

COORDINATION EQUILIBRIA IN NON-AQUEOUS SOLVENTS†

LEONARD I. KATZIN

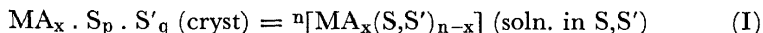
*Chemistry Division, Argonne National Laboratory,
Argonne, Illinois, 60439, USA*

The younger among our colleagues here may wonder why it is necessary to comment on the concept which they have "always" known, that inorganic salts (particularly of the transition elements) are coordination compounds, and as such may be dissolved in a variety of liquid media. There are a number of others here, I know, who, like myself, remember vividly when salts were assemblages of electrically charged spheres whose natural solution medium was "obviously" water, and the properties of such solutions were "obviously" those of electrically charged spheres of an appropriate radius, immersed in a dipolar medium. These same people have contributed to and followed the investigations which make the concepts of 1968 different from those of, say, 1938.

If this were a melodrama, I would nominate for the role of (unintentional) villains the crystallographers whose exciting investigations of the early part of the century demonstrated that the crystals of NaCl and a number of other salts were regular assemblages of charged spheres with essentially constant characteristic radii. Their accessories-after-the-fact would be Born, Haber, Madelung and their followers, whose results fitted so well with the strong electrolyte properties of aqueous salt solutions. We may designate this for short as the world of ideal or sodium chloride chemistry, which (if you will pardon the double entendre) is a colourless world.

It was the transition element world which (again I beg your indulgence) brought colour to the picture. It is peculiarly fitting to the topic of this Conference that the revision of the chemical concepts we are talking about grew in the first instance in response to data developed from solvent extraction studies, initiated during the period of the Manhattan Project and expanded in the rush by all in the post-war period to develop nuclear energy.

The fundamental relationship may be symbolized in equation I,

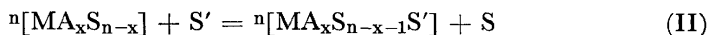


which here represents the solubility equilibrium of a salt in an intermediate-dielectric organic solvent. This is a heterogenous equilibrium, of course, and so perhaps does not properly fall within the title of the present paper. On the other hand, it represents an intersection point for the two chemical worlds we have designated, and a limiting condition on the homogeneous solution, to which we may have occasion to return. The significant point is

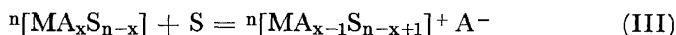
† Based on work performed under the auspices of the U.S. Atomic Energy Commission.

that in the organic solution, the solute demonstrates its character of coordination complex, and under the stated conditions its fundamental nature is that of a neutral molecular species. The early work, first on uranyl nitrate, which directed attention to the current concepts, has been discussed sufficiently elsewhere (*e.g.*, ref. ¹) and will not be covered here. The solution-solid relations epitomized in equation I also suggest that, contrary to the importance for the NaCl type of viewpoint of the crystal lattice energy, with its hypothetical dispersion to the dilute ionic gas, for organic solution the important energetic characteristic is the heat of sublimation of the crystal. This has also been discussed elsewhere² and will not be pursued further here.

Once in solution, the coordination species may become involved in a number of reversible equilibria, which can be grouped into two large categories. The first of these may be designated as substitutional equilibria. One such form of equilibrium, already implied in equation I, is that between competing Lewis bases, not excluding the solvent species (equation II). This needs no further comment.

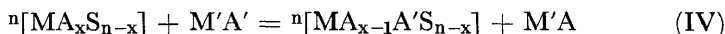


Where the solvent is a sufficiently strong donor, there may be some displacement of anion from the coordination sphere, as suggested in equation III.

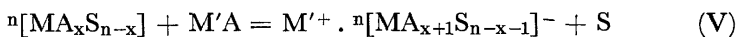


In some cases the formation of ions in this manner can bring us near the solubility limits again. If more than one anion is displaced, solid formation becomes extremely likely. Alcohols are known to displace anions, and of course, stronger bases do so also.

Introduction of a new anion into the solution, for example as M'A', may lead to displacement of one anion by another (equation IV).



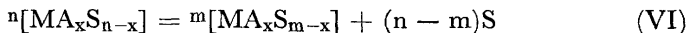
There is a fairly constant displacement series found, with perchlorate most readily displaced, followed by nitrate, thiocyanate and finally halide. In some systems there seems to be almost simultaneous displacement of two anions. If the same anion, rather than a different one, is added, as M'A, one may find solvent displacement to yield an anionic complex ion (equation V), part of an ion pair.



This leads to an increased conductivity of the system. It also exposes the danger of solid phase formation again. The cation M', in order to give a soluble reagent, is most often a tetraorganic derivative of nitrogen, phosphorus or arsenic; the lithium ion; or hydrogen ion. Particularly in the case of the lithium, though sometimes with other cations, especially symmetric forms of the complex anion will lead to formation of relatively high-lattice-energy solids, hence precipitation.

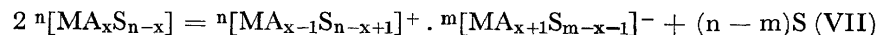
The second main category of equilibria to be considered deals with changes in the coordination configuration around the central metal cation. Though in the "old" version of inorganic chemistry this was a matter of radius ratios, and the packing geometry around a central sphere of given radius, the relations to binding energetics are better appreciated now, even if not yet entirely understood. The majority of cations studied seem to show the possibility for more than one coordination number, the potentialities being determined in the last analysis by the electronic states available. The actual form taken is determined by the ligands. Thus, as one obvious example, Hg^{++} in HgCl_2 is linearly bicoordinate; red, solid HgI_2 or HgI_2 in solution with excess iodide have tetrahedrally 4-coordinate Hg^{++} ; and hexahydrated Hg^{++} has been demonstrated. Most commonly encountered is the octahedral-tetrahedral pair of coordination states, particularly but not exclusively for the *d*-transition elements, and the role of halide and pseudohalide in stabilizing the tetrahedral state has been widely and variously documented.

In some systems, the medium determines whether, say, a solvated chloride is to be found in the octahedral or the tetrahedral state. In a given medium both forms may be found in equilibrium, the proportions being determined by the temperature. This state of affairs is epitomized in equation VI.



In attempting to pin down the quantitative factors involved, one enters a jungle of massive ambiguities, not the least of which is the role of secondary interactions between the ligands attached to the central metal ion, and the solvent medium. In a given system, it is possible sometimes to measure the energetics of the equilibrium, and to verify the anticipated relations between the configuration and the mean bonding energies—*i.e.*, that the mean bond energies in the 4-coordinate form are decidedly greater than in the 6-coordinate.

In systems in which predominately weak bases are present, and the dielectric constant is relatively high (*e.g.*, dimethylformamide solution), the equilibrium takes on a slightly different form, namely that illustrated in equation VII:



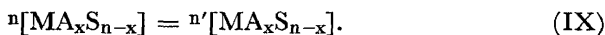
One obvious interpretation of the reaction is that this is a disproportionation primarily, which is facilitated by the high dielectric constant, and the difference in energy of binding of the anionic A^- between the octahedral and tetrahedral configurational states.

In another class of configurational changes, the effect can be traced to the influence of a powerful molecular donor, as indicated in equation VIII.



This class of equilibrium is exemplified by the influence of phosphoryl compounds, for example, on both the lanthanide and the last-row elements. In both of these series of salts, relatively high aqueous coordination numbers for water are reduced on incorporating the phosphoryl compound into the molecule. Pyridine-N-oxides and similar sorts of compounds may behave analogously.

Though there are few examples so far, one more equilibrium must be listed—the configuration change without change in coordination number (equation IX).



The main data on such an equilibrium deal with the tetrahedral-square planar states of Ni(II) and Co(II). In such a system the factor of interactions of the secondary level—*i.e.*, between the ligands and the solvent environment—becomes crucial indeed. This is exemplified in the literature data on the variations of the configurations and their relative stabilities with peripheral structural differences in the chelating ligands. In the case of monodentate ligands of relatively simple structure, we have found in our laboratory that the behavior is solvent and temperature sensitive, as well as showing influences of peripheral structural alterations.

As the general subject of this meeting is solvent extraction, I take the liberty to digress from my title for a few minutes to indicate some of the obvious points of intersection of the prior considerations and this topic. In solvent extraction, two phases are in equilibrium, and the activities of all species are the same in both phases. The compositional differences between them depend on activity coefficients. These in turn can be described in terms of differing “solubility parameter” relations, in the Hildebrand sense.^{3, 4} In other words, the differences in secondary effects of intermolecular interactions of the equilibrium species with the solvent or with each other become determinative. Protruding polar groups on a ligand, for example, will give strong water interaction, if not actual polymerization or precipitation, thus lowering the extraction. Very often the exact species involved in equation II, the exchange of Lewis bases, may be significant. Cobaltous chloride serves as a simple illustration. Equal volumes of water and of acetone can be separated into two phases by 10 per cent by weight of CoCl_2 . The acetone-rich phase is coloured blue by the $\text{tet}[\text{CoCl}_2 \cdot 2\text{H}_2\text{O}]$. A higher-molecular weight, immiscible ketone extracts little or no cobalt, presumably because the interaction of the coordinated water groups is much stronger with solvent water than with the organic ketone. Addition of some pyridine to the system, however, gives good extraction, as the $\text{tet}[\text{CoCl}_2 \cdot 2\text{Py}]$ formed through equation II has better interaction with the organic phase than with the aqueous. A number of analogous examples are reported in the solvent extraction literature, and no doubt the so-called synergistic effects express similar relations. The acetone- CoCl_2 -water experiment above illustrates another point, that the different coordination states of a cation (*cf.* equation VI) have sharply different activity coefficient relations. Comparing other systems—*e.g.*, the TBP-type exemplified in equation VIII, the HCl-dependent systems, and the difference between HgCl_2 , which is 2-coordinate, with higher coordination forms of mercuric halides—one can visualize the operation of a relation in which the coordination number is inversely related to the covalent bond strength. The latter can be related to low intermolecular polar interaction in turn, with its correlates of species volatility and increased potential for solution in organic solvents of similar character.

References

- ¹ L. I. Katzin. *J. Inorg. Nucl. Chem.* **4**, 187 (1957).
- ² L. I. Katzin. *Transition Metal Chemistry* (R. L. Carlin, ed.), **3**, 56 (1966).
- ³ J. H. Hildebrand and R. L. Scott. *The Solubility of Nonelectrolytes*, Reinhold Publishing Co., 1924.
- ⁴ L. I. Katzin. *The Chemistry of Non-Aqueous Solutions* (J. J. Lagowski, ed.), Academic Press, Vol. I, 173 (1966).