

The 'Caesium Effect' Revisited

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The so-called caesium effect, encountered in synthetic organic chemistry, is tentatively explained in terms of potential surfaces. It is presumed that salts in solution exhibit at least short-range order due to neighbour and next-neighbour interactions. The arrangement of the ions provides zero- and equi-potential surfaces, the geometry of which are used in the interpretation.

Two different but related effects depend on the presence of caesium ion in organic synthetic chemistry: (i) the efficient alkylation of caesium carboxylates with e.g. alkyl halides^{1,2} and (ii) macrocyclization involving hydrocarbon or polyether chains.^{3,4} In the first case alkylation proceeds more readily with caesium as the counter-ion when compared with the other alkali-metal ions. In the second case, the presence of caesium ion favours intramolecular substitution over intermolecular, providing easy access to large-ring compounds. The nucleophilic nature of both substitution processes has been convincingly demonstrated.

Hitherto no clear-cut explanation accounting for both effects has been offered. Indeed, the authors of a recent paper conclude that the emerging picture is complex, but, subtleties in chemistry should come as no surprise to anyone working in that field.⁵

In this paper a model based on knowledge inherent to inorganic rather than organic chemistry is presented.

Discussion

In recent years solid-state chemistry has been enhanced by an entirely new conceptual tool, differential geometry.⁶ Although mathematically non-trivial, it has provided ideas and theories comprehensible to the non-mathematician. Numerous inorganic structures, as well as a number of natural products and organic compounds, have been described using concepts borrowed from differential geometry. Minimal surfaces, or infinite periodic minimal surfaces (IPMS) have been successfully employed in structural descriptions ranging from zeolites⁷ to starch.⁸ The structure of ionic compounds has been interpreted in terms of periodic equipotential surfaces (PEPS) or periodic zero-potential surfaces (POPS).⁹ An alternative description of an ionic lattice is provided by the so-called tangential-field surface (TFS), utilized in the delineation of the fast-ion conductor α -AgI; the conductivity has been interpreted as silver ions moving on the TFS set up by the iodine ions.^{10,11}

IPMS are characterized by vanishing mean curvature and negative Gaussian curvature, i.e. every point on the surface is a hyperbolic, or saddle, point.¹² PEPS and POPS are not minimal surfaces in a strict mathematical sense (the mean

curvature fluctuates around zero) but the overall features are essentially those of minimal surfaces. In a POPS the surface is defined by points in space where the potential arising from the oppositely charged components is zero; the TFS, an IPMS if the POPS is an IPMS, is a surface defined by like charges, providing points in space where an opposite charge will be subject to equal attraction. Hence, in any ionic lattice, the POPS and TFS are co-existent and related through the symmetry of the particular structure.

It has been shown that, for the alkali-metal halides, the POPS can be described as a set of orthogonal planes (a plane is a special case of a minimal surface) forming closed cubes around the charged centres.⁹ However there is one exception, caesium. The POPS for, e.g., caesium chloride can be represented by Schwartz's P-surface (Fig. 1), composed of a central Cs^+ , surrounded by 8 Cl^- in a *bcc* fashion. The TFS for caesium chloride is identical with the POPS of, e.g., sodium chloride, forming closed cubes around each Cs^+ and Cl^- , respectively. Each cube around Cs^+ , constituting the TFS where a negative charge would be equidistant from the positively charged lattice components, embraces the repetitive unit of the P-surface. In sodium chloride, where the like charges are *fcc* (or, alternatively *bct*), the TFS can be illustrated with the T-surface (Fig. 2).

The notion of POPS and TFS is strictly valid in the solid state only, but, the short-range order always present in solution will most certainly promote a potential distribution around an ion that is closely similar to that in the solid state.

Caesium in intermolecular reactions. A number of discrete species can be envisaged in a solution of a caesium salt in an organic solvent. Depending on the solvent and the particular salt, the solvate structure can span anything from tight ion pairs to completely dissociated ions. In the most popular solvents, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), the degree of ion pairing seems negligible. This has been taken as substantiation of the presence of 'naked' anions, responsible, at least in part, for the synthetic effectiveness.



Fig. 1. Schwartz's P-surface.

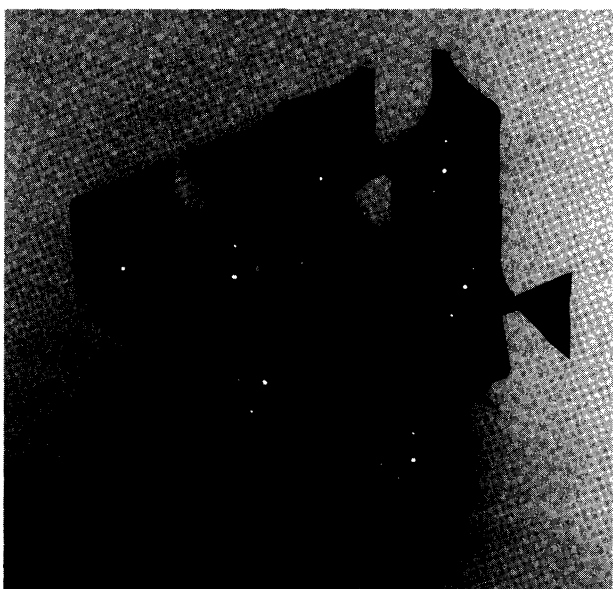


Fig. 2. The T-surface.

The appearance of a POPS related to a particular metal ion is a function of the features of the metal ion itself; any counter-ion will give the same POPS, provided that the counter-ion can be regarded as a point charge or has spherical charge symmetry. Hence the assumption that a caesium carboxylate will display a POPS (and a TFS) similar to, e.g., CsCl is eminently reasonable. The POPS being an IPMS, in this special case the P-surface, can be said to be composed of elements resembling the simplest analytical minimal surfaces; helicoids and catenoids. It has been shown that organic compounds can be described as nets tessellating minimal surfaces;¹³ simple molecules can be fitted to helicoids and catenoids, more complicated molecules can be fitted to more elaborate surfaces, e.g. resembling parts of the analytical P-surface. It follows that the caesium-related POPS is a favourable area of distribu-

tion for a hydrocarbon chain since: (i) the chain can easily adjust itself to the surface by means of 'topological recognition' and (ii) on the POPS the hydrocarbon chain is at the maximum distance from any charged moiety. Any polarized (or polarizable) or charged part of an organic molecule will be on the TFS. Thus a caesium carboxylate can be envisaged as being distributed with its charged end on the TFS set up by the counter-ion and the hydrocarbon chain on the POPS as defined by the two oppositely charged ionic entities. If an S_N2 reaction is attempted the other component of the reaction, usually a halide, methanesulphonate, or *p*-toluenesulphonate, is obviously quite polarized. The polar end will be found in the vicinity of the TFS and the rest of the molecule, the non-polar end, will consequently be located close to the POPS. If a complex system, such as the above, is considered as a set of different continuous compartments, it follows that the reactive parts of the interacting molecules, i.e. the parts necessary for reaction, will be situated in the same compartment. The continuous nature of the compartment is vital in that it enables *all* the interacting molecules to maintain close contact throughout the reaction. If, e.g., sodium was responsible for the arrangement of the POPS and the TFS, the former being cubes and the latter the T-surface (a more illustrative picture of this TFS is a set of parallel orthogonal layers of tunnels penetrating the lattice), an entirely different situation would arise. The local discontinuity of the tangential field, being non-intersecting tunnels, results in a local inhomogeneity with respect to the reactants. Confined to the TFS, the polar, reactive parts of the interacting molecules would occupy different tunnels and hence be less likely to meet, i.e. react. Any movement away from the TFS, constituting ideal paths for polar entities, would have to be against a higher field gradient; reactants jumping from one tunnel to another will dissipate energy.

Caesium in intramolecular reactions. A well-known difficulty in organic chemistry is the formation of large-ring compounds. Usually the problems are solved by consecutive ring expansions or by the utilization of so-called templates. The use of templates commonly requires the presence of polar or polarizable groups able to interact with the metal ions employed. Normally the templating ions are regarded as spheres of differing sizes, providing suitable moulds around which the desired molecule can form. In the case of caesium, both the composition and the size of the rings formed overthrow this rather casual picture. Applying the arguments stated above it is easily realized that the templating effect of caesium is more sophisticated than simply providing a spherical mould.

In the formation of large rings from essentially non-polar compounds it seems natural to use the POPS of the caesium salt as the template. The minimal surface nature of the POPS is highly compatible with most organic residues and its continuous features allows accommodation of literally infinitely long segments, capable of forming very large rings. The actual bond-forming charged parts of the mole-

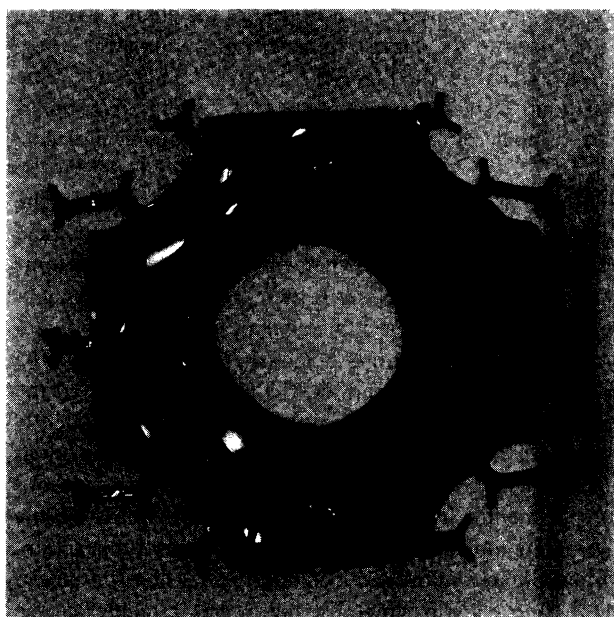


Fig. 3. The carcerand fitted to the P-surface.

cule would be expected to be close to the TFS. A striking example of this reaction can be found in Cram's synthesis of the so-called carcerand^{13,14} (Fig. 3).

Caesium fluoride is employed as an effective agent in the formation of large-ring polyethers.¹⁵ Analogously to the non-polar rings discussed above, the template could be a combination of the POPS and the TFS. The polarizable ether groups could be accommodated close to the TFS where the bond-forming charged units would be located; the non-polar residues would stay close to the POPS.

A plane, or a cube, the POPS of the other alkali-metal ions, would be less likely to promote the formation of rings. In fact, the preferential formation of open-chain di- or oligo-mers from bifunctional precursors would be anticipated. Furthermore, the non-intersecting nature of the related TFS would be expected to increase that general trend.

Conclusion

Caesium, responsible for spectacular effects when applied in organic synthesis, differs from the other alkali metals in the composition of the POPS and TFS. These unique potential distributions, due to neighbour and next-neighbour interactions, described by these surfaces, account for the performance of caesium ions both in terms of synthetic efficiency and structure-modelling ability.

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