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The fractionation of isotopes of elements which are included in multi-nuclear anions, first of all of carbon and oxygen at sedimentation of salts from a solution has been studied in many works. At the same time fractionation of isotopes of chlorine is insufficiently investigated from the theoretical point of view, that it is possible to explain mainly by complexity of the isotope analysis of chlorine and that the long time was considered, that the division of isotopes of chlorine in nature does not occur. The present work is devoted to theoretical consideration of a question about fractionation of isotopes of chlorine at sedimentation of halite.

Hydration of chloride anion.

Hydration of a chloride ion in water solutions has been studied both experimentally and theoretically, first of all by method of molecular dynamics (see review [1]). It has been shown that hydration of a chloride ion is weak and is reduced to the formation of hydrogen bonds between atoms of hydrogens of water molecules and anion. According to the most researches, the coordination number of a chloride ion in the diluted water solutions lays in limits from 6 up to 8.

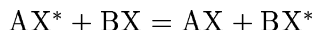
The *ab initio* quantum-chemical calculations have been carried out in work [2] and especially in [3]. The results of these calculations prove to be true also by results of our calculations of clusters $\text{Cl}^- - (\text{H}_2\text{O})_n$ (see Fig. 1). In all cases one can see that the ion Cl^- prevents molecules of water to bond with each other in an optimal way; at small n the molecules of water even try as though “to push out” the chloride ion on a surface of a cluster.

In the works mentioned above the equilibrium geometrical structure of complexes $\text{Cl}(\text{H}_2\text{O})_n^-$ has been investigated in detail. It has been shown that the energy distinctions between the possible forms are insignificant and most likely they will be leveled in real water solutions because of thermal movement and influence of cation.

The additional source of information about hydration of a chloride ion is served by data about diffusion in water solutions of the isotope forms $^{35}\text{Cl}^-$ and $^{37}\text{Cl}^-$ [4]. According to these data, the relation of mobility of light and heavy ion weakly depends from nature of a chloride salt¹. It allows us to assert that a condition of an ion Cl^- and the laws of its separation at sedimentation from solution are of general character and does not depend on a nature of a chloride salt.

Calculation of frequencies of vibrations and $\ln(s/s')$ of hydrated chloride ion.

As it is known from thermodynamics of chemical isotope exchange [5], at reaction



of exchange of isotope of element X isotope separation factor $\alpha_{\text{X}^*/\text{X}}$ (here X^* is heavy isotope of element X), equal by definition to

$$\alpha_{\text{X}^*/\text{X}} = \frac{\{[\text{X}^*]/[\text{X}]\}_{\text{in A}}}{\{[\text{X}^*]/[\text{X}]\}_{\text{in B}}},$$

can be calculated as

$$\alpha_{\text{X}^*/\text{X}} = \frac{(s/s') f(\text{A})}{(s/s') f(\text{B})}.$$

¹In quoted work it has been shown also that this relation practically does not depend on temperature.

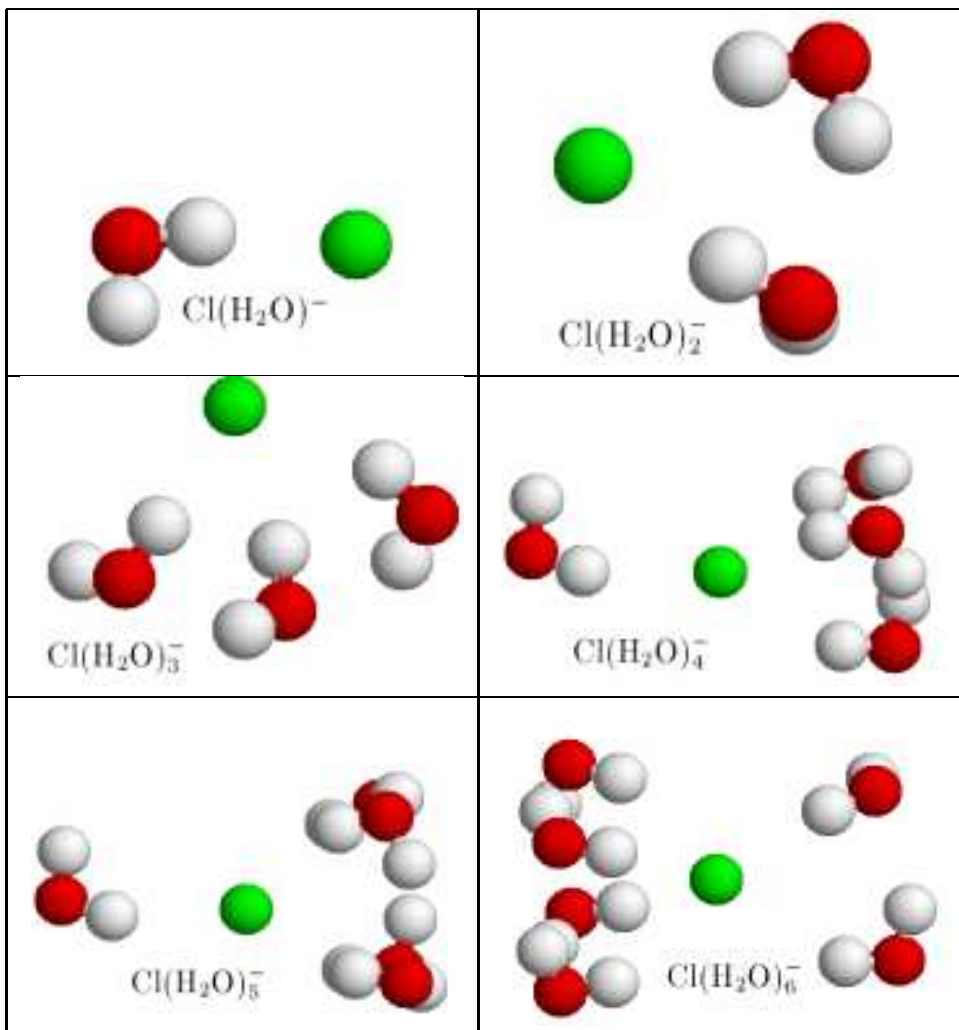


Figure 1: Models of aqua complexes of an ion Cl^- .

Here $[X]$ and $[X^*]$ are the concentration of isotopes in the appropriate substance, $(s/s') f(A)$ and $(s/s') f(B)$ are the so-called reduced partition function ratios or “ β -factors”, representing the relation of the quantum statistical sums for the isotope forms of the given substance, divided on the same relation for the classical statistical sums. For an estimation of separation factors of isotopes of chlorine at crystallization it is necessary first to calculate $(s/s') f$ values of hydrated chloride ion. The experimental data, necessary for such calculation, on frequencies of vibrations of aqua complexes $\text{Cl}^-(\text{H}_2\text{O})_n$ are absent, and the only possible way is to use quantum-chemical methods.

The calculation of frequencies of vibrations and $(s/s') f$ values for hydrated chloride has been carried out by us with the help of the program PC GAMESS [6, 7]. The extended basis RHF/6-311++G**(3df,3p) was used. The effective core potentials (ECP) of SBK type [8] were used. The results of calculation are given in the Tab. 1.

As one can see from the table, values of $\ln(s/s') f$, calculated in MP2 approximation, are greater than those calculated without taking into account the electron correlation. The dependence between these values are almost strictly linear, and this allows us to estimate the MP2 data for $n=5$ and $n=6$ (such approximate data are given in the Tab. 1 by italics).

Table 1: Values of $\ln(s/s')f$ for aqua complexes of Cl^- ion, calculated by *ab initio* methods (T=300K).

Complex	Method of calculation	
	RHF/6-311++G**(3df,3p)	MP2/6-311++G**(3df,3p)
$\text{Cl}^- - (\text{H}_2\text{O})$	0.000487	0.000748
$\text{Cl}^- - (\text{H}_2\text{O})_2$	0.000844	0.001263
$\text{Cl}^- - (\text{H}_2\text{O})_3$	0.001110	0.001670
$\text{Cl}^- - (\text{H}_2\text{O})_4$	0.001264	0.001902
$\text{Cl}^- - (\text{H}_2\text{O})_5$	0.001364	<i>0.002046</i>
$\text{Cl}^- - (\text{H}_2\text{O})_6$	0.001444	<i>0.002165</i>

Experimental data on separation of isotopes of chlorine at sedimentation of halite.

In [9] the experiment on separation of isotopes of chlorine in the system halite – water solution of NaCl has been carried out. However, low accuracy of the analysis has not allowed the authors to measure the isotope separation factor reliably. The separation factor measured has appeared to be 1.0002 ± 0.0003 (halite was enriched by a heavy isotope). In [10] large number of samples, including halite samples from various deposits have been studied. It was found that, as a rule, halite samples are enriched with a heavy isotope of chlorine in relation to the standard (ocean water). In particular, the enrichment of halite samples depending on a deposit varied from 0.52‰ up to 0.24‰. In [11] separation of isotopes of chlorine at halite sedimentation from saturated salt solution has been studied experimentally. Measured separation factor ($\ln \alpha$) in the system NaCl(solid) – solution has been found to be 0.00026 ± 0.00007 at $22 \pm 2^\circ\text{C}$, that confirm the results of work [9].

The correlation between enrichment of a sample by a heavy isotope and concentration of NaCl affirms the idea that the thermodynamic contribution to separation of isotopes in this case is dominant. Really, at formation of a crystal from the saturated solution, solid phase should be enriched by heavy isotope of chlorine ^{37}Cl because $\ln(s/s')f$ of a solid halite exceeds $\ln(s/s')f$ of a hydrated chloride ion. On the contrary, if isotope fractionation were controlled by kinetics of sedimentation, the layers of a solid phase formed first should be enriched by light isotope.

Model of separation of isotopes of chlorine at evaporation of reservoir with salty water.

Quasi-equilibrium mode of sedimentation.

The equations describing separation of isotopes of mononuclear ions at crystallization in quasi-equilibrium mode were deduced by us earlier. The basic equation is the equation similar to the Doerner-Hoskins formula [12], describing co-crystallization in quasi-equilibrium mode:

$$\ln \left(1 - \frac{{}^{35}n_{solid}}{{}^{35}n_0} \right) = \alpha_{35/37} \cdot \ln \left(1 - \frac{{}^{37}n_{solid}}{{}^{37}n_0} \right). \quad (1)$$

Here ${}^{35}n_{solid}$ is amount of substance of isotope ^{35}Cl in solid phase, ${}^{35}n_0$ is total amount of this isotope in the system, $\alpha_{35/37}$ is isotope separation factor at quasi-equilibrium sedimentation. The equation (1) allows one to calculate $\delta^{37}\text{Cl}$ in a superficial layer of a crystal and in stock solution.

Estimation of the value of isotope separation factor α needed for this calculation presents some problem. Our quantum-chemical calculations of $\ln(s/s')f$ for hydrated ion Cl^- give

$\ln (s/s') f \approx 0.002$ at 300K. $\ln (s/s') f$ of solid NaCl has been calculated in [13] and is ≈ 0.003 at 300K. However it is necessary to take into account, that calculated $\ln (s/s') f$ for solid NaCl refers to an ion in depth of a crystal of solid salt (bulk ion), while the isotope exchange really occurs on a *surface* (in near-surface zone). In this case as a first approximation for $\ln (s/s') f$ of an ion on a surface of a crystal it is possible to take an average value between $\ln (s/s') f$ for a crystal and solution [14]. It gives $\ln (s/s') f_{surface} \approx 0.0025$ and $\ln \alpha \approx -0.0005$ at 300K.

Because $(s/s') f$ for halite exceeds $(s/s') f$ for hydrated chloride ion, in the process of sedimentation of salt from a solution crystal is enriched by a heavy isotope, and solution, on the contrary, by light isotope. Thus sedimentation of a heavy isotope occurs non-uniformly — at sedimentation of a salt stratum the lowermost layers sedimented first should be enriched with a heavy isotope to the greatest degree. If the composition of an initial solution corresponded to SMOC², the lowermost layer of salt should have enrichment

$$(\delta^{37}\text{Cl}_{solid})_{bottom} = 1000 \cdot \left(\frac{1}{\alpha} - 1 \right) \approx 0.50\text{‰}.$$

That is, the most part of a salt stratum should be really enriched with a heavy isotope. The top layer of salt at exhaustive evaporation should be enriched with light isotope, however in real conditions this layer represents a mixture of potassium and magnesium salts.

Diffusion mode of sedimentation.

Because the halite sedimentation occurs at nonzero speed, it is necessary to take into account the corrections caused by diffusion in the process of sedimentation. This question is considered by us in detail in the previous work. Here we remind the basic results. It is possible to consider separation of isotopes in the process of sedimentation of a crystal from saturated solution containing two or more isotopes of an element as a special case of co-crystallization.

In the process of sedimentation in diffusion mode the layer of a liquid phase by thickness δ (diffusion layer) is always formed at a surface of crystal. The calculations given in detail in previous paper result in the following expression for isotope separation factor for sedimentation in diffusion mode:

$$\alpha_{35/37} = \alpha_{35/37}^{eq} \frac{SA + [1 - SA] \exp\left(-\frac{\delta G}{37D}\right)}{\alpha_{35/37}^{eq} SA + \left[1 - \alpha_{35/37}^{eq} SA\right] \exp\left(-\frac{\delta G}{35D}\right)}, \quad (2)$$

where $\alpha_{35/37}^{eq}$ is isotope separation factor in quasi-equilibrium mode, G is speed of linear growth of a crystal, D is diffusion coefficient of an ions in a liquid phase (strictly speaking, in near-surface zone), $A = \frac{1 + SMOC}{\alpha_{35/37}^{eq} + SMOC}$, the value $S = \frac{{}^{35}c_{solid} + {}^{37}c_{solid}}{{}^{35}c_{aq} + {}^{37}c_{aq}}$ is constant which

depends on solubility of salt. The maximal value of the fraction $\frac{{}^{35}D}{37D}$ is equal to a square root from the relation of reciprocal weights of atoms. However, actually this relation is significantly (approximately ten times) less. The experimentally measured relation of mobility in saturated solution of sodium chloride is 1.0022 [4]. Diffusion in near-surface zone favors to enrichment of salt by light isotope. Thermodynamic isotope effect, on the contrary, favors the enrichment of solid phase by heavy isotope ^{37}Cl . Thus, kinetic (diffusion) and thermodynamic factors in the process of sedimentation of chloride work in opposite directions. For quantitative estimation of influence of speed of sedimentation on isotope separation factor it is necessary to have numerical values of quantities included in equation (2). The value S depends on solubility of salt, for NaCl it is 6.951 and weakly depends on temperature. As an estimate for diffusion coefficient in near-surface zone we have used the diffusion coefficient of ion Cl^-

²SMOC (“Standard mean ocean chloride”) is the relation of concentration $^{37}\text{Cl}/^{35}\text{Cl} = 0.324$ in ocean water accepted as the standard.

in solution ($6 \cdot 10^{-6} \text{ cm}^2/\text{s}$). The relation $\frac{35}{37} \frac{D}{D}$ and equilibrium separation factor $\alpha_{35/37}^{eq}$, as noted above, are equal 1.0022 and 0.9995 accordingly. As one can see from formula (2), the value of α depends on product of growth rate of a crystal on thickness of diffusion layer. In works on study of the mechanism of crystallization performed recently [15, 16], it has been established that the thickness of diffusion layer varies for various salts in limits from $5 \cdot 10^{-3}$ up to 10^{-5} cm, and this value does not strongly depend on speed of a flow in the vicinity of a crystal.

It is also visible that logarithm of separation factor can change its sign, that is, at high speed of crystal growth (high δG) the direction of separation of isotopes reverses, and the crystal enriches by light isotope. Such enrichment in natural samples of halite has never been observed. Therefore, it is possible to conclude that the separation of isotopes at sedimentation of halite is controlled mainly by thermodynamic isotope effect.

The experimental data on speed of crystal growth of halite

For practical use of formula (2) it is necessary to know growth speed of crystals G , which is fully determined by speed of evaporation of a solution. To estimate the latter, it is possible to address to the data on speed of evaporation of water from natural reservoirs, such as lakes and seas. Besides, we carried out experiment on sedimentation of sodium chloride from the freely evaporating saturated solution. The solution was placed in the glass cylinder. The cylinder was established in room and the solution was given an opportunity to evaporate freely. We have not protect the surface of solution against dust because in natural conditions such protection is absent, and the dust particles can serve as artificial germs of crystallization. The results are given in the Tab. 2.

Table 2: Average speed of evaporation of water from water reservoirs and corresponding linear speed of growth of crystals NaCl.

Reservoir	Average speed of evaporation of water, mole/(cm ² · s)	Average linear speed of crystal growth G, cm/s
Caspian sea	$1.82 \cdot 10^{-7}$	$5.5 \cdot 10^{-7}$
Global Ocean	$2.20 \cdot 10^{-7}$	$6.6 \cdot 10^{-7}$
Cylinder	$(1.2 \div 1.5) \cdot 10^{-7}$	$(3.6 \div 4.5) \cdot 10^{-7}$

It is necessary to emphasize that in all works devoted to separation of isotopes of chlorine at crystallization of halite it is meant that the growth of crystals occurs inside a solution, and the concrete mechanism of process of growth of these crystals has not been considered. Meanwhile, the isotope separation factor can be influenced by this mechanism in a great extent.

The question on the mechanism of growth of crystals of NaCl was considered for the first time a long ago by Mendeleev [17]. From recent works it is necessary to note the Internet report [18]. In this report, alongside with study of NaCl pyramids described by Mendeleev, the growth of dendrites on walls of vessels is marked. Between dendrites and solution there is a strip of free space covered with a thin film of a solution, and the solution is delivered to place of growth (dendrite surface) mainly in capillaries inside of dendrites. It is clear that at such growth the solution caught by dendrite is exhausted, and for width of diffusion layer δ in formula (2) it is necessary to accept width of strip between a solution and dendrites. This width can be large that according to the equation (2) can result in realization of kinetic control on separation of isotopes. At the same time, because real reservoirs have the large areas of surface, the dendrites formed only on coast hardly increment essential contribution to total amount of the resulting solid salt. It seems that more important is the pyramidal

mechanism of crystallization. At evaporation of solutions of NaCl the salt particles float on a surface in the form of very small cubes, joined with each other as pyramidal tetrahedral funnel (pyramid revolved top inside). Such a funnels float on a surface because of emptiness inside a pyramid and grow from edges, the solution for growth of a funnel is delivered to the top edge of a funnel due to the capillary forces. The funnels can long keep on solution surface, stick together among themselves and forming salt crust. After reaching of certain critical mass (or at hit of water inside) they drown and fall on the bottom of the reservoir, then the described mechanism repeats. That is, at crystallization there is a formation of dissipative structure, during which crystal stratum is formed. As a result, salt deposit at the bottom of reservoir represents a congestion of crystallites formed on a surface.

As it is possible to understand, the most essential in the given mechanism is the delivery of a solution to a point of growth (tops of pyramids) by capillary forces. This mechanism determines the size of diffusion layer δ . In described conditions δ can considerably surpass values of about 10^{-5} and can achieve 10^{-2} cm or even more, that according to the equation (2) can considerably increase kinetic contribution to separation of isotopes and reduce separation factor.

Conclusion

As it is visible from the article, the offered model of fractionation of isotopes of chlorine at sedimentation of salts corresponds to experimental data observed in nature. However, the experimental data are scarce. Consequently, detailed research of isotope structure of chlorine in salt sediments taking into account non-uniformity of a $^{37}\text{Cl}/^{35}\text{Cl}$ on depth of a layer would be extremely useful. Such researches could be an important source of information about geological conditions in which sedimentation of halite occurred.

At the same time, on the basis of the available data showing enrichment of halite by a heavy isotope, it is already possible to assert that the basic contribution to separation of isotopes in the process of halite sedimentation gives thermodynamic isotope effect, and diffusion can only reduce size of this effect, but is not capable to change a qualitative picture as a whole.

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