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Lack of evidence of dilution history-dependence upon solute aggregation in water. A nuclear magnetic resonance determination of self-diffusion coefficients

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NMR-PFG (pulsed field gradient) diffusion coefficient measurements of aqueous solutions of sodium chloride, sodium azide, 18C6 crown ether, β-cyclodextrin and of a mixture of sodium azide and 18C6 crown ether, did not reveal any solution history-dependence, indicating that the unexpected solute aggregation upon dilution, reported by Samal and Geckeler (*Chem. Commun.*, 2001, 2224), is inconsistent with these as well as other experimental results.

Recently, Samal and Geckeler[1] reported studies on cluster–cluster aggregation phenomena in aqueous solutions of fullerene–cyclodextrin conjugates, β-cyclodextrin, sodium chloride, sodium guanosine monophosphate, and a DNA oligonucleotide, in which they found an inverse relationship between the aggregate size and concentration in all these solutes. Their results indicate that there exist larger aggregates in dilute aqueous solutions than in more concentrated ones. Considering the case of cyclodextrin, their concentration *vs.* particle size curves did not merge into one line for all solutions, and the extent of particle size increase was higher for cyclodextrin solutions of lower starting concentrations than for solutions of higher initial concentration, indicating that solution history is an important factor in the growth dynamics of the aggregates. As Samal and Geckeler mentioned,[1] their finding 'could be of importance to the universal understanding of diverse phenomena involving dilution and dilute solutions'.

One way of monitoring cluster formation is by measuring diffusion coefficients of the nuclei involved using NMR-PFG[3] techniques. We recently measured[2] sodium self-diffusion coefficients, in aqueous solutions, of 18C6 crown ether complexes with sodium ions using this method. We found that small concentrations of 18C6 in aqueous solutions of sodium ions, while having negligible effect upon the macroscopic viscosity, cause, for some counter ions, a quite significant suppression of sodium diffusion. This effect suggests that, for some counter ions, each (Na^+; 18C6) complex may associate with a surprising number, typically six to eight, of Na^+ ions, forming stable aggregates.[2] Since the formation of aggregates and their size has a substantial effect upon the sodium diffusion coefficient in this system, we decided to investigate† whether the size of the aggregates was also affected by dilution history.

For 18C6 as well as for several other systems, we then measured diffusion coefficients for two different dilution histories. Two solutions of identical final solute concentrations were prepared for each system; one in a single dilution step and the other through six successive dilutions. After each dilution, we allowed the intermediate solution to rest for a day.

Consider Stokes–Einsten equation for a spherical particle, $D = kT(6\pi\eta r)^{-1}$, where: D is the diffusion coefficient, k is Boltzmann's constant, T the temperature, η the dynamic viscosity of the solution, and r the hydrodynamic radius of the particle. Asssuming that the final viscosities are equal, any decrease in the diffusion coeficient, due to dilution history, for a given solute concentration, can be safely interpreted as due to an increase in the radius of the aggregate in solution.

We started with an aqueous solution of NaN_3 and 18C6, with concentrations of 4.0 and 0.12 M, respectively, and diluted it in six steps, down to 0.4 and 0.012 M. We then compared its ^{23}Na diffusion coefficient with that from a 0.4 and 0.012 M solution prepared in a single dilution. The results turned out to be the same (see Table 1), without any evidence of enhanced solute aggregation on successive dilutions. Of course, the final viscosities are equal. We then repeated the experiment, first with sodium azide only, where we measured the ^{23}Na diffusion coefficient and later with 18C6 dissolved in D_2O, where we measured the ^1H diffusion coefficient. Once more, our results did not reveal any difference in diffusion coefficients due to solution history, indicating that at least, for these systems, there seems to be no solute history-dependent aggregation in water upon dilution (see Table 1).

We next considered some of the systems described by Samal and Geckeler, namely: aqueous solutions of NaCl and β-cyclodextrin. In particular, for NaCl, Samal and Geckeler reported that when they successively diluted a 5.5 M solution to 0.785 M, they observed an increase in the aggregate size from 1.491 to 4.95 μm, more than three times its original size. Comparing these results with existing measurements of diffusion coefficients of alkali ions in aqueos solution,[4] one must

Table 1 Diffusion coefficients of various aqueous solutions prepared with and without six successive dilutions

	Solute concentration[a]/M		Diffusion coefficient/10^{-9} m² s⁻¹	
Solute	Starting	Final	Six successive dilutions	Single dilution
NaCl	4.0	0.4	1.30[b]	1.30[b]
NaN_3	4.0	0.4	1.29[b]	1.29[b]
NaN_3 and 18C6	4.0 and 0.12	0.4 and 0.012	1.05[b]	1.05[b]
18C6	0.1	0.01	0.50[c]	0.49[c]
β-Cyclodextrin	0.006	0.004	0.66[c]	0.67[c]

[a] Starting concentrations for the six successive dilutions . Final concentrations are identical for both histories. [b] Diffusion coefficient measured with PFG pulse sequence using the resonance frequency of ^{23}Na (average of three measurements). [c] Diffusion coefficient measured with PFG pulse sequence using the resonance frequency of ^1H and D_2O as a solvent (average of three measurements).

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conclude that they are very difficult to reconcile. Moreover, we addressed the claim of history-dependence also in these cases. To check whether any history-dependent aggregation occurred in NaCl solutions, we started with a 4.0 M solution of NaCl diluting it successively to 0.4 M, the measured diffusion coefficient was found to have the same value as in another solution of NaCl prepared in a single dilution to 0.4 M. Both diffusion coefficients turned out to be identical and equal to 1.30 $\times$ 10^{-9} m^2 s^{-1} as shown in Table 1.

We finally tried β-cyclodextrin, as Samal and Geckeler did. Once again, there was no meaningful difference in ^{1}H diffusion coefficents based on dilution history (see Table 1).

We conclude that, although NMR-PFG is a powerful tool to detect cluster formation in aqueos solutions[2] we did not find any evidence, neither from the results of Table 1 nor from other experiments,[2,4] to support the unexpected solute aggregation in water on dilution, reported by Samal and Geckeler.

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Notes and references

† The reagents are commercially available and were used without further purification. Water was purified by a Mili-Q water purification system (resistivity of 18.2 MΩ.cm). Diffusion measurements were performed at 298 K in a Varian unity plus 300 MHz spectrometer with an actively shielded pulsed field gradient coil system. A standard Stejskal–Tanner[3] sequence ($\pi/2 - \tau - \pi - \tau$) was employed. For diffusion measurements with ^{23}Na, we used $\tau = 26$ ms, a gradient pulse of $\delta = 6$ ms, and a maximum gradient strength of 50 G cm^{-1}. A 0.5 M NaCl solution was employed as a reference adopting the value $D = 1.24 \times 10^{-9}$ m^2/s for the sodium self-diffusion coefficient at 25 °C.[4] For ^{1}H diffusion measurements, we used D_2O as a solvent, with a maximum gradient strength of 47 G cm^{-1}, $\tau = 32$ ms, and $\delta = 3$ ms. Water was employed as a reference value with $D = 2.3 \times 10^{-9}$ m^2 s^{-1} for the ^{1}H self-diffusion coefficient at 25 °C.[5] In order to avoid signal saturation, T_1 was determined for the studied nucleus, using the inversion recovery pulse sequence ($\pi - \tau - \pi/2$).

1 S. Samal and K. E. Geckeler, *Chem. Commun.*, 2001, **21**, 2224.
2 F. Hallwass, M. Engelsberg and A. M. Simas, *J. Phys. Chem. A*, 2002, **106**, 589; F. Hallwass, M. Engelsberg, A. M. Simas and W. Barros, *Chem. Phys. Lett.*, 2001, **335**, 43.
3 E. O. Stejskal and J. E. Tanner, *J. Chem. Phys.*, 1965, **42**, 288.
4 B. M. Braun and H. Weingaertner, *J. Phys. Chem.*, 1988, **92**, 1342.
5 M. Holz and H. Weingaertner, *J. Magn. Reson.*, 1991, **95**, 115.