

SORPTION AND DESORPTION OF INCLUSION COMPOUND GUESTS

Different types of inclusion compounds

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Abstract

The guests present in inclusion compounds participate in bonding with the hosts. The conditions for the sorption and desorption of the guests are decisive for the properties of the inclusion compounds. They are surveyed for many types of inclusion compounds.

Keywords: composites, conditions of sorption and desorption, different guest types, inclusion compounds, thermal behaviour during sorption

Introduction

Our previous work has focused on inclusion compounds [1–5]. The properties of the host or the guest often change during inclusion complex formation [6]. The stability, including the thermal stability, of inclusion compounds is therefore of interest. The sorption of the guest into the host lattice and its subsequent desorption are at the focus of our attention [1–14]. Both processes often depend considerably on temperature. The aspects of sorption and desorption in inclusion compounds are not always studied by the same method; different physico-chemical methods are applied, including thermoanalytical methods. We present here a review of inclusion and supramolecular compounds, mainly as concerns desorption (and also sorption) problems; with the exception of the cyclodextrins, these features are rarely discussed in the literature. The review deals with numerous inorganic and mainly organic compounds serving as guest or host components, where the sorption and desorption of the guest have generally not been sufficiently clarified to date. Great advances have been made as regards the ranges of inclusion and supramolecular compounds since this work started forty years ago. It appears certain, however, that in the near future the inclusion compounds will be studied and mainly clarified by unified methods, and that the problems treated in this review will also be solved in an analogous way.

Mineral materials

The literature contains numerous reports on the thermal behaviour of minerals, including their degradation and the desorption of the volatile parts.

The dehydroxylations of gibbsite $\{\text{Al}(\text{OH})_3\}$ into boehmite and of goethite (FeOOH) into haematite have been studied during DSC analysis [15]. The hydration

of lime pozzolan cement was followed in cementitious pastes by means of DSC after the addition of fly ash from municipal solid urban wastes. The free lime content was determined as a function of the hydration time [16].

The same DSC method was used to study the dehydration of hydrated calcium aluminates [17]. An activation energy of hydration of $35.58 \text{ kJ mol}^{-1}$ was found. The dehydroxylation of pyrosilicates (vesuvianite) is described [18], and that of Anatolian granulated pumice in [19].

The thermal degradations of alumina, mullite and silica containing vinylbutyrol were followed between 50 and 1278°C by means of non-isothermal thermogravimetry [20]. Multiple layers of ceramic tapes, laminated and sintered for various applications (high-end computers, heat exchangers, turbine blades, etc.) were compared with regard to the thermal decomposition of polymers (15% of organic compound also present) on the ceramic surfaces. The bound water present promoted the degradation and liberation of the sorbed organic guest. Similarly, the surface (acidic or basic) was decisive. Compression of the pellet facilitated desorption.

In zeolites, the possible cation migration from one cation site to another affects the stability of the compacts. The dilatometric behaviour was investigated in [21].

The zeolites [22] contain three types of water: that filling the channels and cavities; that interacting with extraframework cations; and that bound to the framework by strong chemical bonds (OH groups).

Study of guests in natural zeolites of laumontite type [23] by means of NMR and other spectral measurements provided an insight into the arrangement and disorders in the guest species and their interactions in the zeolite pores. Transformations were found in the desorbed glassy state arrangements (H_2O) in the channels, with $n=14.40$; 16.18 at $27\text{--}57$ and $32\text{--}42^\circ\text{C}$.

Different characteristic species of zeolites have been described in the literature. Natural zeolitic vein mineral or replacement product of volcanogenic rock (heulandite or laumontite) from India exhibited the thermal behaviour [24] of zeolites which undergo no major structural changes while exhibiting a continuous mass loss as a function of temperature. Most of the water content was stable up to 280°C . The occluded water was lost up to this point and the structural water continued to be lost up to 498°C . Above this temperature, no further loss of water was observed. At 570°C , a structural collapse occurred.

Endoprocesses (a sharp one at 182°C , involving dehydration without structural changes, and another at 241°C , involving structural rearrangement on dehydration) generally reflect physical changes. Broad one-phase behaviour depends on the dehydration temperature of the chemical system. A broad exoprocess denotes chemical reaction.

The Anatolian zeolites of clinoptilolite (CT) type were analysed [25] by special methods for prediction of their sorptive properties, as were those of Slovakian type in [26].

The natural zeolites of Slovakian origin (deposit: Nižny Hrabovec) with prevailing CT content are sorptive materials for various guest components [7]. Desorption of the guest from CT zeolites is slow; the guest is thermally stabilized. In this manner, we have prepared a series of slow-releasing agrochemicals [1, 3, 26, 27], fertilizers, pharmaceuticals [10, 12–14] and other products [28–32].

Samples of alumina in montmorillonite (MMT) [33] differed in mass loss (9%) in the interval $20\text{--}300^\circ\text{C}$ relative to other non-pillared samples (19.5%). Alumina as guest in pillared compounds permitted a better diffusion of water molecules through

the pillared host during the loss of OH groups from the octahedral network of MMT up to about 700°C.

Other compounds

Cyano complexes form well-known clathrate compounds. The original Hofmann type and those with bidentate or more complicated ligands replacing the original NH_3 have recently been prepared in pillared forms. In the classical forms, the benzene molecule can be enclosed [7, 34–36] and its CH out-of-plane vibration band in the IR spectra is shifted to higher frequency relative to that of the liquid benzene molecule, with H-bonding between the electrons located above and below the plane of the C_6H_6 ring and the host lattice. The shift does not attain that for a chemical bond [37], e.g. in chromocenes (796 cm). This molecule as guest is taken as starting point for other guest motions [38, 39]. In many compounds, the C_6H_6 molecule undergoes a reorientation in the plane about the 6-fold axis, and the motion of this kind is well analysed in the literature.

The following appears probable: if benzene has spatial freedom as regards its out-of-plane directions [39] in a cavity, then an out-of-plane reorientation motion with low amplitude can readily occur as compared with an in-plane motion. This does not seem easy to confirm experimentally except by X-ray structure determination. However, NMR measurements were declared [39] to be a useful method revealing the state of $\text{C}_6\text{H}_6(\text{g})$ during and after its sorption in the host lattice. The activation energy value for jumps between neighbouring sites on C_6H_6 rings is 18.2 kJ mol^{-1} . The frequency of the out-of-plane motion has a very low activation energy in comparison with that of the in-plane motion. The bipyridyl ligands in metal(II) tetracyano-nickelates [40] reveal no coordination effect of the bipy, but only their presence as guest component. In tris(bipy)nickel(II) tetrakis(cyano)nickelate(II) hexahydrate, Černák [41] described the $\text{Ni}(\text{CN})_4$ as forming the host moiety in the compound with H_2O molecules, while the guest components involves the $\text{M}(\text{bipy})$ cations and the non-coordinated bipy molecules.

The gradual formation and thermal degradation of tetracyano complexes [42] demonstrated the effects of the surroundings on $\text{Ni}[\text{Ni}(\text{CN})_4]$ and its thermal stability [43–45]. The unusual properties of the intermediates were illustrated. The tetracyano-nickelate clathrate could in some directions be partially enclosed to natural zeolitic material [46].

Morphological studies on cyano complexes and their intermediates [10, 11] led to interesting results (Fig. 1). Some memory effects were considered to exist in the intermediates and final oxides. The product oxides exhibited new properties.



Fig. 1 Freshly prepared sample, a) Sample after 3-month-long standing; b) Sample heated to 280°C C_6H_6 and NH_3 decomposed; c) Sample heated to 373°C C_6H_6 and NH_3 decomposed and partially CN decomposing

Werner complexes have long been known [47] as useful inclusion compounds in separation and electrochemical processes. The structural aspects affecting their desorption have been dealt with by Lipkowski and his group. Guest desorption [45] is observed in discrete processes; pyridine and its derivatives are sometimes present at two sites simultaneously: as guest and ligand.

Cholic acid is a naturally-occurring steroid and a four channel type inclusion compound [47]. Its guest affects the channel form and this determines the channel-guest interaction. The channel form is responsible for its dipole moment. When it contains aromatic substituents or a cyclic lactone, the channel type structure persists. Otherwise, if an alcohol molecule is used as guest, one finds the cage type of cholic acid. The reaction kinetics and the decomposition kinetics were dealt with recently by Scott.

Urea in the presence of an appropriate organic molecule may act as a host lattice with modelling cavities [48]. Such are peptides in the biological systems. The urea channels were distorted by the host-guest interaction when 1,8-dicyanooctane was used. The host structure was extensively hydrogen-bonded to the linear, parallel, infinite hexagonal channels [49] prepared for the guest. The urea lattice remains intact after heating above its *m.p.*

Crowning started its history 20 years ago [50] at Brigham Young University. Calorimetry was used to study the $\log K$ values in order to interpret the reactions of various liquids with metal ions by Izatt and Christensen. They found that the strongest complex of potassium was formed with dicyclohexane-18 crown-6. The synthesis was ameliorated [1, 2, 4]. The incorporation of rigid groups into crown ether molecules can be a useful tool for organizing the macrocyclic cavity towards the binding of specific guests.

Calixarenes ($C_{11}H_{14}O_4$) have their origin in the tetrameric structure of an oligomer extracted from a condensation product mixture obtained by reacting *p*-tert-butylphenol with formaldehyde in the presence of sodium hydroxide [51]. Fifty years of work on calixarenes has seen their application in many different areas of chemical research, such application increasing in the past 15 years in particular [52]. The synthesis of the inclusion complex is best performed in a one-pot reaction [52–54]. Study of the host-guest interaction by optical methods led to knowledge of their selective receptor properties and hence also to their use in chemical sensors [55]. Simple inorganic ions (copper, lead and mercury) and organic compounds have been studied as guests. Among others, several ferrocene derivatives [56] were complexed by the calixarenes. The 1H NMR results indicated that the oxidized form of the guest (ferrocenium) is more readily bound than the reduced form (ferrocene) [57].

Cyclodextrins (CDs) are molecules with a conical shape and interior that are moderately nonpolar. The relatively hydrophobic cavities (6.5 Å) are known to be able to bind organic molecules in solution and in the crystalline state [58, 59]. Besides the hydrophobic cavity, they also have a hydrophobic exterior. They can recognize a variety of organic compounds in solution.

The study of antibiotics (18 types) in complexation with HPB CD revealed that the intensity increased with increasing specific hydrophobic surface area of the entering guest molecule. The intensity of interaction increased significantly with increasing concentration of methanol in the environment. Methanol enters the CD cavity and competitively inhibits the formation of an inclusion complex.

The desorption was studied [58] by means of TA for the control of drugs vs. arthritis and primary dysmenorrhoea.

Antitumour activity studies after the discovery of *cis*-Pt(NH₃)₂Cl₂ led to the preparation of other drugs [59]. The problem of the extremely low solubility of rhodium(II) carboxylates (a serious drawback to their use as antitumour agents) was bypassed by the use of CDs as solubilizers [60]. The dehydration of B CD occurs at 80–90°C, whereas in the inclusion compounds where the H₂O molecules are substituted by the new guest it takes place at 250–300°C.

The solubilization of lanthanide ions in basic aqueous solutions has been described by means of the formation of non-inclusion outer-sphere complexes with CDs [61]. This is interesting as concerns the molecular design of highly active and selective catalysts in the cleavage of nucleic acids and others, with prospects of new carriers of Ln ions into biological systems, in biotechnology and gene therapy.

The otherwise insoluble Ln ions are used in consequence of the formation of hydroxide gels in most cases.

Gas hydrates were thoroughly studied by Djadin *et al.* [67]; they contain different guest molecules. The system Xe–H₂O has been studied recently and the critical dimensions of the guest have been established. The sorption of the guest is governed by this: if it is less than 5.2–5.4 Å, hydrates of type I are formed; if it is 5.8–7.0 Å, those of type II are formed. In the intermediate range, both structures are stabilized [68]. Molecules larger than the above values do not form hydrates. Double clathrate hydrates have been dealt with by Udachin and Lipkowski [69].

A *layered double hydroxide* with intercalation character is known [62]. When Mg/Al=0.73/0.27 hydroxide was intercalated with *p*-toluenesulphonate, the layer expanded from 4.77 to 17.7 Å. The layered double hydroxide in the prepared form has potential applications in catalysis and in electronic devices and exhibits reversible photochromic properties.

Aluminium dihydrogen triphosphate has been described with bases and polymerized aniline between its layers [63].

The formation of polyaniline in the layers resulted from the chemical oxidation of the intercalated guest. It is proposed for use in electronic devices and heterogeneous catalysis. Aniline as a weak base ($pK_a=9.42$) was intercalated under ultrasonic wave irradiation. As the reaction proceeded, swelling occurred. An inorganic hybrid material resulted. Similarly, in [64] it was shown that H₂O was sorbed together with aniline in the zeolite.

Vanadyl phosphate has also often been studied. Thermomechanical and X-ray studies showed that H₂O molecules are intercalated into the interlayer space of α -VOPO₄ randomly, and create a disordered layered lattice, composed of VOPO₄ and VOPO₄·2H₂O layers. The same authors [65] described ethanol intercalation and reported an expansion from 4.7 to 13.17 Å in VOPO₄·C₂H₅OH. A two-step intercalation mechanism was found. Ethanol first enters the interlayer space at the edges of the crystals. In the second step, the intercalation zone spreads into the internal parts of the crystals.

General aspects

Inclusion compounds belong in the supramolecular domain and attract attention for their role in molecular recognition. There are specific conditions for their exis-

tence and specific features of their constituent host and guest molecules during sorption and desorption of the guest in certain cases. Some of these will be discussed:

The glass transition is often reported for inorganic and organic substances; this phenomenon is mostly studied by DSC and TMDSC methods. It is important in natural products, low molecular mass liquids and others, mainly for the acquisition of dynamic information, independently of the nature of the material studied.

The complexes of LiAlO_4 crown ethers and dicyclohexanes also exhibit a glass transition. The presence of glasses in the thermal history is responsible for anomalies in their behaviour, e.g. difficulty in obtaining perfectly crystallized products from the oily fluids formed by the solvates of the complexes.

One of our zeolite products likewise displayed a glass transition [10]. The complex was prepared from a natural CT type of zeolite, cyclodextrins and an antibiotic, spironolactone. Changing the sequence of adding the components changed the amount of guest present and mainly the thermal stability of the product.

The natural CT zeolite containing sorbed iodine or iodide released the guest only at 200°C, whereas products obtained by other methods of preparation contained some iodine up to 900°C [2, 28]. Analogously, the synthetic zeolite ZSM-5 sorbed and contained silver iodide, as did synthetic mordenite [13]. Different methods of identification and desorption control were chosen, including measurements of electrochemical behaviour, which confirmed the constrained state of the enclosed guest species. The mode and rate of desorption always depend on the interactions and strengths of the bonds between the host and guest molecules. These are affected by many factors: the contact area, the hydrophobic interactions, van der Waals-London forces and H-bonding. This holds especially for CDs [59], where a specific steric situation is necessary for bonding. H-bonds have been documented in many cases in pillared and other cyano complexes [38–41], Werner complexes [66], cholic acids [47, 48] and urea [49].

Our zeolitic product that slowly releases acetophenone or methylbenzoate as a base for perfume exhibited some interactions between the host and guest components in the UV-VIS spectra. The hindered desorption was checked by TA: the original 5.88% of methylbenzoate decreased to 4.475% at 50°C; and after heating to 205°C 3.22% of methylbenzoate was still present in the complex. In this connection, the aspect of solubility is to be remembered, similarly as in the case of CDs, cyano complexes [34, 39, 40] and Werner complexes [69].

The dimensions of the guest affect the structures in the case of hydrates [67, 68] and double hydrates [69]. The basic shape of the guest in cholic acid affects the shape of the spaces [70].

In our zeolitic products, when a quantity of the guest was still present in the host component, we could find small hollows or pits in the morphological pictures. A loss of crystallinity was also typical after the sorption of the guest. This phenomenon occurred only after sorption of the guest via impregnation on the product surface [7]. The electronmicroscopic pictures [7, 10, 11, 64] of the intermediates and products [7, 11–13] of thermal degradation of other compounds were characteristic of the presence of the guest as it diminished during desorption.

Films are also related with the inclusion systems and demonstrate the importance of the mode of their preparation. Such films have been treated by Niinistö [71], and terephthalate films in paper by Dargen *et al.* [72] and others. The tetraethylporphyrin

ntercalated in the hydrated form of V_2O_5 exerts electrocatalytic activity [73] in the reduction of molecular dioxygen and conducting and electrochromic properties of its films. A hydrated bidimensional structure was reported, with an interlamellar distance of 1.155 nm, suitable for the intercalation of many inorganic, organic and polymer species. Such films were obtained from polyvanadic gels (composition: $V_2O_5 \cdot xH_2O$, with $x=1.9-2.5$). After reaction with porphyrin solution, the films had a different composition: $V_2O_5(TPyP)_{0.075}H_2O_{0.38}$, where TPyP is mesotetra(4-pyridine)porphyrin. The thermal properties of RuO_2 films prepared with ruthenium(II) liketonate [74] and other stable thin films have been described [75].

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