Influence of H^+, OH^- and Salts on Hydrophobic Self-Assembly

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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Details regarding the experimental and theoretical methods are provided in the Sections 1 and 2, below. Additional archived experimental data and theoretical analysis procedures are available in the Purdue University Research Repository, DOI:10.4231/8GBW-9P30.

1. Experimental Methods

Materials

1,2-Hexanediol (12HD, ≥ 98%), 1-octanol (≥ 99%), 1-hexanol (≥ 98%), LiOH (≥ 98%), HCl (ACS 37%), HBr (ACS 48%), were purchased from Sigma-Aldrich (St. Louis, MO). NaOH (≥ 98.5%) was purchased from Acros Organics (Waltham, MA). LiCl (≥ 99%), NaCl (≥ 99%), and NaBr (≥ 98.5%) were purchased from JT Baker (Phillipsburg, NJ). All were used as received and dissolved in ultrapure water with a minimum resistivity of 18.2 MΩ cm (Milli-Q®). All glassware was cleaned with acetone and ultrapure water and heated in an oven until fully dry before use.

Raman-MCR 12HD Aggregation Measurements

Aqueous counter-ion solutions containing salts, acids and bases were prepared at 2 M in volumetric flasks. 12HD solutions were prepared by weighing 12HD into volumetric flasks that were then filled with either pure water or 2 M counter-ion solutions. The counter-ion concentration of 2 M was used to produce CMC shifts that are more accurately measurable than when using lower counter-ion concentration, and a 2 M counter-ion concentration is sufficiently dilute that the resulting free energies of solvation and micelle formation remain linear in counter-ion concentration up to this concentration.[1, 2] The resulting solutions were transferred to a glass cuvette using a pipet. Raman spectra were obtained using a home built spectrometer and self-modelling curve resolution (SMCR) was used to obtain solute-correlated (SC) spectra from pairs of solvent and 12HD solution spectra, as previously described.[3, 4] Briefly, the cuvette containing the sample solution was placed in a temperature-controlled cell holder (Quantum Northwest,

Liberty Lake, WA) and equilibrated to 20 °C. An argon-ion 514.5 nm excitation laser provided between 10-20 mW of power to the sample cuvette. The backscattered light was collected and transmitted using a fiber-optic-bundle to a thermoelectrically cooled CCD detector (Princeton Instruments, Trenton, NJ) after passing through a 300 mm spectrograph (Acton Research, Inc.) equipped with either a 300 grooves/mm or 1200 grooves/mm grading. The total exposure time for all spectra was 5 minutes and two replicate spectra were obtained during every measurement.

Raman-MCR Partitioning-Based Solubility Measurements

Solutions used to measure partitioning of 12HD between 1-octanol and the aqueous phase were prepared in glass cuvettes. First, 1.4 mL of either pure water or the aqueous salt (or counter-ion) solution was added to a cuvette and then 1.4 mL of a 1 M solution of 12HD in 1-octanol was gently added to the cuvette to form a two-phase system. The 1-octanol solution was dispensed carefully and slowly over the aqueous solutions, as physical mixing of the aqueous and organic phases was observed to lead to irreversible gel formation. The cuvettes containing this two-phase mixture of 12HD were allowed to equilibrate on an orbital shaker for a minimum of 48 hours. The solvent reference solutions, without 12HD, were prepared and equilibrated in the same way, to correct for the slight solubility of 1-octanol in water. Solubility measurements of 1-hexanol were performed similarly, except that 1-octanol was replaced by 1-hexanol, to compare its solubility in pure water and aqueous counter-ion solutions. The same Raman system described in the previous section was used, with the excitation beam focused within the aqueous phase. The Raman-MCR based method for obtaining the influence of ions on the solubility coefficients, k_s, of 12HD were performed by measuring the integrated area of the C-H band in fully equilibrated two-phase solutions created using either pure water and an aqueous counter-ion solution, as previously described[5] and summarized below.

The influence of ions on solubility is often quantified using the Setschenow (or Sechenov or Setchenov) coefficient, defined as $\frac{1}{C_s} log\left(\frac{S_0}{S}\right)$, where S_0 and S are the solubilities in pure water and the ionic solution, and C_s is the salt (or counter-ion) concentration. Here we use the following closely related expression to define the solubility coefficient, k_n, pertaining to the influence of salt (or other counter-ions) on the chemical potential of a solute in an aggregate of size n.

$$\mu_{n,s}^{0} = \mu_n^0 + k_n C_s \tag{1}$$

Thus, k_n is related to the solubility of the oily solute as follows

$$k_n = \frac{RT}{C_S}\ln\left(\frac{S_0}{S}\right) = \frac{RT}{C_S}\ln\left(\frac{P}{P_0}\right) \tag{2}$$

where R is the molar Boltzmann constant and T is the absolute temperature, and P_0 and P are the n-octanol/aqueous partition coefficients in pure water and aqueous ionic solutions, respectively.

The above expressions pertain to the dilute limit, in which the concentrations of both the salt and solute are sufficiently low that the ionic and molecular species (including aggregates) do

not significantly interact with each other. The last equality in Eq. 2 assumes that ions remain primarily in the aqueous phase and thus do not influence the solvation free energies in n-octanol. The experimental determination of k_n is facilitated by the observation that free energies of solvation and micelle formation typically have a linear dependence on counter-ion concentration up at least ~2 M.[1, 2]

2. Theoretical Methods

MCPS Theory

The following is a summary of the MCPS theoretical formalism,[4] as applied to the experimental determination of aggregate size distributions in pure water and aqueous ionic solutions. The equilibrium between free (fully hydrated) solutes and aggregates may be expressed as follows

$$K_n = \frac{[n]}{[1]^n} = \frac{\frac{1}{n}C_n}{(C_1)^n} = \left(\frac{1}{n}\right)(C_A)^{1-n} \tag{3}$$

where $[n]$ is the concentration of aggregates of size n.

The second equality in Eq. 3 introduces the solute concentration-based notation, where $C_n = n[n]$, is the concentration of solutes that are contained in aggregates of size n (and thus C_1 is a free surfactant monomer). The third equality introduces the n-dependent critical aggregation concentration, C^*_A, which may be used to re-express Eq. 3 as $C_n/C_A = (C_1/C_A)^n$, where C^*_A is related to the aggregation free energy and solute chemical potentials as follows.

$$C^*_A = \left[\left(\frac{1}{n}\right)e^{\beta\Delta G^0_n}\right]^{\frac{1}{n-1}} = \left(\frac{1}{n}\right)^{\frac{1}{n-1}}\left(e^{\beta\Delta\mu^0_n}\right)^{\frac{n}{n-1}} \tag{4}$$

Note that C^*_A is equivalent to free monomer concentration above which the concentration of aggregate-bound solutes exceeds that of free solutes. More specifically, when $C_1 = C_A$ then $C_m = C_1 = C_A$, while when C_1 is either less or greater than C_A, then C_m will either be much less than or much greater than C_1, respectively. The aggregation free energy is $\Delta G^0_n = \bar{G}^0_n - n\bar{G}^0_1 = n\mu^0_n - n\mu^0_1 = n\Delta\mu^0_n$, where $\bar{G}^0_n = n\mu^0_n$ and $\bar{G}^0_1 = \mu^0_1$ are the corresponding partial molar Gibbs energies of an aggregate of size n at a standard state concentration of $[n] = [1] = 1$ M, and μ^0_n is the chemical potential of a surfactant that is contained in an aggregate of size n. The multi-aggregation chemical potential surface (MCPS) is $\Delta\mu^0_n = \mu^0_n - \mu^0_1$, which corresponds to the n-dependent chemical potential in the aggregate, relative to the free monomer.[4] The 1M reference solutions are implicitly assumed to be ideal, in the sense that the aggregates and monomers are assumed not to interact significantly with each other. One may alternatively choose some other reference concentration by, for example, expressing all concentrations in mM units, thus implying a reference concentration of 1 mM. Note that Eqs. 3 and 4 are consistent with $\Delta G^0_n = -RT\ln K_n = -RT\ln\left[\frac{1}{n}C_n/(C_1)^n\right]_{eq}$, where C_n and C_1 are the corresponding equilibrium solute

concentrations. This also implies that the Gibbs energy of an n-fold aggregation reaction at any other (non-equilibrium) concentrations, C_n and C_1, may be expressed as follows.

$$\Delta G_n = \Delta G_n^0 + RT\ln\left(\frac{\frac{1}{n}C_n}{C_1^n}\right) \tag{5}$$

Note that C_1 and C_n in Eq. 5 need not be equilibrium concentrations, but if they are then $\Delta G_n = 0$. If the system were entirely composed of free monomers and aggregates of exactly one size $n = n^*$ then C_A^* (at $n = n^*$) would be equivalent to the corresponding CMC. However, in a system containing a distribution of aggregates of various sizes, C_A^* may no longer be equal to the experimentally measured CMC, defined as the apparent free monomer concentration C_f at which the micelle-bound surfactant concentration is $C_m = C_f$, where C_f is defined as

$$\frac{C_f}{C_T} = \frac{1}{C_T}\sum_{n=1}^{n_L}\left(\frac{n_L + 1 - n}{n_L}\right)C_n = \frac{\langle\omega\rangle - \omega_m}{\omega_f - \omega_m} \tag{6}$$

where $n \le n_L$ is the range of low-order aggregate sizes that are included in C_f.[4]

The second equality provides the connection between MCPS and the experimental C-H frequency measurements, where $\langle\omega\rangle$ is the Raman-MCR average C-H frequency at a given concentration of 12HD (and ions), and ω_f and ω_m are the corresponding free and micelle-bound frequencies, which may be obtained by extrapolation of the MCPS fits to 0 and infinite C_T. Equivalently, the following hybrid strategy, described in the Appendix of reference,[4] may be used to obtain free monomer fractions directly from C-H band shape changes, rather than from the corresponding average frequencies. This strategy is equivalent to replacing the right-hand side of Eq. 6 by $(S - S_f)/(S_m - S_f)$, where S, S_f and S_m are the total least squares (TLS) coefficients obtained from fitting Raman-MCR C-H band spectra to a linear combination of a pair of spectra measured at low and high concentration, where all the input spectra are normalized to unit area over the C-H band frequency range of interest. The limiting TLS coefficients S_f and S_m are those extrapolated to 0 and infinite C_T, using the MCPS fits as previously described.[4] More specifically, the coefficients S, S_f and S_m are referred to as S_L, S_L^0 and S_L^∞, respectively, in the Appendix of ref. 4, and Eq. A1 in ref. 4 should be replaced by $S_L = \frac{C_f}{C_T}\left(S_L^0 - S_L^\infty\right) + S_L^\infty$, which is equivalent to $C_f/C_T = \left(S_L - S_L^\infty\right)/\left(S_L^0 - S_L^\infty\right)$. The above hybrid strategy produces the same C_f/C_T values as those obtained using average C-H measurement. The hybrid strategy is somewhat more robust, and thus is preferred, since it relies on information obtained from the entire C-H bandshape rather than only from the corresponding average C-H frequencies.

The total free energy change, ΔG, for such a pseudo-two-component aggregation process with a total surfactant concentration of $C_T = C_f + C_m$ may be expressed as follows

$$\Delta G \approx \Delta G^{0}_{n^*} + RT\ln\left[\frac{\frac{1}{n^*}C_m}{(C_f)^{n^*}}\right] = n^*\Delta\mu^{0}_{n^*} + RT\left[\ln\left(\frac{1}{n^*}\right) + (1-n^*)\ln\left(\frac{1}{2}C_T\right)\right] \quad (7)$$

where the last equality is obtained assuming the (non-equilibrium) solution consists of an equal mixture of free and bound solutes, such that $C_f = C_m = \frac{1}{2}C_T$.

The MCPS formalism is quite general as it can be applied to both micelle formation and other sorts of aggregation processes, depending on the functional form of the MCPS, $\Delta\mu_n^0$. Moreover, it has recently been demonstrated that the aggregation of 12HD and other micelle-forming surfactants, both below and above CMC, are well described by assuming that $\Delta\mu_n^0 = \mu_n^0 - \mu_1^0$ is a quadratic function of n,[4] thus justifying the use of the quadratic MCPS model in the present analyses. The quadratic MCPS model has one primary parameter, corresponding to $\Delta\mu^{0}_{n^*}$, equivalent to the minimum value of $\Delta\mu_n^0$, at $n = n^*$, which determines both the experimental CMC and the characteristic size of the micelles, whose aggregate size distribution is peaked near n^*. The width of the aggregate size distribution is also determined by the above two parameters, since the width is dictated by the curvature of the quadratic $\Delta\mu_n^0$ function, and $\Delta\mu_n^0$ is assumed to be smooth function of n down to $n = 1$ (at which $\Delta\mu_1^0 = 0$), in keeping with the physically grounded requirement that the $\Delta\mu_n^0$ cannot differ much from its values at $n \pm 1$.[4] The only other parameter in the MCPS model is n_L, which determines the range of aggregate sizes that are included in the pre-micellar low-order aggregate size distribution,[4] The values of $\Delta\mu^{0}_{n^*}$ and CMC may be more accurately determined than the values of n^* and $n_L$but the uncertainties of the latter two parameters do not significantly influence the resulting CMC (as shown in Fig. 1, and associated text, in the parent manuscript).

Influence of Ions on Solubility and the MCPS

The influence of ions on the MCPS may be expressed as

$$\Delta\mu^{0}_{n,s} = \Delta\mu_n^0 + \Delta k_s C_s \quad (8)$$

where $\Delta\mu^{0}_{n,s} = \mu^{0}_{n,s} - \mu^{0}_{n,1}$ and $\Delta k_s = k_n - k_1$ is the difference between the salt-induced solubility coefficients for a surfactant in an aggregate of size n and a free surfactant, at as salt concentration of C_s.

Thus, the n-dependent aggregation concentrations $C_A(n)$ and apparent CMC in a given salt solution may be obtained using Eq. 4, upon replacing $\Delta\mu_n^0$ by $\Delta\mu^{0}_{n,s}$ and ΔG_n^0 by $\Delta G^{0}_{n,s} = n\Delta\mu^{0}_{n,s}$. The salt-induced solubility coefficients, and thus their influence on micelle formation, may also be described using Kirkwood-Buff and Wyman-Tanford theories, as previously described[3, 5, 6]. Specifically, these theories relate k_n to the partitioning of ions between the bulk aqueous solution and the hydration-shell of a solute, such that a positive or negative k_n indicates either the expulsion or accumulation, respectively, of ions around the solute.

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