ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 9, pp. 633–639. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.K. Lyashchenko, D.V. Loginova, A.S. Lileev, N.A. Ivanova, I.A. Efimenko, 2009, published in Koordinatsionnaya Khimiya, 2009, Vol. 35, No. 9, pp. 643–649.

Dielectric Constant and Dielectric Relaxation in Aqueous Solutions of $K_2[PdCl_4]$ and $K_2[PtCl_4]$

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Received September 8, 2008

Abstract—The MW-dielectric properties of aqueous solutions of $K_2[PtCl_4]$ (**I**) and $K_2[PdCl_4]$ (**II**) were studied at 298 and 313 K in the frequency range (12–25 GHz) corresponding to the maximum dielectric constant dispersion for water and aqueous solutions of these salts. The low-frequency conductivities were measured. The static dielectric constant, the dielectric relaxation time, and the enthalpy of activation of the dielectric relaxation of the solutions were determined. Compared to pure water, in solutions of salts **I** and **II**, the orientational mobility of water molecules is increased and the network of H-bonds is violated more strongly than that of most other ions with hydrophilic hydration. It was demonstrated for the first time that dielectric spectroscopy can be used for analyzing complexation processes in systems containing aqua and hydroxo chloride complexes of metals.

DOI: 10.1134/S1070328409090012

Aqueous solutions of $K_2[PdCl_4]$ and $K_2[PtCl_4]$ are typical examples of systems with complex anions in solution. The ions $[PtCl_4]^{2-}$ and $[PdCl_4]^{2-}$ are similar in structure and size. In binary and ternary aqueous electrolytes with a relatively small excess of chloride ions, the solutions contain aqua and hydroxo chloride complexes of Pt(II) and Pd(II). The compositions of these complexes depend on the concentrations of Cl^- and H^+ ions and the temperature [1]. Compared to chloro complexes of Pt(II), analogous Pd(II) complexes are thermodynamically less stable, much more labile [1, 2], and easily hydrolyzable in aqueous solution.

A comparative study of Pt(II) and Pd(II) complexes are of great interest because of their biological activity. The discovery of a new class of promising antitumor platinum-based drugs [3] prompted a search for substances with cytostatic activity among complexes of other platinum metals, first of all among palladium complexes. However, most Pd complexes (including an analog of *cis*-$[Pt(NH_3)_2Cl_2]$ widely used in oncology) were ineffective [4, 5]. Presumably, this is associated with the higher lability of palladium salts compared to platinum ones. At the same time, a comparative study of the primary effects of Pt and Pd complexes on biological systems revealed that the $PdCl_4^{2-}$ ion is more active than $PtCl_4^{2-}$ [6]. Complexes containing the $PdCl_4^{2-}$ ion were found to exhibit not only antitumor activity but also radioprotective [7, 8] and immunomodulating effects [9].

The description of processes in biological systems is impossible without knowing the character of complexation; in addition, phenomena occurring in interactions of complexes with water should be understood. On the one hand, water molecules are “normal” ligands in the coordination sphere of the central atom. On the other hand, the molecular kinetic properties of water change upon hydration of metal complexes. In the case of Pt(II) and Pd(II) complexes, the hydration is more complicated than common aqueous electrolytes containing simple cations and anions.

To analyze hydration effects, we used MW-dielectric spectroscopy in the frequency range corresponding to the maximum dispersion of the dielectric constants of water and aqueous solutions (7–30 GHz). This technique detects changes in the kinetic mobility of water molecules in the hydration shells of ions. This is one of few direct techniques that allows the characterization of water molecule dynamics over times of $\sim 10^{-11}$ s from experimental data on the dielectric relaxation time τ. The temperature dependence of τ is used to calculate the activation parameters of dielectric relaxation ($\Delta H_\varepsilon^{++}$, $\Delta G_\varepsilon^{++}$, $T\Delta S_\varepsilon^{++}$), which reflect changes in the degrees of binding and structuration of the network of H-bonds in solution.

Another important hydration characteristic of aqueous electrolytes is static dielectric constant $\boldsymbol{\varepsilon}_s$. This quantity cannot be determined directly because of the high conduction of electrolyte systems. Yet it can be calculated from high-frequency data on dielectric constant $\boldsymbol{\varepsilon}'$ and dipole-associated losses $\boldsymbol{\varepsilon}''_d$ by extrapola-

Table 1. High-frequency dielectric constant and dipole-associated dielectric losses in aqueous solutions of $K_2[PdCl_4]$ and $K_2[PtCl_4]$

m, mol/kg H_2O	12.17 GHz		13 GHz		14 GHz		16 GHz		18.9 GHz		22 GHz		25 GHz	
	ε'	ε''_d	ε'	ε''_d	ε'	ε''_d	ε'	ε''_d	ε'	ε''_d	ε'	ε''_d	ε'	ε''_d
298 K $K_2[PdCl_4]$–H_2O														
0.2			52.6	30.4			48.9	32.7	41.6	33.6	36.1	33.8	32.4	33.1
0.3			52.3	29.5			46.8	31.7	41.2	32.6	36.0	32.8	32.1	32.5
0.4			51.9	28.5			46.1	30.7	41.1	31.6	35.8	31.9	32.0	31.3
$K_2[PtCl_4]$–H_2O														
0.2	53.9	30.8			51.5	31.7	47.2	33.1	41.0	33.4	36.0	33.6	31.9	33.5
0.3	52.8	29.4			50.5	30.5	46.4	31.9	40.4	32.0	35.7	32.3	31.9	32.1
0.4	51.3	28.2			49.5	29.3	45.6	29.9	40.1	30.8	35.6	30.9	31.8	30.7
318 K $K_2[PdCl_4]$–H_2O														
0.2			58.2	23.9			53.6	26.7	49.0	29.3	45.3	30.7	41.0	31.0
0.3			57.5	22.6			52.7	25.5	48.0	28.2	43.6	29.1	40.5	30.3
0.4			56.6	21.4			51.9	24.2	46.8	26.8	42.7	28.4	39.4	28.9
$K_2[PtCl_4]$–H_2O														
0.2	57.9	22.8			56.0	24.9	54.0	26.4	48.1	28.9	44.3	30.2	40.9	31.3
0.3	56.8	21.8			55.1	23.8	53.0	24.8	47.6	27.9	43.5	28.7	40.5	29.8
0.4	56.2	20.9			54.4	22.7	52.2	23.8	46.7	26.6	42.9	27.8	39.7	28.7

tion to the zero frequency. Using experimental ε' and ε'' values, one can determine the above relaxation characteristics of water molecules in the context of a particular relaxation model [10]. The literature data on the MW-dielectric characteristics of aqueous solutions of salts with complex anions are lacking. With solutions of $K_2[PtCl_4]$ (**I**) and $K_2[PdCl_4]$ (**II**) as examples, one can find out whether the complex ions have a different effect on water compared to the well-studied [10–13] singly and doubly charged simple anions such as Cl^-, NO_3^-, SO_4^{2-}.

EXPERIMENTAL

We determined ε' and ε'' values in solutions of salts **I** and **II** at frequencies of 12.17, 13, 16, 18.9, 22, and 25 GHz at 298 and 308 K. The temperature was maintained constant with an accuracy of ±0.1°C. The experimental and calculational procedures are described in [13, 14]. We used the method of thin cylindrical rods in a waveguide [15], which allows studying highly conducting liquids (and, in particular, solutions of electrolytes) with great losses. The errors in the determination of ε' and ε'' were ε' ± (1–1.5)%, ε'' ± (2–2.5)%, respectively. The data obtained are given in Table 1.

The low-frequency conductivity σ required to calculate the ionic component of the losses (ε''_i) was determined in a cell with Pt electrodes at a frequency of 1 kHz with an E7-8 automated ac bridge. The cell was temperature-controlled to within ±0.1°C. The error in the determination of σ did not exceed ±0.5%. The data obtained are given in Table 2.

Table 2. Conductivity, the energy of conduction activation, and the ionic component of the dielectric losses in aqueous solutions of $K_2[PdCl_4]$ and $K_2[PtCl_4]$ at (1) 298 and (2) 313 K

m, mol/kg H_2O	*k*, S/m	E_a^*, kJ/mol	ε_i''						
			12.17 GHz	13.00 GHz	14.00 GHz	16.00 GHz	18.9 GHz	22.00 GHz	25.00 GHz
$K_2[PdCl_4]$ (1)									
0.2	3.89	14.6		5.38		4.37	3.70	3.18	2.80
0.3	5.54	14.3		7.67		6.24	5.28	4.54	3.99
0.4	7.13	12.9		9.87		8.02	6.79	5.84	5.13
$K_2[PtCl_4]$ (1)									
0.2	4.29	13.1	6.34		5.51	4.82	4.08	3.51	3.09
0.3	5.93	13.1	8.78		7.63	6.67	5.65	4.85	4.27
0.4	7.39	13.1	10.9		9.50	8.32	7.04	6.05	5.32
$K_2[PdCl_4]$ (2)									
0.2	5.16	14.6*		6.95		5.64	4.78	4.10	3.61
0.3	7.30	14.3		10.1		8.21	6.95	5.97	5.26
0.4	9.14	12.9		12.7		10.3	8.70	7.47	6.58
$K_2[PtCl_4]$ (2)									
0.2	5.52	13.1	8.16		7.09	6.20	5.25	4.51	3.97
0.3	7.64	13.1	11.3		9.82	8.59	7.27	6.25	5.50
0.4	9.52	13.1	14.1		12.2	10.7	9.06	7.79	6.85

* E_a was calculated for the temperature range 298–313 K.

The initial platinum and palladium compounds employed for preparation of solutions were synthesized as described in [16]. Potassium tetrachloroplatinate was prepared by reduction of $K_2[PtCl_6]$ with hydrazine sulfate; potassium hexachloroplatinate was prepared from a saturated solution of KCl and an aqueous solution of $H_2[PtCl_6] \cdot 6H_2O$ (“ч.”). $K_2[PdCl_4]$ (high-purity grade). Potassium tetrachloropalladate was prepared by addition of an excess amount of KCl to a solution of $PdCl_2$ (high-purity grade) acidified with HCl. The resulting solution was concentrated and the crystalline precipitate that formed was filtered off and recrystallized from water.

To monitor the stability of 0.2 m solutions of salts **I** and **II** with time, we measured their conductivities and pH for ~100 h since the instant they had been prepared (these solutions are most prone to hydrolysis). The pH values of solutions were measured with a Radelkis OP-110 pH meter (accuracy ±0.02 pH units). The results obtained are shown in Fig. 1. One can see that the conductivity and pH change only slightly with time and are within the measurement error. Therefore, one can believe that the ionic compositions of the solutions remained constant during our dielectric measurements.

The complex dielectric constant ε* was calculated by the equation [10]

$$\varepsilon^* = \varepsilon' - i\varepsilon'', \tag{1}$$

where ε' is the high-frequency dielectric constant and ε'' is the total losses at a particular frequency

$$\varepsilon'' = \varepsilon_d'' + \varepsilon_i''. \tag{2}$$

The ionic component of the losses was calculated by the formula [10]

$$\varepsilon_l'' = \sigma/\varepsilon_0\omega,$$

where ε_0 is the dielectric constant in vacuum and ω is the angular frequency at which ε* was measured.

For a single macroscopic relaxation process in the system under study, the frequency dependence of the dielectric parameters can be described in terms of the Debye or Cole–Cole model [10]:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\tau\omega^{(1-\alpha)}}, \tag{3}$$

where ε_s is the low-frequency limit of the dispersion range or static dielectric constant (provided that no other relaxation processes associated with the lower-frequency dispersion ranges take place in the system),

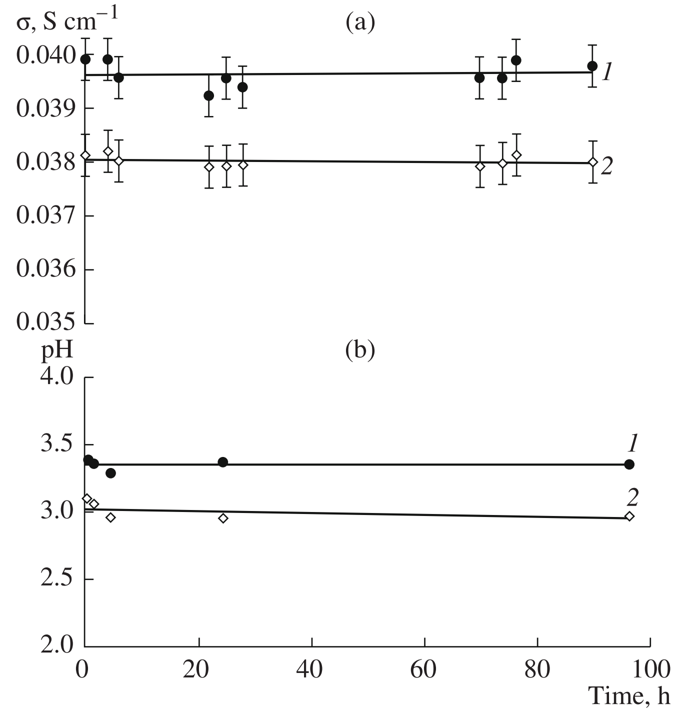

Fig. 1. Plots of (a) conductivity and (b) pH vs. time for 0.2 m solutions of (*1*) $K_2[PdCl_4]$ and (*2*) $K_2[PdCl_4]$ at 298 K.

τ is the most probable dielectric relaxation time, α is the parameter of the relaxation time distribution ($0 \le \alpha \le 1$), and ε_∞ is the high-frequency limit of the dielectric constant for the dispersion range under consideration. As in [11–13], ε_∞ for water and aqueous solutions was taken to be five.

According to experimental data, Eq. (3) can be use to describe relaxation processes for water molecules in the solutions studied (with the observed small relaxation time distribution α = 0.01–0.06). The ε_s values were determined from the Cole–Cole plots by circular extrapolation to a zero frequency. Some examples are shown in Fig. 2. The relaxation times of water molecules in solutions were estimated graphically from the frequency dependence of the function $f(\omega) = [((\varepsilon_s - \varepsilon')^2 + (\varepsilon'')^2)/((\varepsilon' - \varepsilon_\infty)^2 + (\varepsilon'')^2)]$ by using the Cole–Cole equation. In logarithmic coordinates, this dependence is linear, with a slope of $(1 - \alpha)$. Its *x*-intercept corresponds to the frequency at which the dipole losses are the highest ($\omega_{\max} = 1/\tau$). Using the equations of the absolute reaction rate theory, we calculated the activation parameters of dielectric relaxation. This is possible because, as a first approximation, the plot of $\ln\tau - 1/T$ is linear in the above temperature range. The data obtained are given in Table 3.

RESULTS AND DISCUSSION

The relaxation of water molecules in aqueous solutions of salts **I** and **II** occurs in the same frequency range as for solutions of simple electrolytes. These frequencies correspond to the dispersion range in pure water and in solutions of electrolytes and non-electrolytes [11–14]. Therefore, the parameters τ and $\Delta H_\varepsilon^{++}$ can be used to estimate the degree of binding and structuration of the network of H-bonds in salt solutions. A typical case of the hydrophilic hydration of ions occurs

Table 3. Dielectric properties of aqueous solutions of $K_2[PdCl_4]$ and $K_2[PtCl_4]$

m, mol/kg H_2O	298 K			313 K			$\Delta H_\varepsilon^{++}$ kJ/mol*	$T\Delta S_\varepsilon^{++}$ kJ/mol
	ε_s	τ, ps	α	ε_s	τ, ps	α		
$K_2[PdCl_4]$								
0	78.4	8.25	0.00	73.2	5.8	0.00	15.6	6.2
0.2	72.4	7.8	0.00	69.6	5.7	0.03	13.5	4.1
0.3	70.7	7.6	0.00	68.0	5.8	0.04	11.9	2.6
0.4	70.0	7.6	0.02	66.8	5.8	0.06	10.9	1.6
$K_2[PtCl_4]$								
0	78.4	8.25	0.00	73.2	5.8	0.00	15.6	6.2
0.2	73.4	7.9	0.01	68.2	5.6	0.01	15.5	6.2
0.3	72.2	7.9	0.03	67.1	5.6	0.04	15.5	6.2
0.4	70.9	7.8	0.06	66.2	5.6	0.06	14.4	5.1

* $\Delta H_\varepsilon^{++}$ was calculated for the temperature range 298–313 K.

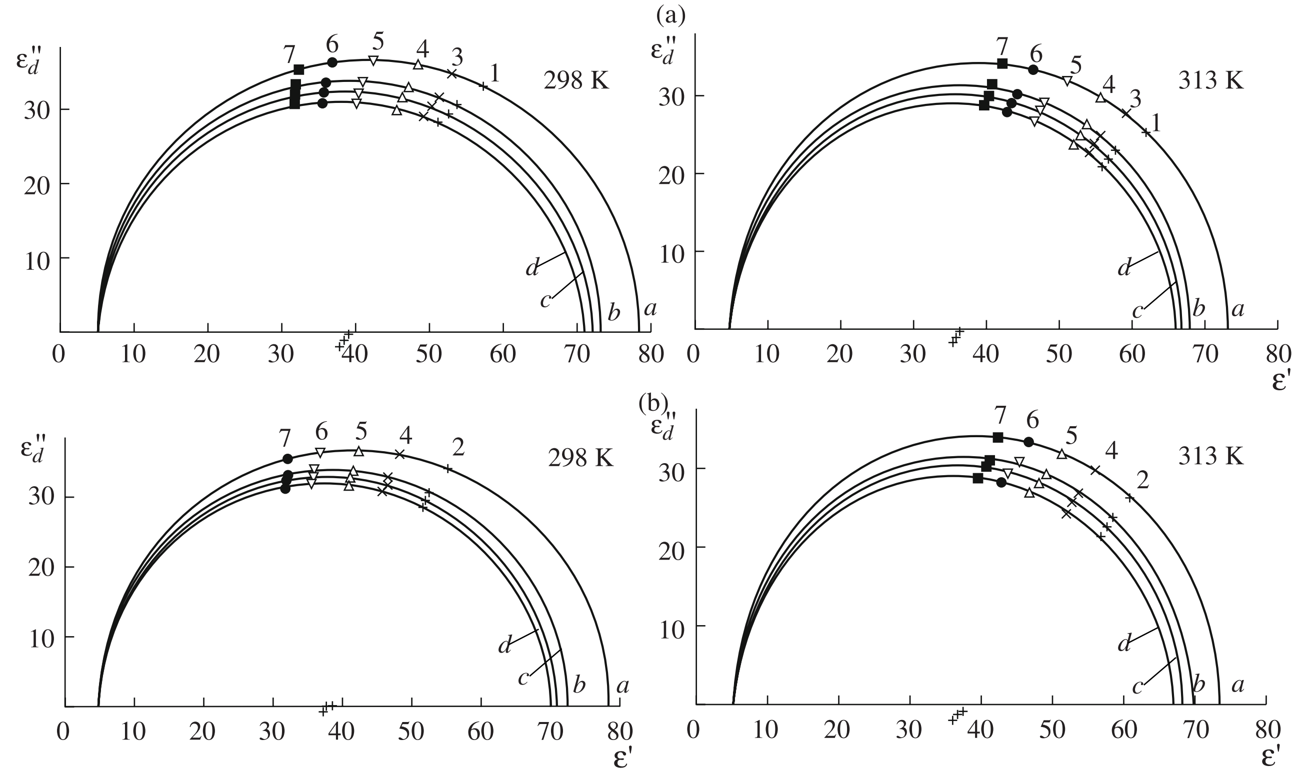

Fig. 2. Cole–Cole plots for aqueous solutions of (a) $K_2[PtCl_4]$ and (b) $K_2[PdCl_4]$. The frequencies are (1) 12.17, (2) 13, (3) 14, (4) 16, (5) 18.9, (6) 22, and (7) 25 GHz. The concentrations of the solutions are (*a*) 0, (*b*) 0.2, (*c*) 0.3, and (*d*) 0.4 mol/kg of H_2O.

when $\tau^{p-p} < \tau^{H_2O}$, and $\Delta H_\varepsilon^{p-p} < \Delta H_\varepsilon^{H_2O}$ [11–13, 17, 18]. Analogous changes take place in the solutions studied. Thus, according to molecular kinetic changes of water, solutions of $K_2[PtCl_4]$ and $K_2[PdCl_4]$ serve as a characteristic example of the hydrophilic hydration of ions. The decrease in τ and $\Delta H_\varepsilon^{++}$ when passing from water to aqueous solution suggests an increased orientational mobility of water molecules and violation of the initial network of H-bonds. The concentration dependences of τ at 298 K are more pronounced than at 308 K, when the initial structure of water is more strongly violated by the thermal motion of its molecules. This should diminish the effect of ions. That is why τ virtually does not change at 308 K or its changes are within the measurement error.

For salt **II**, the decrease in τ and $\Delta H_\varepsilon^{++}$ at 298 K is more pronounced than in solutions of salt **I** (Fig. 3). This can be explained by the higher dissociation degree of Pd(II) complexes compared to Pt(II) complexes; because of this, the concentration of chloride ions in solution increases after their displacement from the first coordination sphere of the central atom by water molecules or OH^- ions. Chloride ions and partially H^+ ions (due to hydrolysis) additionally violate the network of H-bonds in the bulk of solution. The violating effects of these ions were found in solutions of HCl [17]. A comparison with data for other solutions of 1 : 2 electrolytes (with K_2SO_4 as an example [12]) revealed that complex Pd(II) ions have a stronger violating effect than Pt(II) ions. In solutions of salt **II**, the Pd(II) ions produce one of the strongest violating effects on water because of the presence of additional Cl^- and H^+ ions in solution. In the reaction $[PdCl_4]^{2-} \longrightarrow \longrightarrow [Pd(Cl_3H_2O)]^- + Cl^-$ [1, 19], the destabilization of the network of H-bonds in solution should be approximately double as much as in a solution of KCl, provided that the effect of the complex anion $[Pd(Cl_3H_2O)]^-$ is close to that of Cl^-. This is observed experimentally. Thus, the character of changes occurring in water during the dissolution of $K_2[PdCl_4]$ depend on not only the hydration of the complex ion but also the number of Cl^- and H^+ ions produced by hydrolysis. This is confirmed by substantially lesser changes in the water structure upon the dissolution of $K_2[PtCl_4]$, when the displacement of Cl^- ions from the first coordination sphere by water molecules is less pronounced.

The ε_s values also decrease when moving from water to solutions of salts **I** and **II** (Table 3, Fig. 4). The least decrease in ε_s takes place in solutions of KCl containing singly charged cations and anions. At 298 K, ε_s

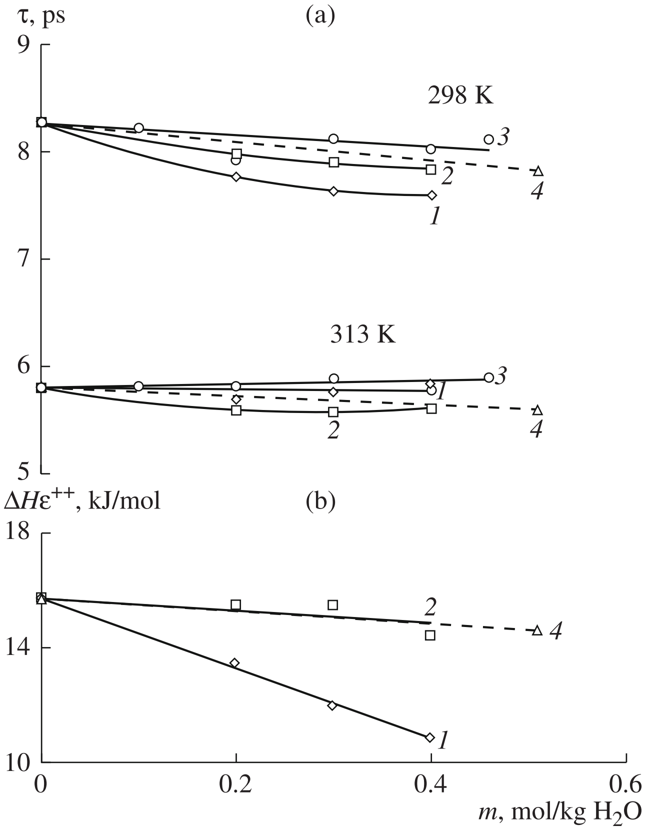

Fig. 3. Plots of (*a*) the time τ and (*b*) enthalpy $\Delta H_{\varepsilon}^{++}$ of dielectric relaxation vs. the concentration for aqueous solutions of (*1*) $K_2[PdCl_4]$, (*2*) $K_2[PtCl_4]$, (*3*) K_2SO_4, and (*4*) KCl.

falls more noticeably for $K_2[PdCl_4]$ than for $K_2[PtCl_4]$. The reasons are the same as with τ. Note that the stronger decrease in ε_s for a Pt–Pd pair correlates with the stronger fall of τs. For solutions of simple salts with singly charged ions, a correlation between a stronger decrease in τ and a less strong fall of τ_s is common [10–13]. This behavior is due to the fact that for stronger ion–water (ions with a smaller radius) interactions and a greater fraction of "frozen" water molecules (or their "frozen" degrees of freedom) in the first coordination sphere of the metal ions, water molecules become less mobile, thus more weakly affecting the orientational dynamics of the whole hydration shell. A different order of decreasing τ and ε_s for Pt(II) and Pd(II) ions is explained by the aforesaid displacement of Cl^- ions from the first coordination sphere of the central atom by water molecules (or OH^- ions if hydrolysis takes place). The stronger hydrolysis of the palladium salt produces a greater number of hydrated Cl^- and H^+ ions in solution, resulting in the corresponding changes in τ and ε_s.

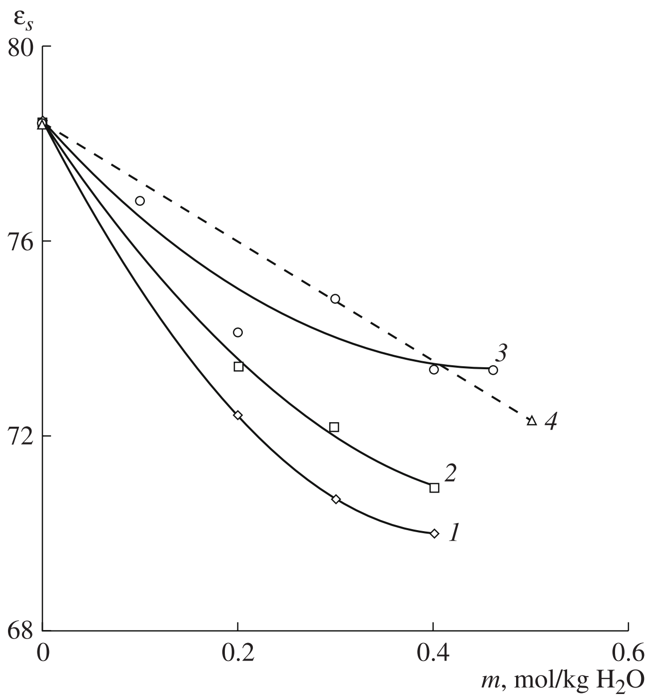

Fig. 4. Plots of the static dielectric constant ε_s vs. the concentration for aqueous solutions of (*1*) $K_2[PdCl_4]$, (*2*) $K_2[PtCl_4]$, (*3*) K_2SO_4, and (*4*) KCl at 298 K.

Hence, the complexation processes under discussion change not only the coordination sphere of the central atom but also the state of the aqueous medium. These changes are reflected by τ and ε_s values, which substantially differ from those for other salt solutions. These changes are most pronounced in solutions of $K_2[PdCl_4]$ because of considerable displacement of Cl^- ions from the first coordination sphere of the central atom by water molecules and OH^- ions. This process noticeably changes the dielectric properties of its solutions. Such a distinctive feature of the behavior of $PdCl_4^{2-}$ and its derivatives can be important for analysis of the differences between the biochemical effects of complex Pt(II) and Pd(II) anions in aqueous biological fluids.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 08-03-00095.

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