Russian Journal of General Chemistry, Vol. 74, No. 3, 2004, pp. 335–340. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 3, 2004, pp. 372–378.

Change in Volume Properties of and Complex Formation in the System $Hg(NO_3)_2$–KX–H_2O (X^- = Cl^-, Br^-, I^-)

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Received December 27, 2002

Abstract—The chemical nature of the anions in step complex formation in $Hg(NO_3)_2$–KX–H_2O systems (X^- = Cl^-, Br^-, I^-) manifests itself in different trends in variation of the molar volumes of the solutions.

At present increasing interest in thermodynamic studies on solutions is given to their volume properties. Although these properties reflect only an integral state of the system, they notably surpass other thermodynamic parameters in sensitivity to structural features of the solution. Analysis of volume characteristics of chemical interactions may provide information on structural changes not only in the immediate environment of ions, but also in the solution as a whole. Volume properties are best studied by a comparative method, since it allows one to reveal specific features of interactions for separate complex systems and thus to gain a deeper insight into the chemistry of aqueous salt solutions.

In this work we have studied the volume changes produced in solutions of mercury(II) nitrate by its complex formation with a number of halide ions X^- at varied concentrations of the components and varied X^- [$Hg(NO_3)_2$–KX–H_2O systems (X^- = Cl^-, Br^-, I^-)].

Mercury(II) ions form a series of complexes HgX_i^{2-i} (i = 1–4) with halide ions X^- (X^- = Cl^-, Br^-, I^-) [1] in step reactions [scheme (1)].

$$Hg_{i-1}^{3-i} + X^- = Hg_i^{2-i}. \quad (1)$$

It is necessary to note that the neutral complex species $HgBr_2$ and HgI_2 are practically insoluble in water, but they transform to soluble anionic species HgX_3^- and HgX_4^{2-} in excess of the corresponding halide. Vice versa, all complexes with chloride ions, $HgCl_2$ among them, are readily soluble in water. Thus, complex formation in $Hg(NO_3)_2$–KX–H_2O systems (X^- = Br^-, I^-) starts in solution, goes on in a heterogeneous system, and completes again in solution. Doubtlessly, reactions that occur in such a complex system should exert effect on physicochemical properties of the solution, and the strength of this effect should depend on reagent concentrations. However, heterogeneous systems are most frequently quite difficult to study experimentally.

In this work we made use of dilatometric titration [2–7] which permits to go around these difficulties. Using this method we directly and continuously measured volume changes as a result of chemical reactions and corresponding structural modifications in the systems under study.

The volume change ΔV which is given by the equation $\Delta V = V_{exp} - (V_1 + V_2)$ is in essence a deviation from additivity (the difference between the experimentally observed volume of the whole system V_{exp} and the sum of the volumes of the interacting solutions V_1 and V_2). The resulting data are shown in Figs. 1–3 as plots of molar volume change ΔV_m ($cm^3\ mol^{-1}$) on complex formation in $Hg(NO_3)_2$–KX–H_2O systems (X^- = Cl^-, Br^-, I^-) against molar ratio N = $[X^-]:[Hg^{2+}]$.

Furthermore, in addition to dilatometric measurements, we calculated fraction distributions of HgX_i species (i = 1–4) as a function of N (Figs. 1–3) on the basis of published step stability constants of mercury(II) complexes {system $Hg(NO_3)_2$–KCl–H_2O: $\log K_1$ 6.72, $\log K_2$ 6.51, $\log K_3$ 1.00, $\log K_4$ 0.97 [8]; system $Hg(NO_3)_2$–KBr–H_2O: $\log K_1$ 9.04, $\log K_2$ 8.40, $\log K_3$ 2.18, $\log K_4$ 1.36 [9]; system $Hg(NO_3)_2$–KI–H_2O: $\log K_1$ 12.81, $\log K_2$ 11.11, $\log K_3$ 3.79, $\log K_4$ 2.04 [9]}.

As usual, comparative analysis allows us to reveal common and specific features of different systems. In our case, at first glance, similar shapes of the $\Delta V_m = f(N)$ curves is a common feature.

The shapes of the dilatometric curves for the systems under study (Figs. 1–3) show that they all are a combination of several straight-line sections cor-

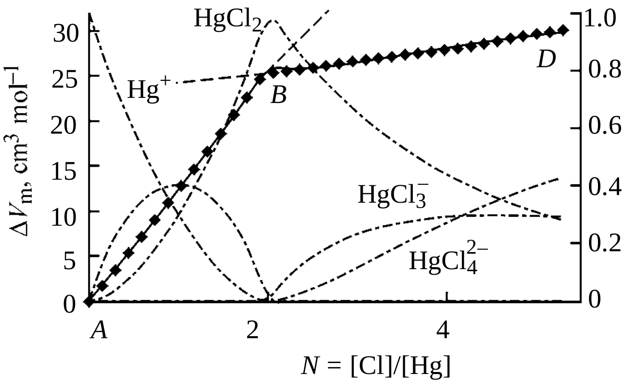

Fig. 1. Dilatometric titration curve for the system $Hg(NO_3)_2$–KCl–H_2O. Here and hereinafter $[Hg(NO_3)_2]$ 0.172 and [KX] 0.60 M; (points) experiment, (solid line) calculation, and (broken line) distribution diagram of complex species.

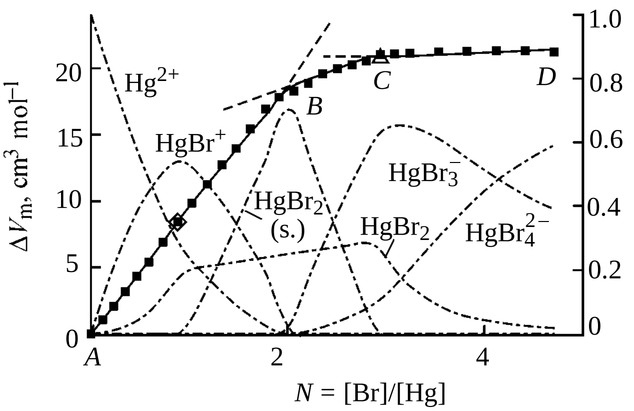

Fig. 2. Dilatometric titration curve for the system $Hg(NO_3)_2$–KBr–H_2O. Here and hereinfter, (rhombs) precipitation onset points and (triangles) full precipitate dissolution points.

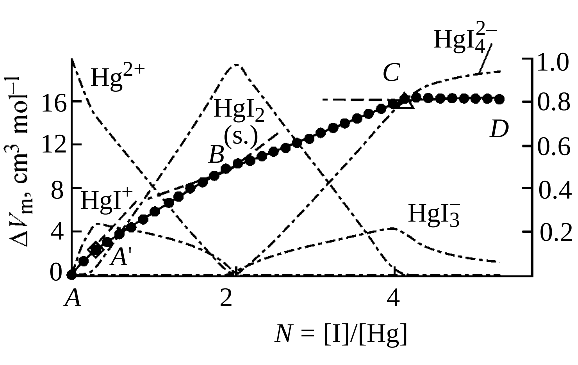

Fig. 3. Dilatometric titration curve for the system $Hg(NO_3)_2$–KI–H_2O.

responding to different chemical reactions and intersecting in the singular points *A*, *B*, and *C*.

In all the three cases, the volume appreciably increases up to *N* 2 (i.e. up to the singular point *B*) corresponding to the first two steps of complex formation. After *N* 2, the positive volume effect noticeably attenuates.

Complex formation is known to be most frequently accompanied by an increase in volume. Two reasons can be responsible for it. First, this is dehydration of the ions forming a complex. Generally, there are several possible schemes of complex formation [schemes (2)–(4)].

$$A_{aq}^{y+} + B_{aq}^{z-} = AB_{aq}^{y-z} + aq + \Delta V_1, \qquad (2)$$

$$A_{aq} + B_{aq}^{z-} = AB_{aq}^{z-} + aq + \Delta V_2, \qquad (3)$$

$$A_{aq}^{y-} + B_{aq}^{z-} = AB_{aq}^{y-z} + aq + \Delta V_3. \qquad (4)$$

Here A is an ion or a neutral molecule and B is an acido ligand.

Water in the hydration shells of initial ions is in a structured, i.e. in a contracted state (as compared to the structure of free water) owing to the so-called electrostriction effect. This effect can be considered as a result of electrostatic interaction between an ion and the water dipole. Complex formation liberates water molecules from the hydration shells of each ion, and they become a part of the solvent structure and occupy a slightly larger volume compared to the initial state. Furthermore, the formation of a complex species by scheme (2) is accompanied by charge neutralization. In the system under study, this takes place when first two complex species have been formed [reaction (1), *i* = 1 and 2], i.e. at *N* from 0 up to 2, and affects the state of water molecules in the hydration shell of the complex species. The electrostatic interaction of these water molecules and the weaker charged complex species formed attenuates, thus introducing an additional positive contribution (ΔV_{elong} [10]) to the total volume change.

It is seen from Figs. 1–3 that the singular point *B* at *N* 2 fairly correlates with the maximal content of the HgX_2 form in all the systems under study. Let us consider the correlation between the molar ratio *N* and the maximal content of a complex in solution, calculated with use of stability constants (potentiometry [8, 9]). The anion (complex) contents c_{max} and *N* are as follows: Cl^- ($HgCl_2$) 2, 2; Br^- ($HgBr_2$) 2, 2; ($HgBr_3^-$) 3.4, 3.4; I^- (HgI^+) 0.2, 0.2; (HgI_2) 2, 2, and (HgI_3^-) 4, 4.

In fact, the independent data obtained by different methods are nicely consistent with each other, thus providing further evidence for our dilatometric data. Change of the dominating process in solution occurs at *N* corresponding to the singular point *B* in the dilatometric curve, which is also seen in the distribution diagrams (Figs. 1–3). Actually, HgX_2 formation and precipitation dominate up to *N* 2 [except for the system $Hg(NO_3)_2$–KCl–H_2O], and at $N > 2$ the precipitate dissolves to form HgX_3^- and HgX_4^{2-} complexes in solution.

Thus, our analysis shows that $N = [X^-]: [Hg^{2+}] = 2$ in the singular point *B* of the dilatometric curve is a characteristic of the composition of the complex both in solution ($HgCl_2$) and in the solid phase ($HgBr_2$, HgI_2) (Figs. 1–3).

Let us consider specific features of the systems under study. For $X^- = Br^-$ and I^-, there is also the singular point *C* at the maximal content of HgX_3^- species. This point for Br^- anions, as well as the maximum for HgX_3^- species are reached at a lower mole ratio (*N* 3.0) than for I^- (*N* 4), which results from the higher solubility of $HgBr_2$. The HgX_3^- form is not always dominating, but it is its maximal content which manifests itself in dilatometric curves as the singular point *C*. The absence of the point *C* for $X = Cl^-$ is natural, because the distribution diagram of $HgCl_3^-$ shows no well-defined maxumum and, therefore, further volume increase is observed. With the other systems, addition of halide ions at $N > 4$ produces no noticeable volume changes.

Mercury halides HgX_2 that form precipitate in two of the three systems (iodides at *N* 0.2 and bromides at *N* 0.8; the precipitation points are marked by special symbols in Figs. 2 and 3). It is necessary to note that solid phase formation differently affects volume properties of solutions. Amari *et al.* [11] contend that precipitation should be accompanied by a greater volume increase compared to complex formation ($\Delta V_p > \Delta V_{cf}$) as a result of the formation of the inherent structure of the precipitate. However, we did not observe changes in the volume effect in going from complex formation in solution to precipitate formation (i.e. $\Delta V_p = \Delta V_{cf}$) in one of the systems studied ($X = Br^-$, Fig. 2). We can conclude that precipitate formation in this case is accompanied by the dehydration of ions in the same way as in the case of complex formation [scheme (2)] and, correspondingly, by the same structural changes of water in solution. In the case of $X = I^-$, the positive volume effect decreases at the moment of precipitation onset ($\Delta V_p < \Delta V_{cf}$). Thus, the iodide system in distinguished from the other systems by the presence of the singular point *A*' (Fig. 3) at *N* 0.2, which corresponds to the maximal concentration of HgI^+ and to HgI_2 precipitation onset.

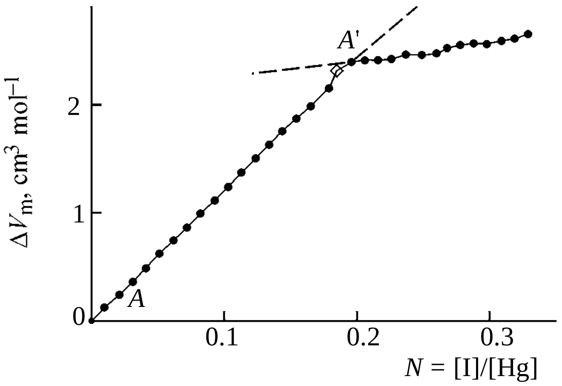

Fig. 4. Dilatometric titration curve for the system $Hg(NO_3)_2$–KI (*c* 0.30 M)–H_2O.

To check this feature of the $Hg(NO_3)_2$–KI–H_2O system, we carried out an additional dilatometric titration at low *N* values (Fig. 4). As seen, this experiment gave evidence for our earlier results. The presence of a singular point at *N* 0.2, when HgI_2 starts to precipitate, is connected to structural features of this solid phase compared to $HgBr_2$.

Such a difference in the effects of precipitate formation on volume properties of the system suggests that in considering volume characteristics of precipitation one should take into account the composition and structure of the particular solid phase and also specific features of its interaction with solvent molecules.

At $N > 2$, i.e. in the third and fourth steps of complex formation, the positive volume effect decreases. Unlike the first and second steps of reaction (1), $i = 1$ and 2, where charge neutralization takes place according to scheme (2), at $N > 2$, there is the transition from the uncharged complexes HgX_2 to the negatively charged complexes HgX_3^- and HgX_4^{2-} by schemes (3) and (4). The total ionic charge in these systems remains unchanged, which is undoubtedly responsible for the smaller ΔV_3 and ΔV_4 values compared to the first two volume effects.

It is probable that structural changes of halide complexes themselves can introduce their own contribution to the volume changes in all the steps [7]. It is known that the initial mercury hexaaqua complex $Hg(H_2O)_6^{2+}$ has an octahedral structure, and the final tetraaqua complexes HgX_4^{2-} are tetrahedral. As for the intermediate complexes HgX_i (i = 1–3), there are different opinions concerning their structure in solution. First of all this variance is connected to the rather low concentrations of these species within the entire range of molar ratios. Griffiths and Anderson [12], having investigated a great number of electronic spectra, found that the $HgCl_3^-$ anion has a planar structure (D_{3h} symmetry) and is completed to trigonal bipyramid by two coordinated H_2O molecules. At the same time, HgI_3^- has a pyramidal structure (C_{3v} symmetry) and is completed to tetrahedron by one H_2O molecule. In turn, according to [12], $HgBr_3^-$ occupies an intermediate position, but still its structure is closer to pyramidal. From a comparative analysis of published structural characteristics of mercury halide complexes, on the one hand, and data on volume changes in the systems under study (Figs. 1–3), on the other, we can conclude that the volume effects in the latter case are primarily controlled by changes in the charges of the starting and final species, affecting the structure of the solution as a whole.

Different molar reaction volumes (ΔV_{mi}) in all steps of complex formation can also be related to specific features of the systems under study. Analysis of ΔV_{mi} values gives information on structural changes of the solution as a whole.

The ΔV_{mi} values for each step of complex formation of mercury with halide ions [reaction (1), $i = 1–4$] were calculated using the CPESSP simulating program [13, 14] using step complex formation constants for $Hg(NO_3)_2–KX–H_2O$ systems ($X^- = Cl^-, Br^-, I^-$). The ΔV_1, ΔV_3, and ΔV_4 values for all the three systems, as well as ΔV_2 for $X = Cl^-$, were obtained with account for the stability constants of complexes in solution, whereas ΔV_2 for $X^- = Br^-, I^-$ were obtained using the solubility products of precipitates [ΔV_2 (s.)], since the fractions of HgX_2 complexes in solutions of these systems are small and insufficient for correct calculation of ΔV_2(sol.). Thus, along with the stability constants of complex species, we took into account the solubility products of the poorly soluble HgX_2 (the SP values calculated by the CPESSP program are $10^{-18.9}$ for $HgBr_2$ and $10^{-27.5}$ for HgI_2). The calculated ΔV_{mi} values are as follows, $cm^3 mol^{-1}$: $Hg(NO_3)_2–KCl–H_2O$: ΔV_1 12.95, ΔV_2 12.94, ΔV_3 2.71, and ΔV_4 1.66; $Hg(NO_3)_2–KBr–H_2O$: ΔV_1 8.75, ΔV_2 8.84, ΔV_3 2.83, and ΔV_4 1.98; and $Hg(NO_3)_2–KI–H_2O$: ΔV_1 8.64, ΔV_2 1.35, ΔV_3 3.97, and ΔV_4 2.54.

It is seen that the volume effects ΔV_1 and ΔV_2 for $X^- = Cl^-, Br^-$ are rather close to each other, which also shows up in the fact that the corresponding plots from the point of origin up to the point *B* (Figs. 1 and 2) are straight lines. The system $Hg(NO_3)_2–KI^-$ H_2O is an outlier, as its ΔV_2 is much smaller than ΔV_1, which manifests itself in the presence of the singular point *A*' in the dilatometric curve at the moment of precipitation onset (*N* 0.2).

By the volume effects ΔV_1 and ΔV_2 of complex formation with mercury at molar ratios *N* from 0 up to 2 within the studied range of concentrations, the halide ions form series (5).

$$\Delta V_1,\ \Delta V_2(Cl^-) > \Delta V_1,\ \Delta V_2(Br^-) > \Delta V_1,\ \Delta V_2(I^-). \quad (5)$$

On the one hand, this series does not correspond to the widespread notion that the more stable are the resulting complexes, the greater positive volume effects should accompany their formation (see published stability constants of mercury halide complexes). According to this logic, the series of volume effects should be reverse. However, on the other hand, when considering mercury(II) halide complexes with stability constants ranging from 10^6 up to 10^{13}, one should take into account that the degree of ion binding into a complex is close to 100% even in the case of chloride ions that form the “least stable” complexes with Hg^{2+} ions.

Thus, most emphasis in interpreting the series of halide ions arranged in terms of the volume effects of their complex formation with Hg^{2+} ions should be paid to the nature of the halide ions themselves. Analysis of published partial molar volumes of the ions {$V_0(Cl^-)$ 17.83, $V_0(Br^-)$ 24.71, and $V_0(I^-)$ 36.22 $cm^3 mol^{-1}$ [15]} and available data on the effect of the ions on the water structure in their immediate environment [16] allows us to propose the following explanation of the described regularity. In the range of *N* values under consideration, Hg^{2+} reacts with X^- by scheme (1) ($i = 1, 2$), and, therefore, the volume change in the reaction can be written as $\Delta V_{mi} = \Delta V_{Hg} + \Delta V_X$ [ΔV_{Hg} is the contribution of dehydration of Hg^{2+} ions to the change in molar volume; ΔV_X is the similar contribution of X^- ions; the ΔV_{mi} values are given above and the ΔV_{Hg} value is constant for all the systems, as the initial concentration of mercury(II) ions and the degree of their binding in complexes (~100%) are equal for all the systems]. Series (5) can be explained in terms water structuring–destructuring in the ionic field. On complex formation in $Hg(NO_3)_2–KX–H_2O$ systems, destructurized water molecules from the immediate environment of halide ions pass into the structure of the free water. This introduces a negative contribution into the total volume effect ($\Delta V_X < 0$), but, nevertheless, the positive volume effect from dehydration of Hg^{2+} ions ($+\Delta V_{Hg}$) and from transfer of water structured around mercury ions into the free volume override this negative contribution, and the total volume effect remains positive. In going from iodide ions with the strongest destructuring effect on water to bromide and chloride ions, the negative contribution to the ΔV_1 and ΔV_2 values decreases.

Thus, the volume changes ΔV ($cm^3\ mol^{-1}$) at N 0–2 should decrease along series (5), and this is observed experimentally.

Unlike the above-considered ΔV_1 and ΔV_2 series ($N > 2$), the ΔV_3 and ΔV_4 series for the halide ions under study is reversed.

$$\Delta V_3,\ \Delta V_4(I^-) > \Delta V_3,\ \Delta V_4(Br^-) > \Delta V_3,\ \Delta V_4(Cl^-). \quad (6)$$

It follows from the formation constants of HgX_3^- and HgX_4^{2-} complexes and from the distribution curves that the degree of ion binding (α) in this region is lower than 100%. If we designate the volume effect of a 100 % reaction as ΔV_{100}, the observed volume effect ΔV_m will be determined by Eq. (7).

$$\Delta V_m = (\Delta V_{100}\alpha) \times 100\%. \quad (7)$$

The ΔV_{100} value is positive for all the three systems. The degree of ion binding into a complex is maximal for $X^- = I^-$ and minimal for $X^- = Cl^-$, which is responsible for the series reversal. Thus, in the region of molar ratios, where the degree of anion binding into a complex is not 100%, the stability of the resulting complexes (see the K_3 and K_4 values) and, correspondingly, the degree of ion binding into these complexes become dominating factors (though, apparently, not unique). This order agrees with the above-mentioned reasoning concerning the correlation between the stability of a complex and the strength of the positive volume effect of its formation [17].

Thus, in this work we have studied volume effects in step complex formation of mercury(II) ions with halide ions in the $Hg(NO_3)_2$–KX–H_2O ($X^- = Cl^-$, Br^-, I^-) systems by means of dilatometric titration. A quantitative characteristic of volume changes in these systems is given. The effects of the chemical nature of the anions on the volume changes are shown to be different. It was established that at the molar ratios N from 0 to 2 the formation of HgX^+ and HgX_2 complexes for all X^- is accompanied by volume increase resulting from dehydration of the reacting ions, the volume effect of halide ions decreasing in the series ΔV_1, ΔV_2 (Cl^-) > ΔV_1, ΔV_2 (Br^-) > ΔV_1, ΔV_2 (I^-), in parallel with the partial molar volumes of the corresponding anions and their effect on the structure of water. Formation of anionic complexes HgX_3^- and HgX_4^{2-} ($N > 2$) is accompanied by weaker positive volume effects for all the systems. In this case, the volume-effect series is reversed: ΔV_3, ΔV_4 (I^-) > ΔV_3, ΔV_4 (Br^-) > ΔV_3, ΔV_4 (Cl^-). This dependence was explained in terms of the stability of the resulting complexes.

EXPERIMENTAL

Solutions of potassium halides were prepared with chemical grade potassium chloride, officinal potassium bromide, and pure grade potassium iodide. The initial solution of mercury(II) nitrate was prepared from chemical grade mercury(II) nitrate monohydrate; to prevent spontaneous hydrolysis, this solution was acidified with nitric acid. The concentration of mercury(II) was determined using thiocyanate ions in the presence of iron(III) ions. Dilatometric titrations we performed using an 0.172 M solution of mercury(II) nitrate containing 0.195 M nitric acid and an 0.60 M solution of corresponding potassium halide. In one of titrations (Fig. 4), an 0.3 M solution of potassium iodide was used. The ionic strength of 1 M was maintained by continuously adding potassium nitrate. Directly before titration the working solutions were degassed in a vacuum desiccator for 15–20 min, then placed in a dilatometer (detailed description of the device and operating technique are given in [18, 19]). The temperature of 25°C was maintained in the course of titration with an accuracy providing stable volume changes (±0.005°C). The required temperature constancy during measurements was provided with the help of a sequence of two UT2/77 ultrathermostats and an air thermostat. The lower reaction chamber of the dilatometer was hermetically connected to a calibrated measument capillary tube 0.0401 cm in diameter; the displacement of liquid meniscus by 1 mm of the capillary tube length corresponded to the volume change of 1.261×10^{-4} cm^3. For faster equilibration, the solution in the lower chamber was continuously stirred with a magnetic stirrer. Precipitate formation during titration was controlled with a laser beam. The titration was carried out by adding certain amounts of the titrant to a solution containing a mercury(II) aqua complex at regular intervals (10 min) sufficient for liquid meniscus to stabilize the measurement capillary tube. Initially, the experimental data were obtained as a dependence of the meniscus displacement in the capillary tube (S, cm) on the number of revolutions of the dilatometer rod (U). The U value for each point was recalculated to the molar ratio N by formula (8).

$$N = (UV_{1U}c_x)/(V_{l.c.}c_{Hg^{2+}}). \quad (8)$$

Here V_{1U} is the volume corresponding to one revolution of the dilatometer rod, c_X is the concentration of halide ions, $V_{l.c.}$ is the volume of the lower chamber of the dilatometer, and c_{Hg} is the concentration of mercury(II) ions in the initial solution. The meniscus displacement S was recalculated to the change in molar volume ΔV_m by formula (9) (V_{1cm} is the volume corresponding to 1 cm of the capillary tube length).

$$\Delta V_{\mathrm{m}} = (V_{1\mathrm{cm}}S)/(V_{\mathrm{l.c.}}c_{\mathrm{Hg}}). \qquad (9)$$

Quantitative characteristics of volume changes associated with step complex formation in the systems under study, we fulfilled mathematical simulation using the CPESSP program [14, 15]. The model for treatment of dilatometric data is based on additive scheme (10), according to which (with reference to volume properties) the total volume change ΔV_{tot} in a reaction is a sum of the effects ΔV_i of separate reactions.

$$\Delta V_{\mathrm{t}} = \sum_{i=1}^{N}\alpha_i \Delta V_i. \qquad (10)$$

Here ΔV_i is the volume change on the formation of one mole of the ith form and α_i is its fraction.

The calculation involves constructing a composition matrix which includes a set of basis and complex species present in the solution. Each species is assigned the initial value of the property ΔV_i and the value of formation constant.

On the basis of Eq. (1), a set of M equations [M is the number of experimental points (30–38 for the reactions in study) was set up and solved using the nonlinear regression techniques by iteratively fitting ΔV_i values. Using the K_i constants, α_i values for all species in each titration point and, correspondingly, $\Delta V_{\mathrm{tot}}^{\mathrm{calc}}$. The goodness of fit of calculated values to experimental was estimated by Fisher's criterion (F) calculated as a sum of weighted rms deviations related the number of degrees of freedoms m [Eq. (11)] ($m = M - k$, k is the total number of parameters to be determined).

$$F = \{\Sigma(\Delta V^{\mathrm{exp}} - \Delta V_{\mathrm{tot}}^{\mathrm{calc}})^2/[(\sigma\Delta V^{\mathrm{exp}})^2 + (\Delta\Delta V)^2]\}/m,$$

$$F_{\mathrm{lim}} < 2. \qquad (11)$$

Here ΔV^{exp} is the experimental volume change, σ is the relative error of the determination (accepted σ 0.05), and $\Delta\Delta V$ is the absolute error of the determination (accepted $\Delta\Delta V$ 0.007 cm^3). For the basis species were used Hg^{2+} and X^- and for the complex species, mononuclear species HgX_n^{2-n} (n = 1–4) known from the literature.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project no. 02-03-32 750) and the *Universities of Russia* Program (project no. UR.05.01.004).

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