper is to verify this hypothesis and thus resolve the mystery of TBA aqueous solutions. We show that the formation of mesoscale particles in these solutions can be triggered by trace amounts of propylene oxide, which is expected to be present in all commercial sources of TBA. We believe that our findings are relevant to the resolution of the controversies surrounding mesoscopic inhomogeneities and structures in other aqueous systems.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. Aqueous solutions with a concentration of 0.07−0.08 TBA mole fraction were prepared by the procedure described in ref 15. Filtration under cold conditions was carried out with the help of RHV0CTC variable speed pump, purchased from Fluid Metering Inc. The sample was continuously filtered through 200 and 20 nm filters at cold conditions, at a flow rate of about 7 mL/min for about 30 min. After cold-filtering the sample, about 2 μL of cold propylene oxide (purchased from Sigma Aldrich, with a purity of 0.997+) was added to 10 mL of this sample. In another experiment, methane gas (0.999+ purity, purchased form Airgas) was injected at 5 °C for about 10 min into 10 mL of another cold-filtered TBA aqueous sample.

2.2. Light-Scattering Technique and Procedure. The light-scattering experiments in aqueous TBA solutions were carried out with the setup described in ref 15. The sample was subjected to various temperatures ranging from 8 to 50 °C, with a temperature control better than ±0.1 °C. The heating rate was about 8 °C/h, while the cooling rate was about 5 °C/h. At each temperature, the sample was allowed to equilibrate for about 2 h before a reading was taken. The dynamic autocorrelation function in the homodyne mode was obtained by using a Photocor correlator. "Dust cutoff" software was occasionally used to disregard any segments during which the scattering intensity spiked beyond a preset limit.[15]

For two exponentially decaying relaxation modes, the intensity autocorrelation function $g_2(t)$[16] obtained in the homodyning mode is given by

$$g_2(t) - 1 = \left[A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \right]^2 \quad (1)$$

where A_1 and A_2 are the amplitudes, t is the lag time, and τ_1 and τ_2 are relaxation times. If the relaxation times are associated with the diffusion of molecules or particles, then the decay rate for each mode is

$$\frac{1}{\tau_{1,2}} = 2D_{1,2}q^2 \quad (2)$$

where $q = (4\pi n/\lambda) \sin(\theta/2)$ is the wavenumber (n is the refractive index of the scattering medium, λ is the wavelength of the laser, and θ is the scattering angle) and $D_{1,2}$ is the translational diffusion coefficient either for the fast mode (D_1) or for the slow mode (D_2). For monodisperse, spherical Brownian particles

$$D_{1,2} = \frac{k_B T}{6\pi\eta R_{1,2}} \quad (3)$$

where k_B is Boltzmann's constant, T is the temperature, η is the shear viscosity of the medium, and $R_{1,2}$ are the corresponding hydrodynamic radii.[16]
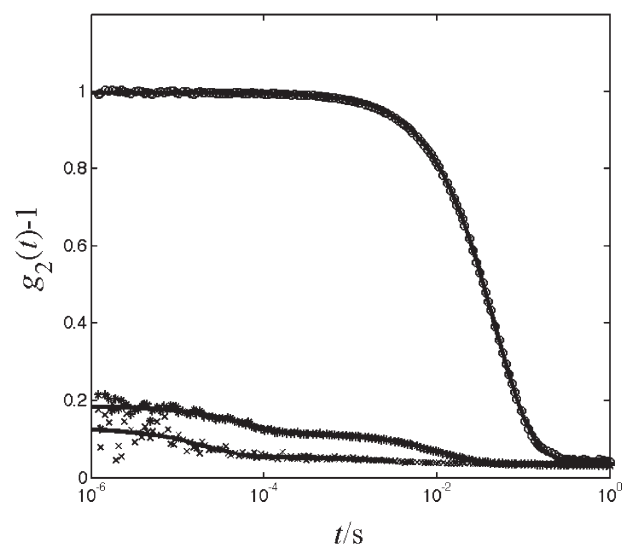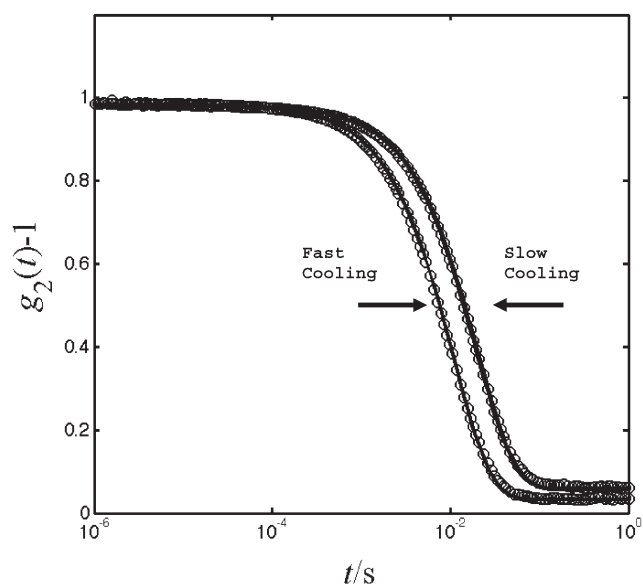

Figure 1. Intensity autocorrelation functions for TBA aqueous solutions at the scattering angle $\theta = 45°$. Open circles and asterisks are for 0.083 mole fraction TBA solution at $T = 8.5$ °C and $T = 22.8$ °C, respectively. The crosses represent the autocorrelation function for the 0.073 mole fraction TBA aqueous solution obtained at $T = 8.5$ °C after cold filtration. The solid curves represent fits of the data to eq 1.

3. RESULTS AND DISCUSSION

Figure 1 shows light-scattering intensity autocorrelation functions obtained at a scattering angle of 45° for aqueous TBA solutions at room temperature (22.8 °C) and at low temperature (8.5 °C), before and after cold filtration. At room temperature, two relaxation modes are detected—a fast mode, with a decay time of about 65 μs, and a slow mode, with a decay time about 20 ms. As reported in ref 15, both modes obey the q-dependence of eq 2, which confirms that the fast mode corresponds to molecular diffusion, in good agreement with the data reported in refs 12 and 13 and the slow mode corresponds to the Brownian diffusion of near-spherical aggregates, ranging in size from a few hundred nanometers to about a micrometer. Therefore, the diffusion coefficient and the corresponding particle size reported in ref 15 by a fit of the slow mode to a single exponential are average parameters, whose standard deviations include the polydispersity. The amplitude ratio A_1/A_2 indicates the contribution from the two detected modes into the total light-scattering intensity, while the limiting value of the correlation functions at zero lag time, $g_2(0)$, depends on the static light-scattering intensity and the optical scheme. Upon cooling below room temperature, a sharp increase in the light-scattering intensity is observed and the mesoscale mode almost entirely dominates the correlation function. The correlation function essentially becomes a single exponential. On cold filtering the sample, the light-scattering intensity drops to a level typical for ordinary molecular binary solutions. After cold filtration, the molecular diffusion mode can still be clearly detected despite the very low light-scattering intensity. However, the contribution from the mesoscale particles becomes marginal. Since the refractive index of the solution does not significantly change after the cold filtration, from $n = 1.3442$ before the filtration to $n = 1.3440$ after the filtration, we conclude that the change in the TBA concentration is insignificant.

We conclude that cold filtration removes the source of the mesoscale particles in the solution and thus hypothesize that the
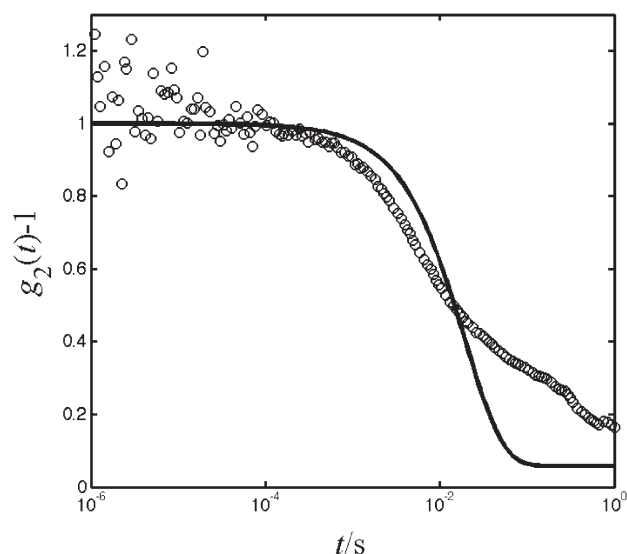
Figure 2. Intensity autocorrelation functions for the 0.073 mole fraction TBA cold-filtered aqueous solution, doped with 7×10^{-5} mole fraction PO, at the scattering angle $\theta = 60°$ and $T = 8.5$ °C. The correlation function with the steeper slope corresponds to a fast cooling rate of 3 °C/min, while the correlation function with the shallower slope corresponds to a slow cooling rate of 5 °C/h. The solid curves represent fits of the data to single exponentials.

Figure 3. Intensity autocorrelation function for the 0.073 mole fraction TBA aqueous solution, cold-filtered and saturated with methane gas, at a scattering angle $\theta = 60°$ and $T = 8.5$ °C. The solid curve is a normalized single-exponential fit (Figure 2, slow cooling) which describes the autocorrelation function obtained by the addition of PO to a TBA solution under same conditions.

mesoheterogeneities can be regenerated in a controlled fashion. To verify this hypothesis, we added 2 μL (7×10^{-5} mole fraction) of propylene oxide (PO) to the cold-filtered 10 mL TBA sample. TBA is derived commercially from isobutane as a coproduct in the production of propylene oxide,[17] which is a known hydrate former.[18] Thus, propylene oxide is an expected impurity that might be present in trace amounts in all commercial TBA samples. Figure 2 shows the intensity autocorrelation function of the cold-filtered TBA aqueous solution after the addition of 7×10^{-5} mole fraction PO. One can see from the figure that the mesoscale mode reemerges. The appearance of the mesoscale particles is also manifested by a sharp increase in the light-scattering intensity, especially at small scattering angles. When we added larger amounts of PO, up to 80 μL, we observed a significant increase in the number of particles, manifested by a corresponding increase in the light-scattering intensity.

We added other impurities, such as 10^{-4} mole fraction isopropanol, 10^{-4} mole fraction isobutanol, and 4×10^{-5} mole fraction cyclohexane, to the previously cold-filtered sample. No significant changes in the light-scattering intensity or in the autocorrelation function were observed. Experiments were also carried out by adding 6×10^{-5} mole fraction PO to a cold-filtered 0.073 mole fraction isopropanol aqueous solution and by adding 5×10^{-5} mole fraction PO to dust-free pure water. Again, unlike the avalanche of mesoscale inhomogeneities, which emerged in TBA solutions upon cooling, no significant effects were observed in these samples. We conclude that the formation of mesoscale inhomogeneities in some aqueous solutions requires specific interactions with an impurity, such as the interaction between TBA-induced solution structure and PO.

In order to investigate whether the observed inhomogeneities were related to the presence of possible gaseous nanobubbles,[4,5] a methane-saturated TBA aqueous solution was investigated.

Unlike the observed strong opalescence upon adding PO, the total light-scattering intensity did not rise as significantly after injecting methane gas, though it showed irregular oscillations and occasional sharp spikes, most likely associated with nonequilibrium gas bubbles. At the same time, as seen in Figure 3, the autocorrelation function shows the presence of an extremely broad spectrum of relaxation times, as compared with the results shown in Figure 2. We conclude that gaseous nanobubbles do not play a significant role, if at all, in the formation of the observed mesoscale particles in TBA aqueous solutions.

We explain the origin of the mesoscopic particles formed in TBA aqueous solutions by a coupling between fluctuations of a short-ranged, short-lived clathrate-like structure in the homogeneous phase and the clathrate-forming ability of propylene oxide. The structural fluctuations in TBA solutions are most pronounced around a certain "stoichiometric ratio", possibly 1TBA:17 H_2O.[7,19,20] In particular, the thermodynamic anomalies in TBA solutions are attributed to the formation of these short-range clathrate-like structures.[21] Furthermore, some experiments and computer simulations indicate a molecular clustering in TBA aqueous solutions on the nanometer scale.[19,20,22−31] However, such a molecular clustering without further aggregation cannot cause the anomalous scattering associated with the mesoscale inhomogeneities.[12,13,15] As suggested by Malomuzh and Slinchak,[30] strong hydrogen bonds between water molecules and alcohol molecules can be responsible for the formation of solvent−solute molecular clusters which can further aggregate due to van der Waals-type interactions.

We assume that PO could stabilize the short-range fluctuations in TBA aqueous solutions and lead to the formation of long-range, mixed clathrate-hydrate precursors. Such an effect is caused only by specific impurities, such as PO, in TBA solutions and possibly in some other aqueous solutions with similar structural fluctuations. A similar concept of concentration fluctuations stabilized by electrons was developed by Krivoglaz in the

1970s.[32] The interaction with electron can compensate the free-energy increase caused by the fluctuations and lead to the formation of stable quasi-particles, called "fluctuons". At certain conditions, the size of the fluctuons may significantly exceed the molecular scale. It seems possible that a similar effect exists in TBA aqueous solutions if a hydrophobic "foreign molecule", such as a PO molecule, stabilizes the structural fluctuations. The mesoscale particles may be trapped in a metastable state and hence could be kinetically stable for a long time, similar to what Jacobson et al. have demonstrated through molecular dynamics simulations.[33]

We want to emphasize the difference between conventional concentration fluctuations, which are pronounced in nonideal solutions, and stable mesoscale inhomogeneities. Conventional concentration fluctuations are characterized by the correlation length and are responsible for the molecular diffusion mode in the dynamic autocorrelation function, as shown in Figure 1. Alternatively, mesoscale inhomogeneities, such as those found in microemulsions, are usually formed through the "Lifshitz-point" mechanism, describing stabilization of fluctuations by strong selective interactions with a solute.[34] Such interactions may stabilize molecular clusters at a nanoscale; however, a further attraction between these clusters may result in the formation of larger long-lived aggregates.

We have also made a preliminary study of the effect of the rate of cooling on the formation of the mesoscale particles. The solution was warmed up to about 50 °C and cooled to about 8 °C at a fast rate of 3 °C/min and at a slow rate of 5 °C/h. As seen in Figure 2, the autocorrelation function obtained after fast cooling has a faster decay time ($\tau = 20$ ms) while the slow cooling leads to a slower decay time ($\tau = 40$ ms). The mesoscale particles obtained on fast cooling correspond to a particle size of about 120 nm in radius, calculated with eq 3, while the slow cooling produced particles of about 240 nm. The viscosity data for aqueous TBA solutions were taken from the measurements of Euliss and Sorensen.[12] The refractive index was measured by using an Abbe refractometer. The characteristic width of the particle size distribution, about 5 nm in the case of fast cooling and about 40 nm in the case of slow cooling, is estimated as a difference between the position of the maximum in the software distribution analysis and the radius obtained from eq 3.

The colloid obtained by fast cooling of aqueous TBA solutions, doped with PO, is surprisingly stable. It has been monitored for more than 6 months, and no significant change of the particle size during this time has been observed. If the colloid is kinetically stable, the characteristic aggregation time can be approximated as $\tau_a = [(3\eta)/(4k_BTn)]W$, where n is the number of particles per unit volume and W is the stability ratio.[35] For a 10 mL aqueous TBA sample, doped with 2 μL of PO, assuming that all PO molecules in the solution are involved in the formation of aggregates of 100 nm size, the particle density is estimated as $n \cong 10^{17}$ m^{-3}. To maintain the stability of the system for months, one expects the stability ratio to be very high, of the order of thousands.

4. CONCLUSIONS

We conclude that the formation of stable mesoscale particles in tertiary butyl alcohol aqueous solutions is triggered by the presence of trace amounts of propylene oxide. We thus resolve the long-standing dispute on the origin of the light-scattering anomaly in these solutions, whether it is an artifact due to the presence of impurities or associated with a genuine solution structure. In fact, both views are relevant. The mesoscale particles are formed due to the fluctuations of the solution structure stabilized by interaction with a specific hydrophobic impurity.

However, a microscopic picture of this phenomenon still needs to be formulated. There are several unanswered questions. What controls the size of these mesoscopic aggregates? Are they thermodynamically stable or kinetically arrested? The fact that the aggregate size depends on the rate of cooling may favor the latter. Another effect, which could play a role in the formation of the aggregates, is the possible polymerization of PO to poly-(propylene oxide), which is known to occur in water, with an alcohol as initiator.[17] However, as noticed in the previous section, when TBA was replaced by isopropanol, the mesoscale particles were not pronouncedly detected.

The results obtained in this work may have an impact that goes far beyond the specific systems investigated. The mesoscale inhomogeneities observed in other aqueous nonelectrolytes[14,15,36-38] and, more broadly, by Sedlák and other investigators,[1-3,39] are most likely associated with interactions of traces of specific impurities and the fluctuations of the intrinsic structure in aqueous solutions. Hence, there is a need to revisit the previously reported results on mesoscale structures in aqueous systems. More comprehensive molecular dynamics simulations would also be highly desirable.

Another promising implication of the specific response of the aqueous solution structure to an "impurity" is the effect of small amounts of an "antagonistic" (amphiphilic) salt. A stable equilibrium charge-density-wave mesophase was theoretically predicted by Nabutovskii et al. long ago[40] but was only recently observed in an aqueous solution of 3-methylpyridine upon the addition of sodium tetraphenylborate by Sadakane et al.[41] Such a microphase separation, as suggested by Onuki et al.,[42,43] can be induced by preferential hydrogen bonding. We anticipate similar density-wave mesophases in TBA and other similar aqueous solutions.

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