

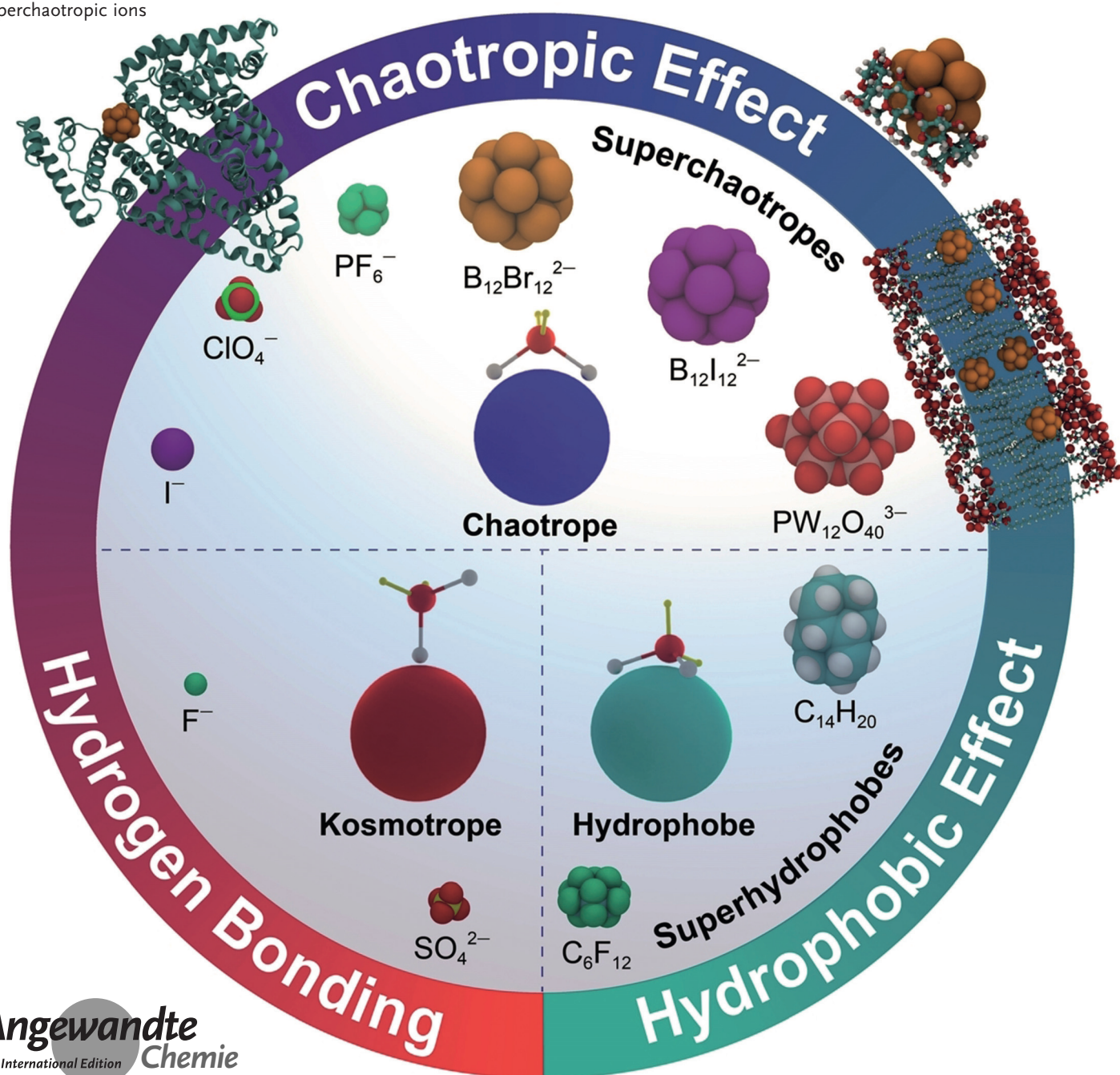
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The Chaotropic Effect as an Assembly Motif in Chemistry

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Following up on scattered reports on interactions of conventional chaotropic ions (for example, I^- , SCN^- , ClO_4^-) with macrocyclic host molecules, biomolecules, and hydrophobic neutral surfaces in aqueous solution, the chaotropic effect has recently emerged as a generic driving force for supramolecular assembly, orthogonal to the hydrophobic effect. The chaotropic effect becomes most effective for very large ions that extend beyond the classical Hofmeister scale and that can be referred to as superchaotropic ions (for example, borate clusters and polyoxometalates). In this Minireview, we present a continuous scale of water–solute interactions that includes the solvation of kosmotropic, chaotropic, and hydrophobic solutes, as well as the creation of void space (cavitation). Recent examples for the association of chaotropic anions to hydrophobic synthetic and biological binding sites, lipid bilayers, and surfaces are discussed.

1. Introduction

Hydrogen bonding and the hydrophobic effect are the two overarching concepts in the understanding of associative and dissociative processes in water, including aqueous solvation, protein folding, and molecular self-assembly.^[1–6] Specific-ion solvation has additionally been related, since Hofmeister, to the kosmotropic (water-structure-forming) and chaotropic (water-structure-breaking) properties of ions.^[7–9] Following up on scattered reports on the unusual behavior of large anions,^[10–18] the propensity of these anions to associate with hydrophobic and neutral polar phases has recently been generalized and named the chaotropic effect, contrasting the hydrophobic effect as a distinct assembly motif in chemistry.^[3,19,20] The effect becomes particularly pronounced for superchaotropic ions that reach beyond the classical Hofmeister scale.^[10,18] The chaotropic effect extends to molecular recognition events with macrocyclic hosts,^[10,12,21–27] biologically relevant interactions with proteins and peptides,^[13,28–32] association to small organic molecules,^[10,33] binding to membranes,^[17,34–38] polymers,^[39] as well as colloids,^[15,18,40] and it manifests itself in solid-state structures between superchaotropic ions and organic components.^[10,12,26,41,42] The terms “chaotropic effect” and “superchaotropic ions” have been readily absorbed by the chemical literature in different contexts.^[11–13,15–18,22,24,28,40,41,43–54] This relevance in several areas of chemistry reveals the chaotropic effect as a generic driving force, orthogonal to the hydrophobic effect. Its operation and impact have been rapidly unfolding during the last three years and are therefore reviewed herein.

We will first propose a conceptual rationalization of different modes of aqueous solvation that seamlessly merge the three principle solvation patterns, which span from hydrogen bonding to the hydrophobic effect and position the chaotropic effect in the transition region. The discrete solvation modes have thermochemical fingerprints, which can be used to pinpoint the dominant driving force of supramolecular assembly processes in water. The individual phenomena, for which the chaotropic effect plays a key role, will be subsequently discussed.

2. Principle Modes of Solvation in Water

The effect of different solutes on the water structure can be understood and visualized by the way that water molecules arrange themselves around a solute (Figure 1a). Keeping in mind the tetrahedral coordination pattern of each water molecule, both the relative orientation of the tetrahedron to the convex solute surface (apical, lateral, and basal) as well as the involved interaction sites at the apex, edge, or base (hydrogen atoms or electron lone pairs) need to be specified. Such a pictorial view of water–solute interactions derives from the previously introduced views by Herzfeld^[55] and Collins,^[56] among others. We stress that even

a well-established phenomenon such as the hydrophobic effect turns out to be extremely intricate at the level of accurate molecular understanding and quantitative predictions remain subject to debate.^[57–62] The same applies for the chaotropic effect addressed herein, such that the presently proposed qualitative arguments and quantitative explanations present our own current stage of rationalization.

Any solvation of a solute requires the creation of a cavity (Figure 1a, right) around which water molecules arrange themselves with the sole objective of retaining most of the stability of the original hydrogen-bonding network. In the absence of intermolecular interactions with the solute, no preferential orientation of the individual water molecules towards the surface of the cavity results, leading to both hydrogen atoms and lone pairs pointing to the convex surface. Common kosmotropic ions are characterized by a small size and large charge density. The positioning of a kosmotropic anion in the cavity results in highly directional hydrogen-bonding or coordinative interaction, which leads to a strong apical orientation of the water molecules (Figure 1a, left). Chaotropic ions are typically large and charge-delocalized. The positioning of a chaotropic ion in the cavity causes less directional ion–dipole interactions to predominate, which results in a lateral orientation of the water molecules under alignment of their dipole moment (Figure 1a, second from the left). The positioning of a hydrophobic solute in the cavity

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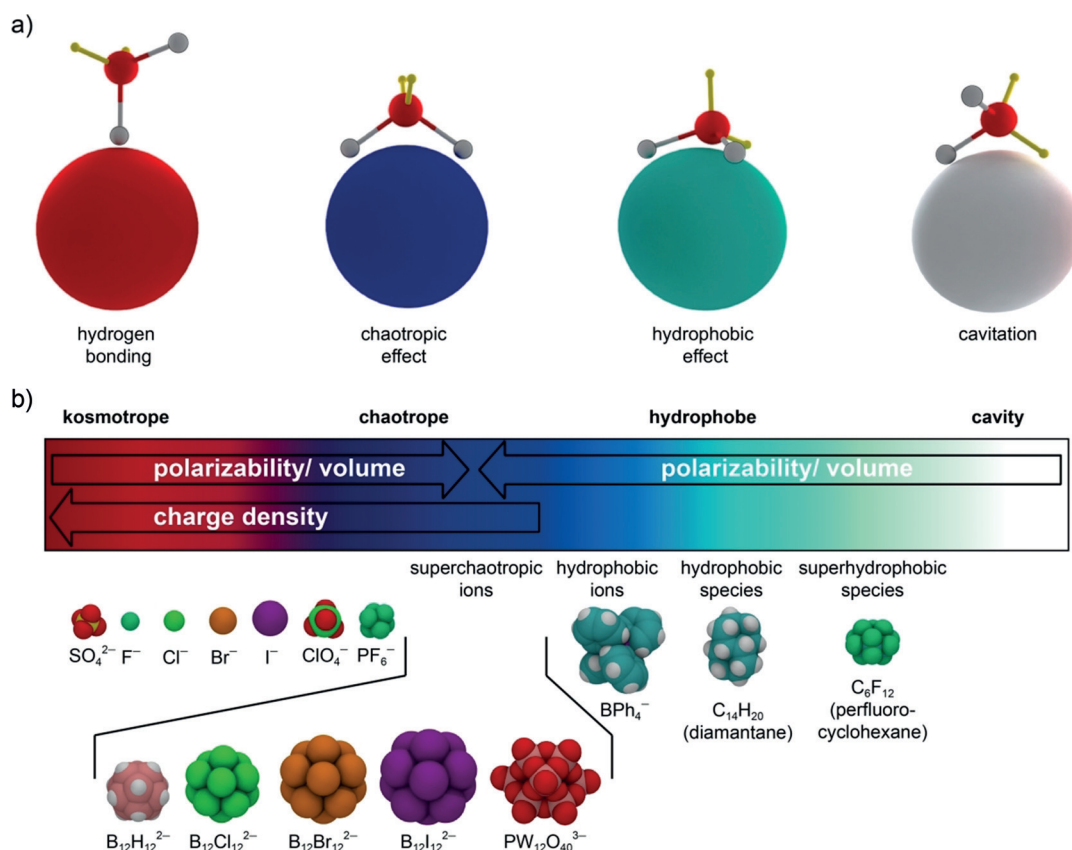


Figure 1. Principal aqueous solvation patterns for anions. a) Presumed favorable orientations of water molecules around a cavity and at the surface of different solutes: kosmotropic and chaotropic ions, hydrophobic molecules, and void space. Electron lone pairs are visualized in yellow. b) Extended Hofmeister scale with specification of the superchaotropic, hydrophobic ionic, and superhydrophobic regions; see Figure S1 in the Supporting Information for a two-dimensional illustration of the solvation pattern dependence on charge density and polarizability.

activates predominantly distance-dependent dispersion interactions, which lead to a preferred basal orientation of the water molecules, maximizing the proximity to bonding electrons, lone pairs, and the oxygen atom (Figure 1 a, second from the right). For cations instead of anions, the principle orientations of the water molecules (apical versus lateral) remain the same except that the interactions occur through the lone pairs instead of the hydrogens, with only the latter variant shown in Figure 1 a.

The pictorial representations of the different aqueous solvation modes allow us to advance a continuum model for solvation, which not only spans from kosmotropes to chaotropes but extends further to hydrophobes and, ultimately, an empty cavity (Figure 1 b).^[63] This continuum view of solvation corresponds to a gradual change of the preferred orientation of the inner-sphere water molecules from apical (left) to lateral to basal. The continuum includes as prominent cases the established effects of hydrogen bonding (coordinative



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bonding) and the hydrophobic effect. As an additional effect, the chaotropic effect emerges in the transition region beyond the classical Hofmeister scale (kosmotrope–chaotrope) and the recognized hydrophobic domain, which spans from hydrophobic ions to neutral species. Others and we have recently introduced the term “superchaotropic”, akin to superhydrophobic, for those ions that exceed common chaotropic properties.^[10,15,16,18,23,41,64] Superchaotropic ions do not display hydrophobic properties by the common definitions but instead give rise to peculiar effects that are summarized in this review and can be understood as being a consequence of the chaotropic effect. The continuum scale for aqueous solvation can be further extended to superhydrophobic species (negligible dispersion) up to vacuum (no interaction); the latter describes the solvation around a formed void in water (cavitation). It is consequential that the water orientations induced by the different types of dominant intermolecular interactions in the first hydration shell (Figure 1a) have characteristic consequences for the hydrogen-bonding network in the entire solvation shell. This accounts for many of the physicochemical and thermochemical properties of the associated solvation processes, including the entropic signature of the hydrophobic effect,^[3,20,65,66] the hydrogen-bond-forming or disrupting effect of kosmotropes and chaotropes,^[67] as well as the associated enthalpic signatures.^[68]

3. Thermochemical Hydration Characteristics

The immersion of a hydrophobic species such as an alkane or noble gas in water is classically thought to be accompanied by a structuring of the solvation shell around the solute and a negative entropic contribution of hydration (Frank–Evans model).^[69] Accordingly, the association of such a hydrophobic species with an organic binding site, such as a macrocyclic cavity, should be characterized by an entropic driving force, which can be traced to the destruction of the structured water shell around the solvated hydrophobic solute. This presents the signature of the classical hydrophobic effect.^[3] For example, the aqueous association of the highly hydrophobic adamantane and triamantane cores to γ -cyclodextrin (γ -CD), a prototypal macrocyclic host, shows this thermochemical behavior (Figure 2).^[70–73] Although the iceberg model suggested by Frank and Evans and the related explanation for the hydrophobic effect have been much debated, it remains appealing today because of the constant and recent experimental support in its favor. For example, the water molecules around noble gases have recently been spectroscopically demonstrated to resemble the structure of ice^[74,75] and the rotational dynamics of water molecules in the solvation shell around hydrophobes is reduced.^[76,77]

Recently, we have observed that the unexpectedly strong binding of large dodecaborate anions ($B_{12}X_{12}^{2-}$) to the same macrocycle, γ -CD, displays a diametric thermochemical signature; that is, it is enthalpically driven with a negative entropic component (Figure 2).^[10,23] Since the driving force for this aqueous binding phenomenon could not be related to the hydrophobic effect (the dianions themselves are not

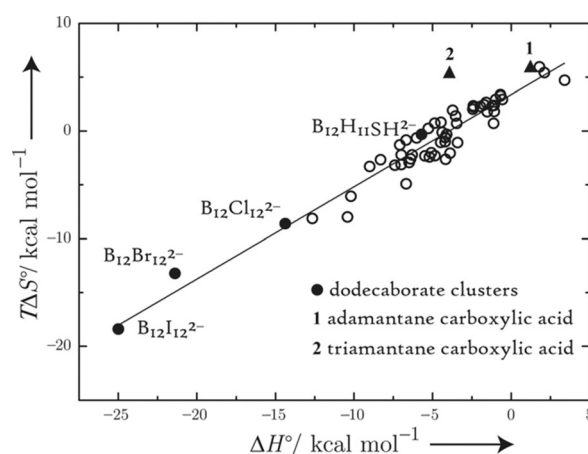


Figure 2. Enthalpy–entropy compensation plot for γ -CD complexes with dodecaborate anions and previously reported γ -CD complexes with diverse organic guests.^[10]

hydrophobic species, see below), we considered kosmotropic and chaotropic ion properties as spanned by the Hofmeister series ($SO_4^{2-} < F^- < HPO_4^{2-} < CH_3COO^- < Cl^- < Br^- < NO_3^- < I^- < ClO_4^- < SCN^-$), a scale originally defined on the basis of salting-out and salting-in effects of ions on egg whites and serum proteins.^[8] Indeed, it turned out that the dodecaborate clusters behave as superchaotropic anions; that is, their chaotropic properties such as salting-in effects exceed those of accepted chaotropes (ClO_4^- , SCN^- , $PF_6^- \ll$ large anions). For example, they significantly increase the solubility of adenine and riboflavin, two established salting-in standards.^[10] Accordingly, we proposed a new effect, the chaotropic effect, as an alternative driving force, which drives the association of (super)chaotropic ions with hydrophobic and neutral matter. The chaotropic effect needs to be differentiated from unspecific Hofmeister effects, in that it accounts for specific chaotrope–solute interactions.

The thermochemical fingerprint for the binding of chaotropic anions can be contrasted to that for the binding of hydrophobic species. Even though both effects relate to desolvation, the hydration shell around a hydrophobe is highly structured while that around a chaotrope is less structured and less hydrogen bonded, relative to bulk water. The desolvation process is therefore classically entropically driven in the case of hydrophobes,^[3] while for chaotropes a dominant negative enthalpic component and an unfavorable entropic term applies. Upon desolvation, the hydration shell around the chaotrope is stripped off and allowed to regain the hydrogen bonds of the aqueous bulk.^[10] This rationalization is fully in line with the original classification of chaotropic ions as being “water-structure breakers”,^[78] such that their desolvation (due to binding to other species) leads formally to a “water structure recovery”.^[10] As is the case with the debate on the origin of the hydrophobic effect, the interpretation of Hofmeister effects has been similarly controversial, with undeniable pieces of evidence in favor of water-structure breaking effects of chaotropic ions in their solvation shell being known, for example, trends of viscosity B-coefficients.^[79]

Marcus has devised, based on experimental ion properties, an empirical scale for water-structural entropies for ionic hydration (ΔS_{struct} , listed in Table 1 for selected anions), which allows also an assessment of the (kosmotropic and chaotropic) properties of ions and of the thermochemical trends related to their (de)hydration.^[68,80] In a chemometric sense, Table 1 can be viewed as a chaotropicity scale, in this case for anions. If the ΔS_{struct} values are positive, the water structure in their surrounding decreases, which can be (again empirically) converted into an effective loss of hydrogen bonds in the entire solvation shell around the ion (negative values of ΔHB).^[68] Ions unambiguously qualify as chaotropes if $\Delta HB < -1$ (or $T\Delta S_{\text{struct}} > 5 \text{ kcal mol}^{-1}$); superchaotropic anions, such as borate clusters, reach values lower than circa -2 (or $T\Delta S_{\text{struct}} > 9 \text{ kcal mol}^{-1}$).

We further concluded that the chaotropic effect presents a generic driving force that accounts for the intrinsic affinity of chaotropic ions, prominently anions, for neutral organic or inorganic matter, including concave macrocyclic binding sites, lipid bilayers, membranes, and polymers.^[11–13, 16–18, 22, 24, 28, 40, 43–48] It should be noted that indications for the affinity of anions to hydrophobic binding sites existed early in the literature^[81–103] but were in part attributed to a putative hydrophobic (or lipophilic) property of large anions, implying the hydrophobic effect as driving force. The hydrophobic and chaotropic effect can and need to be conceptually distinguished for the reason stated above and also because the hydrophobic nature of a solute is subject to a conventional definition, which chaotropic ions do not fulfill. Specifically, as shown in Table 2, hydrophobic species display positive free energies of hydration, small enthalpies of hydration, and large positive heat capacities of hydration,^[104–106] prerequisites that are not fulfilled by chaotropic ions. Rather, chaotropic anions can be classified as hydrophilic on ion-solvation scales.^[107,108] Classifications of chaotropic ions as hydrophobic, occasionally found in the literature,^[109–119] are unfortunate because they may lead to incorrect assignments in terms of the underlying driving force for associative processes. Vice versa, hydrophobic ions do actually exist, such as BPh_4^- , $(\text{C}_2\text{F}_5)_3\text{PF}_3^-$, and AsPh_4^+ ,^[80,120–122] and it is also important not to label these as being superchaotropic^[47,51,52,123] when sequences of ionic properties, scales for ionic solvation, or reasons for aqueous assembly processes are being developed. Superchaotropic and hydrophobic ions are neighbors on the continuum solvation scale in Figure 1 b (because they are both large and highly polarizable), but they would differ in terms of their surface charge density and dominant water-solvation

Table 1: Chaotropicity scale based on the ion hydration parameters proposed by Marcus (Refs. [68,80]): Water-structural entropies of different anions ($T\Delta S_{\text{struct}}$), their size (radius, r), and net effects on the number of surrounding hydrogen bonds (ΔHB).

anion	r [pm] ^[a]	$T\Delta S_{\text{struct}}$ [kcal mol ⁻¹] ^[b]	ΔHB ^[c]
kosmotropes			
SO_4^{2-}	230	-6.7	0.78
HPO_4^{2-}	238	-4.4	0.46
CO_3^{2-}	178	-4.0	0.40
F^-	133	-2.1	0.12
chaotropes			
Br^-	196	5.8	-1.01
SCN^-	213	5.9	-1.03
BF_4^-	230	6.6	-1.12
ClO_4^-	240	7.6	-1.27
I^-	220	8.3	-1.37
PF_6^-	295 ^[d]	8.7	-1.43 (1.93) ^[e]
superchaotropes			
$\text{Fe}(\text{CN})_6^{3-}$	373	12.8	-2.01 ^[e]
$\text{S}_2\text{O}_8^{2-}$	300	13.0	-2.04 ^[e]
$\text{S}_4\text{O}_6^{2-}$	310	13.2	-2.06 ^[e]
$\text{B}_{10}\text{H}_{10}^{2-}$	393 ^[f]	11.5	-1.83
$\text{B}_{12}\text{H}_{12}^{2-}$	400 ^[f]	14.8	-2.31
$\text{B}_{12}\text{F}_{12}^{2-}$	430 ^[f]	12.6	-1.98
$\text{B}_{12}\text{Cl}_{12}^{2-}$	525 ^[f]	15.3	-2.37
$\text{B}_{12}\text{Br}_{12}^{2-}$	560 ^[f]	16.3	-2.51
$\text{B}_{12}\text{I}_{12}^{2-}$	590 ^[f]	17.1	-2.63
$\text{PMo}_{12}\text{O}_{40}^{3-}$	629 ^[f]	18.2	-2.79
$\text{PW}_{12}\text{O}_{40}^{3-}$ ^[g]	654 ^[f]	18.9	-2.89
$\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ ^[h]	701 ^[f]	20.3	-3.08

[a] As tabulated in Refs. [80, 124]. [b] Calculated according to Marcus, see Refs. [80, 124], values for ions for which no hydration enthalpies are known were interpolated (for PF_6^-) or extrapolated (for borate clusters and POMs) from a correlation of ΔS_{struct} versus r for chaotropic anions listed in this table as well as the data for SiF_6^{2-} , PdCl_6^{2-} , PtCl_6^{2-} , $\text{Co}(\text{CN})_6^{3-}$, and $\text{Fe}(\text{CN})_6^{4-}$ ($\Delta S_{\text{struct}} = 4.48 + 0.399r$, $n = 14$, $r = 0.77$).

[c] From eq. 25 in Ref. [68], there abbreviated as ΔG_{HB} . [d] From Ref. [125]. [e] From Ref. [124], multiplied with the correction factor of 1.25 subsequently introduced in Ref. [68]. [f] Calculated from the diameter (the distance between the outer atoms including the vdW radii) obtained from their geometry-optimized structures (for borate clusters) or XRD structures (for POMs). [g] Keggin-type POM. [h] Dawson-type POM.

pattern (Figure 1 a). This is reflected, among other things, in hydration thermochemical data, which in the case of hydrophobic ions are diagnostic for hydrophobic species (Table 2). Note that the primary thermochemical data in Table 2 do not allow a ready distinction between kosmotropic and chao-

Table 2: Thermodynamic hydration data for selected solutes.

	kosmotropic anion F^-	chaotropic anion SCN^- ClO_4^-	superchaotropic anion $\text{B}_{12}\text{H}_{12}^{2-}$	hydrophobic ion BPh_4^- AsPh_4^+	hydrophobic neutral species CH_4
ΔG_{hyd} ^[a]	-112.1 ^[b]	-69.6 ^[b] -54.7 ^[b]	-140 ^[c]	10.8 ^[b] 10.3 ^[b]	2.0 ^[d]
ΔH_{hyd} ^[a]	-121.9 ^[b]	-74.3 ^[b] -58.8 ^[b]	-145 ^[e]	-11.2 ^[b] -11.2 ^[b]	-2.6 ^[d]
$T\Delta S_{\text{hyd}}$ ^[a]	-9.8 ^[b]	-4.7 ^[b] -4.1 ^[b]	-5 ^[f]	-22.0 ^[b] -21.5 ^[b]	-4.6 ^[d]
$\Delta_{\text{hyd}}C_p$ ^[g]	-14.1 ^[h]	1.4 ^[h] -2.2 ^[h]	-	186.7 ^[h] 192.0 ^[h]	52.0 ^[d]

[a] Values in kcal mol⁻¹. [b] From Ref. [126]. [c] From Ref. [127]. [d] From Ref. [105]. [e] Calculated according to $\Delta H_{\text{hyd}} = \Delta G_{\text{hyd}} + T\Delta S_{\text{hyd}}$. [f] From Ref. [128]. [g] Heat capacities in cal K⁻¹ mol⁻¹. [h] From Ref. [129].

tropic character, which led Marcus to introduce the water-structural entropies as diagnostic measure for this ion property (Table 1), with water-structural entropy (ΔS_{struct}) being a function of hydration entropy of the ion (ΔS_{hyd}) and its radius (r).^[68]

It follows that the chaotropic and hydrophobic effect as driving forces in aqueous solution can be empirically and experimentally distinguished by inspection of the hydration characteristics of the involved species (Tables 1 and 2) and also by measurement of the thermodynamics (Figure 2) of the corresponding supramolecular assembly processes.

4. Examples

The chaotropic effect accounts for the association of chaotropic anions to neutral binding sites, surfaces, and phases. Following its nature as a generic driving force in aqueous solution, the chaotropic effect has recently been shown to have an impact on diverse areas of chemistry, ranging from molecular recognition and supramolecular chemistry to biologically relevant interactions with membranes, lipids, and proteins, to polymer and colloid chemistry. While scattered indications for such interactions of chaotropic ions, predominantly anions, were known, the conceptualization and generalization of the chaotropic effect has only emerged very recently, made possible by a sequence of striking observations for very large anions such as borate clusters and polyoxometalates (POMs) for which the effect is particularly pronounced. Accordingly, the unfolding of the chaotropic effect is tied to the appreciation of the superchaotropic character of these large anions.

4.1. Supramolecular Chemistry

Macrocyclic hosts are popular in supramolecular chemistry because they possess hydrophobic cavities that mimic biological binding sites, and which can complex hydrophobic guest molecules. Despite the hydrophobic nature of these cavities, early indications for the competitive binding of ions exist.^[96,99,130] Taraszewska and Wójcik were the first to correlate the small but significant binding of simple anions to α -CD and β -CD with the Hofmeister character of the anions.^[99] Recently, while investigating interactions of large dodecaborate cluster dianions of the type $B_{12}X_{12}^{2-}$ ($X = H, Cl, Br, \text{ and } I$) with γ -CD, we observed exceedingly high binding constants,^[10] which for the first time rivaled the binding of highly hydrophobic guest molecules such as adamantane and triamantane.^[70,71] This study has led to the introduction of the terms chaotropic effect and superchaotropic ions.^[10] We contrasted the distinct thermodynamic fingerprints of host-guest complexation driven by the chaotropic versus the hydrophobic effect and traced the negative enthalpies for binding of the large cluster anions back to the desolvation of these superchaotropic ions. We rationalized the affinity trends of different chaotropic and superchaotropic anions in terms of their water-structuring properties as empirically quantified by Marcus (see Table 1). Host-guest dispersion interactions may

contribute to the chaotropic effect, while for the smaller macrocyclic cavities, the release of high-energy water may also play a supportive role (see the Supporting Information for interplay and differentiation of the chaotropic effect from the non-classical hydrophobic effect and dispersion).

Understanding the driving forces between ions and concave binding sites is therefore of prime importance for the supramolecular design of synthetic receptors with defined affinity and selectivity. Accordingly, the unexpectedly high binding affinities of superchaotropic anions and the chaotropic effect as a generic driving force have recently found their entry into the important area of anion recognition.^[44,65,117,131–143]

In follow-up studies with inclusion complexes, the affinity of dodecaborate clusters to cyclodextrins (CDs) has been extended to the larger CD homologues (Figure 3)^[23] as well as other borate clusters,^[14,144] both in solution and in the gas phase.^[14,23,24] The binding propensity of borate clusters has also been demonstrated for calixarenes^[21] and a tetrathiafulvalene host^[24] as an alternative macrocyclic host (Figure 3). Independent evidence for an intrinsic affinity of other large anions, namely the classical Keggin POM ion ($PMo_{12}O_{40}^{3-}$), to γ -CD had been obtained by Stoddart and co-workers,^[26] and we concluded that the arguments in terms of a chaotropic effect being operative are also transferable to this popular class of large anions.^[10] The actual affinities of POMs with CDs have been studied in detail by Cadot and co-workers^[12,22] as well as others.^[25] The chaotropic effect also accounts for the recently reported binding of chaotropic anions to biotinuril,^[98] bambusuril,^[45,46,97,145] hemicucurbituril,^[146] a tricarbazolo triazolophane (not studied in water),^[147] and the so-called octa-acid (see Figure 3 for structures).^[82,83,148–151] The studied chaotropic anions included not only those in Table 1 but also N_3^- , CNO^- , $SeCN^-$, IO_4^- , ReO_4^- , and SbF_6^- . Noteworthy, the thermodynamic fingerprint (enthalpically driven processes with a negative entropic contribution) is identical in all cases, regardless of which type of superchaotropic anion and which macrocycle are being used.^[10,12,22,23,26,97,98] Finally, the inclusion preference of metallo-macrocyclic cage compounds towards chaotropic anions stands out as well but has not been mechanistically rationalized in comparable detail.^[142,143,152]

In many cases, the aqueous solution interactions of large anions with macrocyclic hosts are retained in their solid-state structures. Inclusion complexes are obtained (Figure 4), mostly with partial inclusion owing to the large anion sizes and frequently host-guest complexes of the 2:1 type. This applies to γ -CD/ $B_{12}Br_{12}^{2-}$ (Figure 4a),^[10] γ -CD/ $PMo_{12}O_{40}^{3-}$ (Figure 4b),^[26] and β -CD/ $PMo_{12}O_{40}^{3-}$ (Figure 4c).^[26] The chaotropic effect can also be exploited for the construction of more complex hybrid and hierarchical assemblies, for example, when superchaotropic Dawson-type anions ($[P_2W_{18}O_{62}]^{6-}$) and cations ($[Ta_6Br_{12}(H_2O)_6]^{2+}$) interact with γ -CD (Figure 4d).^[12] Moussawi et al. extended the design to giant Mo-blue ring-shaped anions, $[Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-}$ (Mo_{154}), which themselves are sufficiently large to encapsulate an entire γ -CD/ $[P_2W_{18}O_{62}]^{6-}$ inclusion complex (Figure 4e); the CDs were also found to associate to the outer surface of the large ring-cluster.^[22] Most recently, Ivanov et al. reported strong binding between γ -CD and chalcogenide

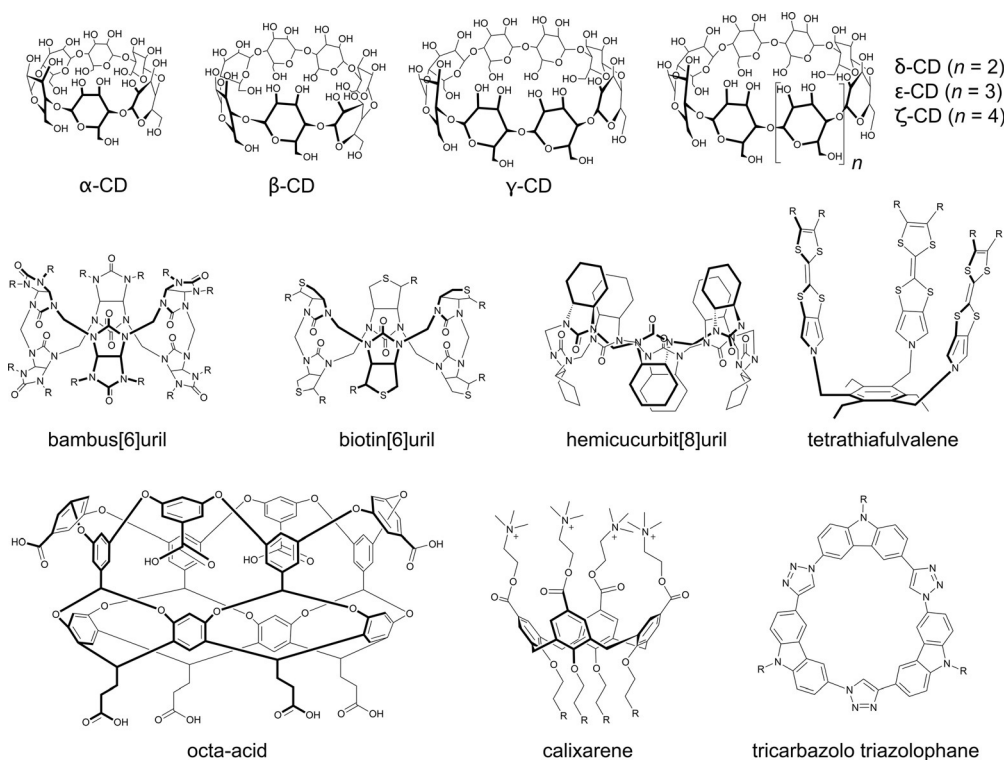


Figure 3. Macrocycles with intrinsic affinity for chaotropic and superchaotropic anions.

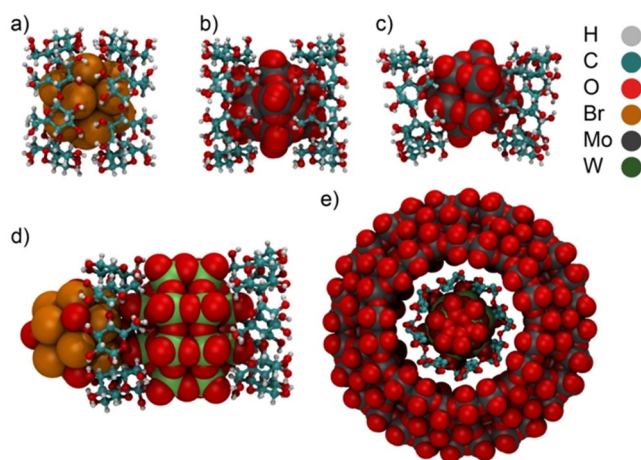


Figure 4. XRD structures for superchaotrope/CD complexes a) γ -CD/ $B_{12}Br_{12}^{2-}$, b) γ -CD/ $PMO_{12}O_{40}^{3-}$, c) β -CD/ $PMO_{12}O_{40}^{3-}$, d) γ -CD/ $[P_2W_{18}O_{62}]^{6-}$ / $[Ta_6Br_{12}(H_2O)_6]^{2+}$, and e) $[Mo_{154}]/\gamma$ -CD/ $[P_2W_{18}O_{62}]^{6-}$.

cluster anions of the type $[Re_6Q_8(CN)_6]^{4-}$ with $Q = S, Se,$ and Te ; their affinities increased in the order $S < Se \ll Te$ and the entropy–enthalpy correlation resembled that of other superchaotropic anions, namely $B_{12}X_{12}^{2-}$.^[27]

The $B_{12}H_{11}SH^{2-}$ ion has recently shown potential as an inorganic capping ligand to stabilize gold nanoparticles.^[21,153] This allows for the creation of hierarchical supramolecular architectures on the surface of gold nanoparticles through

strong host–guest complexation between the dodecaborate anions and an amphiphilic calixarene (Figure 5 a).^[21]

The chaotropic effect accounts for the high affinity of superchaotropic anions to hydrophobic surfaces in general. It is not limited to the interaction with macrocyclic cavities (Figure 3) and the formation of inclusion complexes (Figure 4) but also applies similarly to the interactions with convex surfaces (Figure 6), which accounts for the intrinsic propensity of these large anions to form also exclusion complexes. Indeed, many studies have described their binding to the exterior of macrocycles,^[41,64,84,86–88,90–94,154] where the chaotropic effect applies as well. Most of these cases involve macrocyclic hosts with relatively small cavity size, such that inclusion-type complexes are not possible.^[41,64,94,154] For example, superchaotropic anions, such as POMs and dodecaborate clusters, associate to the hydrophobic exterior of cucurbit[n]uril (CB n) macrocycles (Figure 6).^[41,64,94,154] The large size of superchaotropic anions allows them to interact with several macrocycles in a multidentate manner, which can efficiently induce their precipitation, for example, of CB n . This is counterintuitive because conventional chaotropes are otherwise known to increase the solubility of organic solutes (salting-in Hofmeister effect).^[156] The combination of the chaotropic and hydrophobic effect as assembly motifs has provided a new strategy for engineering multi-responsive supramolecular networks in water (see Figure 5 b and Supporting Information for details).^[41,64]

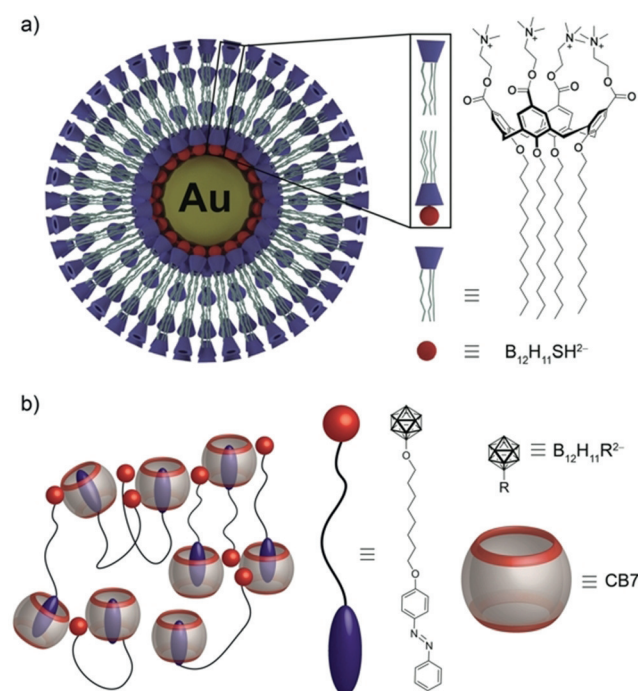


Figure 5. Examples of hierarchical and orthogonal solution-phase architectures exploiting the chaotropic effect as an assembly motif: a) assembly of an amphiphilic calixarene on dodecaborate-stabilized gold nanoparticles and b) assembly of CB7 in the presence of an amphiphilic dodecaborate-functionalized azobenzene. The red residue illustrates a superchaotropic unit as recognition site to the exterior surface of CB7 and the blue unit represents an auxiliary hydrophobic unit that shows a preferential affinity for inclusion complexation with CB7.

4.2. Biologically Relevant Interactions with Proteins, Peptides, and Membranes

The effect of salts on the water-solubility and stability of proteins dates back to the original work by Hofmeister.^[8] Since then, it has become obvious that these salting-in and salting-out effects are unlikely to be primarily related to changes in the bulk water structure; instead, at least in the case of chaotropic anions, direct interactions between the ions and the protein or peptide play also an important role.^[9,157,158] These interactions, which have been demonstrated computationally^[31,32,159] and experimentally,^[7,31,32,56,160] are fully in line with the chaotropic effect, which predicts an intrinsic affinity between chaotropic ions and hydrophobic residues, in this case of biopolymers.

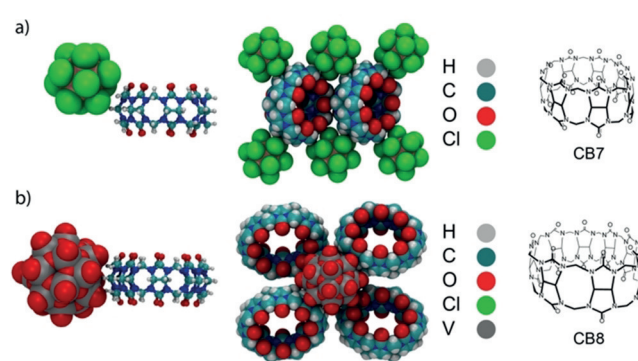


Figure 6. XRD structures of CBn/superchaotropic anion exclusion complexes a) CB7/B₁₂Cl₁₂²⁻ and b) CB8/[H₂O-CV₁₈O₄₂]¹²⁻.

These biologically relevant interactions bear similarities to the host–guest complexation processes discussed above because binding of chaotropic anions to specific binding sites in the protein is also observed. For example, Whitesides and co-workers have shown that weakly hydrated anions (chaotropes) bind to cavities on the surfaces of proteins (the binding pocket of human carbonic anhydrase II) with higher affinity than strongly hydrated anions (kosmotropes).^[161] The thermochemical behavior (Figure 7) for the association process, namely large favorable enthalpic and unfavorable entropic contributions, is in line with the chaotropic effect as a driving force. The authors have also pointed out how the intrinsic affinity of chaotropic anions to proteins relates to other prevalent empirical concepts, such as the law of matching water affinities.^[161] It is worth noting that the large favorable enthalpic contributions for the interactions of large anions with their binding sites are frequently compensated by unfavorable entropic terms resulting from the formation of structured complexes or aggregates.^[10,162]

Indications of interactions of large anions with proteins were known even before their superchaotropic character had been introduced.^[29,163–166] The classification of dodecaborate clusters in 2015^[10] sparked several lines of follow-up work

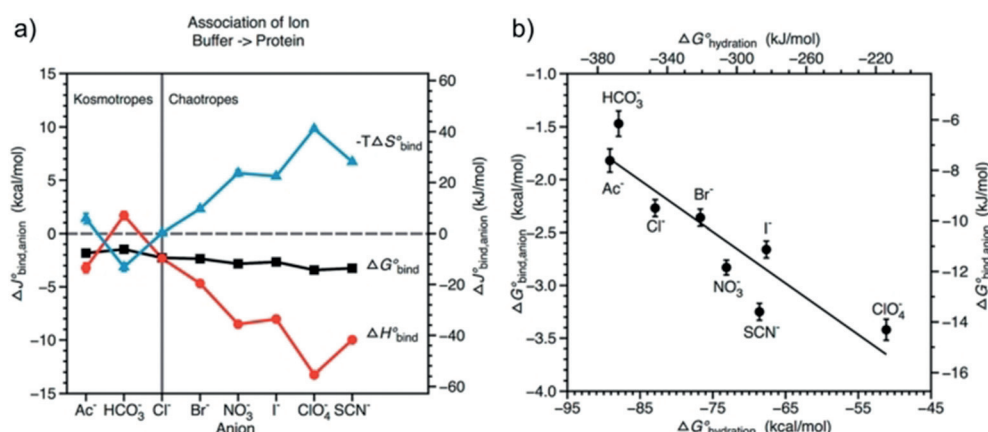


Figure 7. Thermodynamics of anion binding to human carbonic anhydrase II: a) Plot showing the thermodynamic parameters for the association of different anions (298.15 K, pH 7.6, 10 mM sodium phosphate buffer). b) Plot of the free energies of binding ($\Delta G^{\circ}_{\text{bind,anion}}$) versus the free energies of hydration ($\Delta G^{\circ}_{\text{hydration}}$). Reprinted with permission from Ref.[161].

directed towards their direct binding to proteins and led to an interpretation in terms of the chaotropic effect.^[13,28] For example, Kuperman et al. have recently investigated the binding of perhalogenated *closo*-borates ($B_{10}X_{10}^{2-}$ and $B_{12}X_{12}^{2-}$; X: Cl, Br, and I) to bovine and human serum albumins.^[28] The measured binding constants were higher than the values obtained with the parent hydrogen cluster^[165] and varied from 10^4 to $10^6 M^{-1}$. Goszczyński et al. have expanded the interactions with serum albumin from dodecaborates to other hydrophobic or superchaotropic boron cluster types, namely carboranes and metallacarboranes;^[13] they established the affinity order, dodecaborate anion ($B_{12}H_{12}^{2-}$, superchaotropic) \ll carborane ($C_2B_{10}H_{12}$, hydrophobic) $<$ metallacarborane ($[M(C_2B_9H_{11})_2]^-$, superchaotropic).^[13] The interactions of POMs with peptides and proteins, which have recently been reviewed,^[167] are also a consequence of the superchaotropic character and the associated chaotropic effect, as evidenced by the thermodynamic fingerprint (enthalpically driven binding processes with large entropic penalty).^[164] In contrast, some of the interactions of organic ions ($AsPh_4^+$ and BPh_4^-) with proteins are presumably accounted for in terms of their hydrophobic character.^[47,51]

Numerous examples for unspecific interactions of chaotropic anions with biological membranes are also known;^[7,162,168–174] in particular, their membrane-disrupting properties are noteworthy.^[171,172] Gabel and co-workers investigated the interaction between dodecaborate cluster dianions and lipid bilayers;^[34–36,175] at high salt concentrations they observed changes in the morphology of liposomes as well as bilayer leakage (see Figure 8 for an example). The release of the liposomal contents was attributed to interactions between the dodecaborate clusters and lipids, which leads to either the formation of pores or the destruction of the liposomes.^[36] In hindsight, the reported interactions of chaotropic anions with membranes are a prototypal example of the chaotropic effect, which predicts an intrinsic affinity of these anions to associate with hydrophobic phases, such as the interior of bilayer membranes.

Interactions between POM anions and membranes have also been reported.^[37,162,176–178] Jing et al. reported destabilizing effects of a POM macro-ion on the phase and morphology of lipid bilayers.^[162] Nabika et al. reported leakage of egg-

phosphatidylcholine vesicles caused by the Keggin-type POM $SiW_{12}O_{40}^{4-}$ and $PW_{12}O_{40}^{3-}$;^[176] the former anion was also found to interact with a model cell membrane.^[177] Most recently, Nabika and co-workers have traced these interactions, experimentally corroborated through surface-pressure isotherms of ionic and zwitterionic lipids, to the superchaotropic nature of these anions.^[17]

4.3. Interactions with Interfaces and Surfaces

There have been multiple indications of interactions of chaotropic anions with neutral interfaces and surfaces, involving both hydrophobic and polar interfaces as well as hard and soft surfaces. The examples extend from interactions of conventional chaotropic anions with colloids^[121] to their accumulation at the liquid–air interface.^[179–181] Recently, evidence for such interactions has been extended to large anions, including dodecaborate clusters ($B_{12}X_{12}^{2-}$ and $B_{12}X_{11}Y^{2-}$; X = H, Cl, Br, I and Y = SH, OH, NR_3^+) interacting with hydrophilic column materials (Superdex 200, Sepharose 4B, Sephadex G-50, Sephadex G-100, alumina, silica gel, and anion exchange resin)^[182] and carborane clusters (mainly metallacarboranes) accumulating at water–lipid and water–air interfaces.^[183,184] Moreover, akin to the tendency of hydrophobic and classical amphiphilic molecules to form self-assemblies in water, carborane clusters have been found to form micelle-type self-assemblies in water and to show indications of surfactant behavior.^[183,185–188] Halogenated borate clusters accumulate on surfaces by simultaneous adsorption of small neutral molecules.^[189]

With the description of the chaotropic effect as a generic driving force for the assembly of large anions,^[10] these processes can now be described within a uniform mechanistic framework. Indeed, the previously determined thermochemical signature in the solid-phase binding of dodecaborate cluster anions (enthalpically driven binding with large entropic penalty)^[182] fully agrees with this new interpretation. Moreover, in two independent lines of investigation, Matějček and co-workers have established the operation of the chaotropic effect for boron cluster anions,^[11,40,53,190,191] while the group of Bauduin and Diat have expanded the observed

self-assembly and surface-assembly tendencies to POMs as superchaotropic anions.^[15,16,18,192]

In detail, POMs adsorb at micellar surfaces and on monolayers of nonionic surfactants, as shown by using small-angle X-ray scattering (SAXS) and ion flotation techniques.^[16] Cloud point measurements (as a measure of the adsorption strength/association constant of additives with surfactants)^[160] of a triethylene glycol mono-methyl ether solution in the

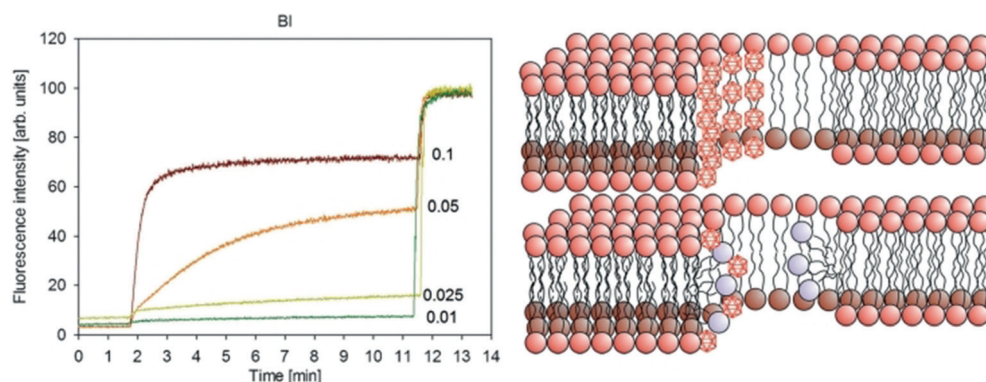


Figure 8. Leakage of carboxyfluorescein (CF) induced by $B_{12}I_{12}^{2-}$ in DSPC liposomes at 37°C. Concentrations of clusters for the individual traces in the graph are given on the left (mM). Suggested mechanism of the interaction between dodecaborate clusters and liposomes (right). Reprinted with permission from Ref. [36].

presence and absence of different anions allowed the classification of POMs ($\text{SiW}_{12}\text{O}_{40}^{4-}$ and $\text{PW}_{12}\text{O}_{40}^{3-}$) as superchaotropic anions, as their effect on the cloud point exceeded those of classical chaotropic anions, indicating strong adsorption of the anionic POMs onto the micellar surfaces (Figure 9).^[16] Most recently, other POMs have also been tested and sorted according to their superchaotropic character, $\text{PW}_{12}\text{O}_{40}^{3-} > \text{PMO}_{12}\text{O}_{40}^{3-} > \text{SiW}_{12}\text{O}_{40}^{4-} > \text{P}_2\text{W}_{18}\text{O}_{62}^{6-} > \text{P}_2\text{W}_{17}\text{VO}_{62}^{7-} \gg \text{SCN}^-$.^[18] The superchaotropic nature of the POM anions was attributed to the efficient charge delocalization over their large surface area (volume), typically at least in the nanometer range. This allows the release of hydration water molecules around the POMs upon adsorption or association, which provides the corresponding driving force,^[18] in line with the entropic component of the water-structure recovery expected for the chaotropic effect.^[10] It should be noted that this alternative experimental scale for (super)chaotropicity is complementary to the empirical scale based on Marcus theory (see Table 1).

The tendency of different boron clusters ($\text{B}_{10}\text{H}_{10}^{2-}$, $\text{B}_{12}\text{H}_{12}^{2-}$, $\text{B}_{12}\text{H}_{11}\text{SH}^{2-}$, 1-carbadodecaborate, and cobalt bis(1,2-dicarbollide)) to self-assemble into aggregates and colloids in water has been detailed by Matějček and co-workers,^[11,188,190,193] while the group of Bauduin and Diat have described the formation of charged nano-colloids from POMs.^[15] The unusual behavior of anionic boron clusters can again be attributed to the chaotropic effect, which complements the classical hydrophobic effect as a supra-molecular assembly and self-assembly motif in water (Figure 10).^[40] The behavior of POMs has also been related to their superchaotropic character.^[16,18] The intrinsic self-assembly tendency of both superchaotropic anions (borate clusters and POMs) accounts also for their high propensity to accumulate at the water–air surface; this leads to surfactant-like behavior, such as a reduction of the surface tension.^[11,40,53,190,191] Accordingly, because they lack the polar head group/hydrophobic tail design of classical amphiphiles,

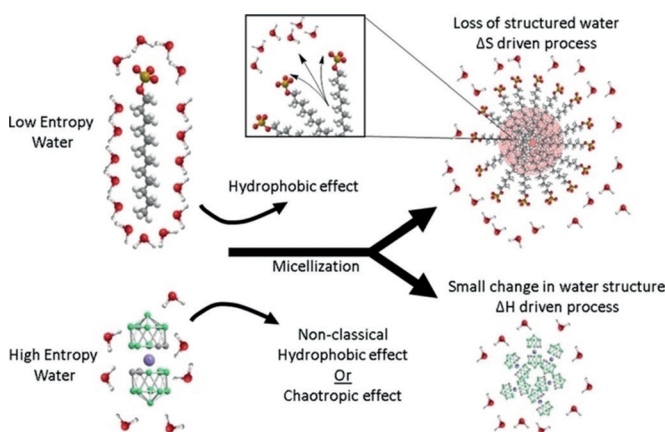


Figure 10. Micellization can be driven by the classical hydrophobic effect (top) or the chaotropic effect (or a combination of the chaotropic and non-classical hydrophobic effect, bottom) with emphasized changes of the hydration shells for the classical surfactant and the large anion cobalt bis(1,2-dicarbollide), COSAN. For a specification of the non-classical hydrophobic effect, see the Supporting Information. Reprinted with permission from Ref. [40].

they have also been classified as non-classical surfactants or “intrinsic amphiphiles”.^[11,40,53,190,191]

5. Conclusions and Outlook

Within less than three years, the chaotropic effect has entered the chemical literature as a generic driving force for diverse assembly processes involving superchaotropic ions. The chaotropic effect can be differentiated from the hydrophobic effect in terms of its characteristic hydration pattern and the thermochemical fingerprint of its associated binding phenomena. Examples include host–guest inclusion complexation, anion recognition, exclusion complex formation and

associated solid-state structures, direct interactions with proteins and membranes, interactions with other interfaces and surfaces, as well as self-assembly. Future research on the chaotropic effect and superchaotropic anions will entail the dissection of dispersion interactions, the design of supramolecular architectures exploiting the hydrophobic and chaotropic effects as orthogonal assembly motifs, and their interactions with inorganic materials.

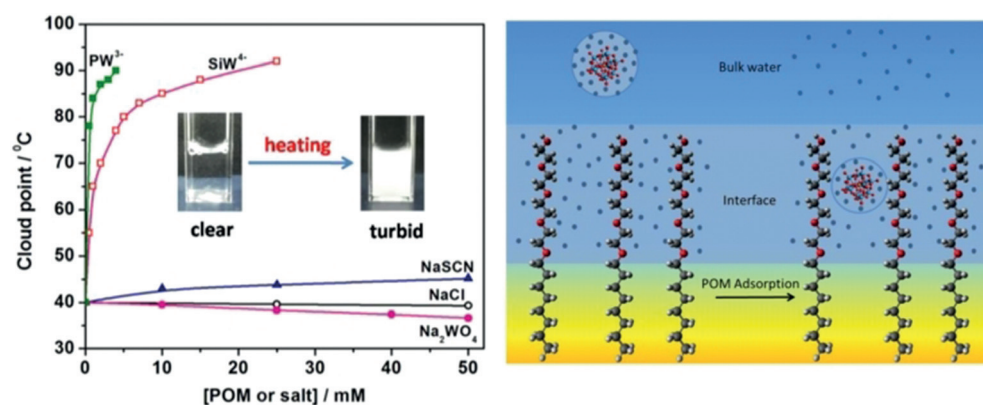


Figure 9. Left: Cloud points of a 60 mM triethylene glycol monomethyl ether solution in the presence of POMs: $\text{SiW}_{12}\text{O}_{40}^{4-}$ ($\text{SiW}_{12}\text{O}_{40}^{4-}$) and $\text{PW}_{12}\text{O}_{40}^{3-}$ ($\text{PW}_{12}\text{O}_{40}^{3-}$) and sodium salts with various representative anions of the Hofmeister series: SCN^- (chaotropic), WO_4^{2-} (kosmotropic), and Cl^- (intermediate between salting-in and salting-out). Inset: Ion-containing surfactant solution at temperatures below (left) and above (right) the cloud point. Right: Schematic of the adsorption of a POM anion on a hydrophilic interface covered by a polyethoxylated surfactant (right). Reprinted with permission from Ref. [16].

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Conflict of interest

The authors declare no conflict of interest.

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