VARIABLE COMPOSITION OF CHLORINE HYDRATES SYNTHESIZED UNDER VARIOUS CONDITIONS

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The composition of chlorine hydrates synthesised by different reaction routes were determined from experimentally measured density values without isolating the gas hydrate crystals. This method is the simplest and accurate for determining the composition of chlorine hydrates prepared under various conditions. The occupancies of each type of the cavities in the clathrate cage have been calculated.

Introduction

Chlorine hydrate is the first gas hydrate discovered by Davy.1 It is widely used as solid chlorine source in various important products and technological processes such as high energy density batteries, refrigerators, disinfection processes and high pressure chlorination reactions.2 The determination of the composition of chlorine hydrate has attracted attention of chemists for long time because of its non-stoichiometric nature and dependence of its composition on the conditions of the preparatory methods.2–11 The use of various oxidants as starting materials for the oxidation of hydrochloric acid e.g. hypochlorites or possible new oxidants such as simple or complex permanganates give new perspectives in the preparation of this compound.12–15 Besides, the composition of the crystals formed depends on the conditions of the methods used for its preparation, a simple and easy method to determine the composition of chlorine hydrate formed without isolation of crystals is required because instability of the crystals during weighing is the main problem in the analysis of the chlorine hydrate.8,10

Results and Discussion

Chlorine hydrate belongs to the type I clathrate hydrates that consist of a 46 membered 3D-network of water molecules including 2 small and 6 large voids. The formula of chlorine hydrate can be written as (8-x)Cl2.46H2O, where x is the number of the unfilled voids in the elementary cell (Z=1).3 This formula can also be expressed as Cl2.nH2O, where n is the number of water molecules, termed as hosts, that encage one molecule of the chlorine gas termed as the guest. It theoretically means that the chlorine hydrate, which is richest in chlorine, could be characterized with the formula derived from the maximal filling ratio, namely Cl2.5.75H2O. Since the density can easily be determined experimentally with high accuracy without separating the crystals from the mother liquor16,17, these density values can therefore be used for calculation of the composition of the chlorine hydrates. The general formula of the chlorine hydrate can also be written as (6θ(Cl2)+2θ(Cl2)).46H2O, where θ1 and θ2 are the occupancies of the larger and smaller cavities respectively. The density can be expressed as the quotient of the molar mass and the molar volume of each clathrate. The molar mass of the hydrate can be calculated as the sum of the weights of the guest and the water cage, and the molar volume can be expressed by using the known temperature dependent molar volume of the blocks of 46 water molecules of the ice lattice by using the additional term ΔV(T,n)18:

\[
V_{\text{clathrate}} = V_{\text{ice}} + ΔV(T,n)
\]

where T is the absolute temperature in K, and n means the occupancy. The ΔV(T,n) term can be divided into two parts,

\[
ΔV(T,n) = ΔV_{\text{w=0}} + ΔV_{\text{a}}(T,n)
\]

where ΔVw=0 value is constant and can be taken as 3.05 or 3.2 cm³/mol19. The value of the additional term, ΔVa(T,n) depends on the number of chlorine molecules and includes the effect of the thermal motion on the strength of the host-guest interactions in each type of the cavities20,21. The contribution of the ΔVa(T,n) term on the ΔV(T,n) values, however, proved to be not substantial because the widening of the clathrate hydrate cage reaches roughly 1 % value at the Dm=5.7 Å22 diameter of the guest molecule, and the DCl2 is only 5.2 Å.3 The calculated n1 values were compared with the n2 values determined from the known lattice constant 3 and experimental density values (Eqn.(3) and (4)).17,18
A density value of 1.37 g/cm³ was given for a chlorine hydrate formed in capillaries. This value is too large even if a complete occupation (8Cl₂·46H₂O) is supposed \((d = 1.325 \text{ g/cm}^3)\), thus the lattice of the chloride hydrate should be contracted in the capillaries \((a = 1.192 \text{ Å})\) or the difference between the molar volumes of the empty clathrate cage and the ice should be diminished from the average 3.1 to 2.5 cm³/mol.² No example for this magnitude of contraction among the clathrate hydrates of gases, even at higher pressures than the observed 10-12 atm could be present in the capillaries and the perfect filling of the cavities should cause dilatation rather than contraction. Therefore, the hydrate formed in the capillaries probably does not belong to the clathrate type I but a different type of chlorine hydrate richer in chlorine is rather formed as mentioned by Maumene, and a rhombic polymorph of the chlorine hydrate was also detected by Nordenskjdö.²²,²⁷

### Conclusions

The composition of chlorine hydrates prepared by different reaction routes were determined based on their experimentally measured density values. This method is the simplest and accurate way for the determination of the composition of chlorine hydrates prepared under various conditions because it does not require isolation of the crystals form the solution. The composition of various chlorine hydrates prepared in the last 200 years was re-determined and the values were found between 6.01 and 7.63H₂O/chlorine molecule. The results found for the chlorine hydrate prepared in capillaries \((d=1.37 \text{ g/cm}^3)\) showed that this chloride hydrate cannot be type I clathrate hydrate but a new modification or an other type of the chlorine hydrate might be formed within the capillaries.

### References


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Variable Composition of Chlorine Hydrates Synthesized under Various Conditions

### Table 1. Experimental densities, lattice constants and composition values of the chlorine hydrates at 273.15 K.³

<table>
<thead>
<tr>
<th>Reference</th>
<th>(d) g/cm³</th>
<th>(n_1)</th>
<th>(n_2)</th>
<th>(\theta_1)</th>
<th>(\theta_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Faraday⁵</td>
<td>1.2</td>
<td>7.63</td>
<td>7.58</td>
<td>1.00</td>
<td>0.03</td>
</tr>
<tr>
<td>Roozeboom⁶</td>
<td>1.220</td>
<td>7.28</td>
<td>7.23</td>
<td>1.00</td>
<td>0.17</td>
</tr>
<tr>
<td>Bjorkman</td>
<td>1.237</td>
<td>7.00</td>
<td>6.95</td>
<td>1.00</td>
<td>0.32</td>
</tr>
<tr>
<td>Wilms</td>
<td>1.239</td>
<td>6.97</td>
<td>6.92</td>
<td>1.00</td>
<td>0.37</td>
</tr>
<tr>
<td>Smirnov</td>
<td>1.31</td>
<td>6.01</td>
<td>5.98</td>
<td>1.00</td>
<td>0.85</td>
</tr>
<tr>
<td>Kislovski⁷</td>
<td>1.37</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Density of two samples prepared in different ways were determined.

Smirnov and Kleschunov reported an experimentally determined value of density \((1.31 \text{ g/cm}^3)\) for the isolated chlorine hydrate which was found to have the formula \(\text{Cl}_2\cdot 6.2\text{H}_2\text{O}\).²⁵ The use of this density value provided the composition of the hydrate to be \(\text{Cl}_2\cdot 6.01\text{H}_2\text{O}\), which is close to the experimentally found value \((n_1=6.2)\).²⁵

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Section A-Research Paper


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