

# Obtaining of hydration parameters of cesium halides in the processes of water absorption and desorption

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Cesium halides were examined in water absorption/desorption processes. A methodology was proposed to obtain hydration parameters of the substances examined. It was established that amount of water in near hydration shell as well as water desorption enthalpy increase in order CsCl–CsBr–CsI. Magnitudes of near hydration shell were established by means of thermogravimetry as 41, 86 and 99 water molecules, correspondingly.

Получен ряд параметров гидратации галогенидов цезия с помощью разработанной методики изучения процессов адсорбции и десорбции воды. Установлено, что в ряду CsCl–CsBr–CsI размер областей ближней гидратации, а также энтальпия десорбции воды увеличиваются. Установленный методом термогравиметрии размер области ближней гидратации исследуемых солей составляет в указанном ряду 41, 86 и 99 молекул воды, соответственно.

**Отримання параметрів гідратації галогенідів цезію у процесах адсорбції та десорбції води.** *О.В.Ващенко.*

Отримано низку параметрів гідратації галогенідів цезію за допомогою розробленої методики вивчення процесів адсорбції та десорбції води. Встановлено, що у низці CsCl–CsBr–CsI розмір областей ближньої гідратації, а також ентальпія десорбції збільшуються. Встановлений методом термогравиметрії розмір області ближньої гідратації солей, що досліджувалися у вказаній низці складає 41, 86 та 99 молекул води, відповідно.

## **1. Introduction**

Cesium halides are widely used as scintillation materials and optical glass constituents. Their hydration properties can be a substantial limiting factor in their practical application [1, 2]. Possible changes in their hydration properties [3] should be accounted for in development of new scintillation materials by doping basic substances.

Hydration properties of materials, e.g. hygroscopicity, have sufficient influence on their practical utilization. They are directly connected with such intrinsic properties of materials as energy of crystal lattice, elec-

tric conduction, viscosity, etc. [4–6]. The great importance of materials hydration in technological aspect results to wide scope of their investigation, from food and medical production to some compounds of modern scientific equipment [7–10].

In the present work, a technique is proposed allowing obtaining some hydration parameters of water-soluble non-volatile compounds. The technique is based on studying of the processes of isothermal water absorption in the atmosphere of saturated water vapor, as well as of water desorption during temperature-control heating by the method

of thermogravimetry analysis (TGA). TGA method was chosen as one of the most used direct methods to hydration study [11]. The indubitable advantage of TGA method is reliable determination of the amount of absorbed/desorbed water. Some energy parameters can also be determined by means of certain calculations [12, 13].

## 2. Materials and Methods

High purity cesium salts produced by "Tekhnoiod" (Russia) and bidistilled water were used in the work. In Fig. 1 the scheme is presented of experimental equipment for preparing hydrated salt samples. A small amount of salt (4 to 6 mg) was placed into 160  $\mu\text{l}$  aluminum oxide crucible (2) with a center-perforated lid (supplied "Mettler" TGA equipment). The crucible was placed into a vessel with saturated water vapor (1) onto a perforated support (4) immediately above water level at the vessel bottom. Water/salt solution (3) was formed into the crucible during absorption processes. The solution concentration  $c$  became persistently reduced during experiment due to continuous water absorption.

Mechanism of such solution formation can be explained by Raoult's law. According to it, relative reduction of saturated vapor pressure above a solution ( $\Delta p$ ) is proportional to molar fraction  $c$  of a solute:

$$\Delta p = p^0 \cdot c, \quad (1)$$

here  $p^0$  is saturated vapor pressure of a solvent.

Relative pressure reduction above the solution (into the crucible) proved to be compensated by water vapor coming from the whole vessel, as far as the crucible with the solution is an open system and water surface into the vessel sufficiently exceeds the solution one. Therefore, there is permanent excess of water vapor pressure above the solution, which leads to permanent water concentration into the crucible and  $c$  reduction.

Such a mode of preparation of hydrated samples provides including all water molecules proximately into water shells of the solute. Using the same crucibles both for absorption and for desorption experiments excludes any mixing in absorption/desorption cycles, which could corrupt water structure of the sample.

Desorption experiments were performed by TGA module TG 50 of thermoanalytical system "Mettler TA 3000" (Switzerland);

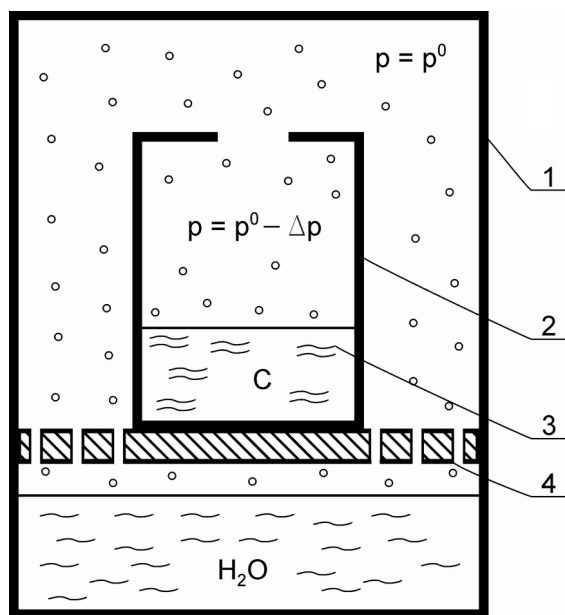


Fig. 1. Scheme of experimental equipment for absorption experiment: 1 — tightly closed vessel with saturated vapor (hygrostat); 2 — crucible with perforated lid; 3 — salt/water solution with concentration  $c$ ; 4 — perforated support.

heating performed in temperature range of 50 to 100°C at 0.5 K/min. Dry sample mass was defined after the end of desorption experiment and additional thermostating under 110°C during 10 min. The dependences were obtained as "the sample mass vs. temperature" (TG) and "rate of mass loss vs. temperature" (DTG). The experimental data processing was carrying out by means of QtiPlot software.

In order to obtain more precise and reproducible data, ordinary salt/water solution were prepared, with salt/water ratio 1 to 80, and examined by TGA method. Then, the crucibles with dry salt were placed into the hygrostat (see Fig. 1) to get hydrated samples. These samples were then repeatedly examined by TGA. Bidistilled water was used as a referring sample.

In the simplest case, desorption processes of water or gas [14] can be described by Boltzman's equation:

$$n_{des} = A \cdot e^{\frac{-\Delta H}{RT}}. \quad (2)$$

Here  $n_{des}$  is a number of water molecules desorbed,  $A$  is a desorption constant,  $\Delta H$  is desorption enthalpy,  $R$  is the universal gas constant, and  $T$  is absolute temperature.

After taking the logarithm of Eq. (2), one can obtain:

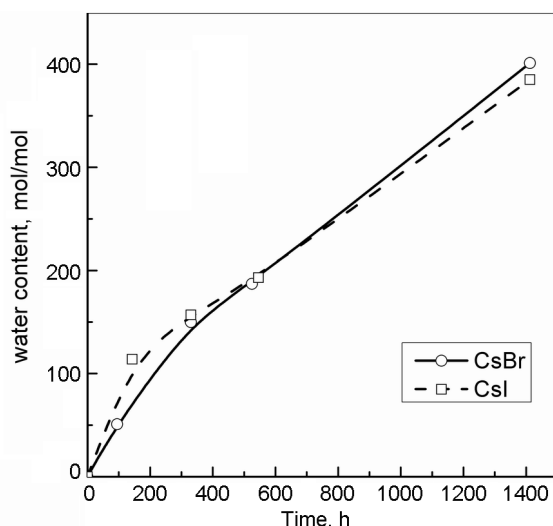


Fig. 2. Water absorption by CsBr and CsI under thermostating in saturated water vapor atmosphere.

$$\ln(n_{des}) = \ln A - \frac{\Delta H_{des}}{RT}. \quad (3)$$

So,  $\Delta H_{des}$  value can be obtained as inclination of line plotted in coordinates  $\ln(n_{des})$  vs.  $(1/T)$ . (Here it should be noted that though desorption enthalpy of pure water varies with temperature, this variation is ab. 5 % within the experimental temperature range.) A segment which is cut off at ordinate axis ( $\ln A$ ) has sense of some structural parameter. It can be referred to as a relative value reflecting changes of water structure in a salt solution relative to pure water:

$$N = \ln A_s / \ln A_w, \quad (4)$$

here  $\ln A_s$  and  $\ln A_w$  are parameters obtained for the solution and pure water.

A similar equation obtained by another way was successfully applied in [8] to determine dissociation (sublimation) heat.

Experimental error calculated as arithmetic mean value of correspond parameters obtained in 3 to 6 measurements.

### 3. Results and Discussions

Water absorption processes can be conveniently presented as "amount of absorbed water molecule per a cation/anion pair vs. time" (Fig. 2). As one can see, the absorption processes do not trend to saturation even in 1400 h of thermostating, so they could be prolonged. In the experiments, the samples hydration came up to 400

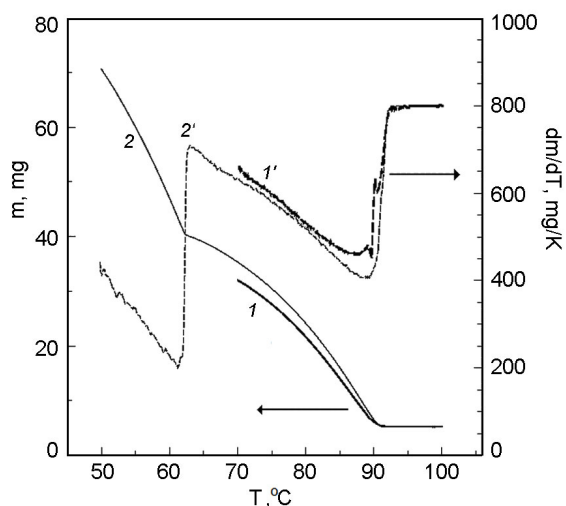
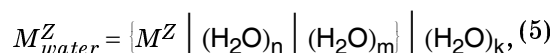


Fig. 3. TG (1, 2) and DTG (1', 2') dependences for hydrated CsI: 1 — solution; 2 — absorbed water.

$H_2O/CsHal$  and more, with resulting solute concentration  $c \approx 3$  % w/w.

The influence of preparation mode is exhibited in Fig. 3, where TG curves are given both for the freshly prepared solution and for the hydrated sample obtained by water absorption. Generally, both TG curves seem very similar, in spite of great difference in initial water content. Though, certain differences are in the range of low water content (corresponding to temperature range 80 to 90°C). So, "absorbed water" curve appears to be much smoother than "solution water" curve, probably due to water structure disturbances during the solution preparation.

The data obtained can be interpreted taking into account commonly accepted water structure of hydrated ion [15] which can be schematically presented by following formula:



where  $M^Z$  is a solute ion/molecule with charge  $Z$ ,  $n$  is amount of the strongest bound water molecules;  $m$  is water amount in near hydrated shell,  $k$  is water amount in far hydrated shell, and  $\mid$  marks thresholds of the shells. (It is worth to note that data of various methods are in good agreement only in  $n$  determination, and thresholds nature remains almost unknown).

Returning to Fig. 3, distinctive jump of curve 2' in at 90° (corresponding to 2  $H_2O$  molecule per cation/anion pair) can be re-

Table. Hydration parameters of cesium halides obtained in TGA experiments

Salt	$n$	Near hydration shell			Far hydration shell		
		$m$	$\Delta\Delta H_{des}$ , kJ/mol	$N$	$k$	$\Delta\Delta H_{des}$ , kJ/mol	$N$
CsCl	$2.1\pm 0.4$	$41\pm 1$	$-6.5\pm 0.5$	$0.78\pm 0.02$	$>80$	$-15.2\pm 0.2$	$0.60\pm 0.02$
CsBr	$2.2\pm 0.5$	$86\pm 1$	$-1.4\pm 0.4$	$0.98\pm 0.01$	$>70$	$-10.3\pm 0.5$	$0.81\pm 0.03$
CsI	$1.9\pm 0.4$	$100\pm 1$	$2.4\pm 0.4$	$1.13\pm 0.08$	$>85$	$-14.8\pm 0.6$	$0.64\pm 0.04$

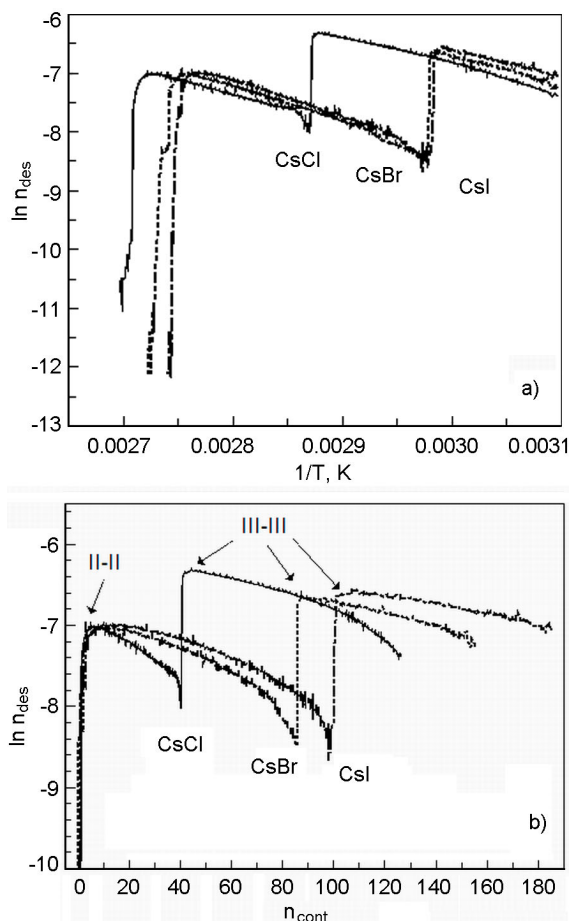


Fig. 4. Amount of desorbed water  $n_{des}$  as a function of reciprocal temperature (a) and of water/salt ratio (b). Thresholds between water shells are marked according to formula (5).

ferred to the threshold II-II (see (5)). The next jump of the curve (corresponding to 99  $H_2O$  molecule per cation/anion pair) probably refers to threshold III-III.

Desorption processes registered by TGA are shown in Fig. 4, where original TGA data are plotted according to Eq. (3). Threshold III-III jump can be determined for CsCl as 41, and for CsBr as 86 water molecules. The water bulk between II-II and III-III thresholds (near hydration shell) seems to be homogenous, because the lines

inclinations remain constant. Deviations from linearity near the jumps could result from structure rearrangement in the neighborhood of the thresholds regions. Increasing of the size of near hydration shell in order CsCl–CsBr–CsI is in agreement with decreasing of their solubility in water [16], though direct comparative data were not found in literature.

Parameter  $n$  refers to not hydration number in classical sense [17], but rather to a number of water molecules which remain between the cation and the anion before final sample drying. This value was determined for CsBr and CsCl as 2  $H_2O$  molecule per cation/anion pair, as much as for CsI. This coincidence seems believable because of linear correlation between the amount of strongly bonded water and the energy of crystal lattice of alkali halides [1]. Taking into account these values ( $\Delta H_{298}$  (kJ/mol) is 669.0 (CsCl); 646.8 (CsBr) and 613.4 (CsI) [18]), one can obtain that  $n$  values for these salts vary within limits of 10 %. This value proved to be less than the experimental error value (see Table).

All the hydration parameters obtained according to (3)–(5) are collected in Table. Water desorption enthalpy ( $\Delta H_{des}$ ) for bidistilled water was obtained as  $\Delta H_{des}^w = 49.0\pm 0.4$  kJ/mol, which is much more than reference one (40.6 kJ/mol). Such disagreement is probably caused by wetting effects which become significant due to small crucible diameter (6 mm) and, hence, may be considered as systematical error. So, it seems reasonable to use relative enthalpy changes,  $\Delta\Delta H_{des}$ , i.e. the difference between these values defined for pure water and for proper salt solution.

As one can see from Table, not only the size of near hydration shell, but  $\Delta H_{des}$  and  $N$  increase in order CsCl–CsBr–CsI. It is interesting that  $\Delta H_{des}$  appears lower than  $\Delta H_{des}^w$  in CsCl and CsBr solutions, whereas in CsI solutions, this values appear slightly more than  $\Delta H_{des}^w$ . Exactly the same tendency was occurred in [19] for the values of

water entropy in the neighborhoods of the anions. Taking into account that Gibbs free energy of the salts solvent decreases in the same order [20], one can suggest more significant growth of the entropy constituent than of the enthalpy one.

Similar clear correlations were not established in far hydration shell. This fact points to the necessity of optimization of the experimental technique. But according to Table,  $N$  in far hydration shell proved to be less than one in near hydration shell, which seems believable.

#### 4. Conclusions

The technique proposed allows one to obtain some hydration parameters of cesium halides and ascertain their distinctions. Among advantages of the technique there are technical simplicity, accessibility, ability to obtain highly hydrated samples, and small amount of tested material required. Among its disadvantages there is rather large experimental time required. The technique can be applied to water soluble and non-volatile compounds, so it could be useful for detailed quantitative study of hygroscopic properties of certain scintillators.

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#### References

1. M.Zhuravleva, L.Stand, H.Weil et al., Nuclear Science Symposium and Medical Imaging Conference, Seoul, South Korea (2013), p.1.
2. Y.Ledemi, L.Calvez, M.Rozza, X.H.Zhang et al., *J. Optoelectron. Adv. Mat.*, **9**, 3751 (2007).
3. O.Ya.Samoylov, I.B.Rabinovich, K.T.Dudnikova, *Zh. Struct. Khimii*, **196**, 768 (1965).
4. L.A.Petrenko, Yu.A.Petrenko, E.F.Ivanova, *Zh. Fiz. Khimii*, **43**, 2967 (1969).
5. K.M.Elkind, I.G.Trunova, *Trudy Nizhegorodskogo GTU*, **4**, 272 (2012).
6. C.Chiappe, M.Malvaldi, C.S.Pomelli, *Pure Appl. Chem.*, **81**, 767 (2009).
7. T.A.Blank, L.P.Eksperiandova, *Visnyk KhNU, Khimia*, **16**, 27 (2008).
8. A.G.Tereshchenko, *Gigroskopichnost i Slezhi-vaemost Rastvorivmyh Veshchestv*, Tomsk, Izdatelstvo TPU (2011) [in Russian].
9. D.S.Sofronov, A.Yu.Voloshko, O.V.Shishkin et al., *Zh. Neorg. Khimii*, **52**, 1783 (2007).
10. J.Han, *Trends In Bio/Pharmaceutical Industry*, **3**, 25 (2006).
11. M.A.Berliner, *Izmereniya Vlazhnosti*, Energiya, Moscow (1973) [in Russian].
12. B.D.Stepin, G.O.Allakhverdov, G.P.Serebrennikova, *Zh. Fiz. Khimii*, **43**, 2452 (1969).
13. G.A.Krestov, V.D.Ovchinnikova, V.D.Baranikov et al., *Termodinamika i Stroenie Rastvorov*, Izd-vo ICHTI, Ivanovo (1979) [in Russian].
14. P.A.Redhead, *Vacuum*, **12**, 203 (1962).
15. G.A.Krestov, *Zh. Struct. Khimii*, **4**, 402 (1962).
16. B.E.Plushchev, B.D.Stepin, *Analiticheskaja Khimija Rubidija i Tsezija*, Nauka, Moscow (1975) [in Russian].
17. R.Robinson, R.Stokes, *Electrolyte Solutions*, London (1959).
18. *Kratkij Spravochnik Fiziko-khimicheskikh Velichin*, Ivan Fedorov, S.-Peterburg (2003) [in Russian].
19. G.A.Krestov, *Zh. Struct. Khimii*, **3**, 137 (1962).
20. *Ionnaja Solvatatsija*, Nauka, Moscow (1987) [in Russian].