Effect of Potentiated Solutions on Mercury(II) Signal in Inversion Voltammetry

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We studied the effects of homeopathically potentiated substances in ultralow doses on physicochemical properties of solutions. Inverse voltammetric signals during Hg(II) oxidation-reduction in the presence of potentiated water, lithium chloride, and mercury nitrate were studied by alternating-current inversion voltammetry. Potentiated substances modified oxidation-reduction processes in the electrochemical system. Potentiated solutions of Hg(II) increased the effective concentration (activity) of mercury ions. The effect was most significant in the presence of mercury nitrate in homeopathic dilutions C6+C12+C24. Our results indicate that potentiated substances specifically modulate kinetic and thermodynamic characteristics of solutions containing the same compounds.

Key Words: *ultralow doses; electrochemical system; mercury nitrate; alternating-current inversion voltammetry; potentiated substances*

Previous studies showed that neurotropic substances in ultralow concentrations (10^{-12} and 10^{-60} M or lower) prepared by the method of homeopathic potentiation possess biological activity. Their physical effects are similar to those observed after treatment with the same substances in standard doses. Moreover, potentiated substances modify the influence of initial compounds in standard doses [1].

Potentiated medicines are obtained by repeated consecutive dilutions and 10-fold shaking of the solution. The number of dilutions is designated “potency”. According to the general molecular theory, these solutions do not contain molecules of the initial substance. In homeopathy the notion “dose” is conditional and reflects dilution of the solution.

Synthesis of homeopathic preparations seems to be simple. However, the process of shaking determines physical properties of the potentiated solution (PS), since molecules of the solvent are oriented around the dissolved substance in a certain (cluster) order [1]. Spatial configuration of clusters stores physical properties of the substance and retains this information during further dilutions.

The specific properties of PS may be evaluated by the method of alternating-current inversion voltammetry (IVA) on a glass-carbon (GC) electrode for $Hg(NO_3)_2$ that allows detecting low concentrations of Hg(II) and various reproducible inverse signals of mercury. The appearance of signals is associated with reduction of mercury ions during accumulation of Hg on the surface of a GC electrode (I) and dissolution of mercury on the anode (II):

$$Hg^{2+}+2e\rightarrow Hg^0 \text{ (I) and}$$
$$Hg^0-2e\rightarrow Hg^{2+} \text{ (II).}$$

This electrochemical system is a simple model for studying basic oxidation-reduction reactions on the electrode. Reaction I illustrates reduction and accumulation of mercury on the electrode surface. Reaction II represents oxidation and dissolution of mercury. Dissolution of mercury with alternating current is accompanied by the peak (maximum current, current-potential dependence). This maximum is proportional to the amount of mercury on the electrode under constant accumulation, concentration, and activity in the solution (effective concentration). The energy state of mercury on the electrode is characterized by the dissolution potential (*E*). Reversibility of the electrochemical process inversely depends on the peak half-width.

Reactions I and II are accompanied by desolvation (reduction) and solvation (oxidation) of Hg(II) ions, respectively. It should be considered that the depolarizer negotiates the electric bilayer near the electrode surface.

The alternating-current signal in IVA has a shape of the peak current. Its amplitude and width depend on kinetic characteristics of the heterogeneous reaction for electron transfer. Trace surface active organic sub-

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stances present on the surface of a working electrode or in the electric bilayer affect kinetic and thermodynamic characteristics of Hg(II) reduction and Hg^0 oxidation. The surface of a working GC electrode (*e.g.*, electrochemical activation by adsorbed mercury ions) plays an important role, particularly during anode oxidation [2].

IVA is widely used for detection of heavy metal ions (Hg^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+}) and surface active substances [3].

Experiments were performed using a PU-1 universal polarograph, PDA-1 bidimensional potentiometer, and 3-electrode detector. Test solutions were prepared in bidistilled water obtained on a glass (quartz) bidistillator. LiCl (1 M) served as the base electrolyte.

PS of the bidistillate, $Hg(NO_3)_2$ (1 g/liter Hg^{2+}), and 1 M LiCl were prepared by the method of S. Hahnemann (potencies CH6, CH12, and CH24).

MATERIALS AND METHODS

The base electrolyte (1 M LiCl) was mixed with 0.100 ml $Hg(NO_3)_2$ (1 g/liter Hg^{2+}) and 1.00 ml PS of the bidistillate. After mixing mercury was accumulated on a working GC electrode for 99 sec. The accumulation potential was 1.60 V (compared to a reference GC electrode). The VA curve for mercury was recorded at a potential scanning velocity of 50 mV/sec (diffuse current 0.25×100; alternating amplitude 10 mV; and potentiometer recording X and Y scales 0.2 V/cm and 20 mV/sm, respectively). The peak current for anode mercury dissolution corresponded to 0.35 V (compared to a reference GC electrode). External polarization of the well was terminated immediately after recording.

The intensity of accumulation and VA curve for mercury were recorded immediately after mixing of components in the test solution (without stirring).VA curves were recorded 7-8 times to evaluate the time dependence for properties of solutions. Blank recordings were performed with an equivalent volume of non-potentiated bidistilled water before and during studies of PS.

Inverse VA curves were constructed under conditions when the blank sample produced a constant signal in 7-fold repetitions. Changes in the area of IVA mercury signals in the presence of potentiated water was statistically analyzed (most informative parameter, Table 1).

We studied changes produced by the potentiated base electrolyte (1 M LiCl). Test solutions were prepared by mixing of 1 ml PS of LiCL (1 M), 0.1 ml $Hg(NO_3)_2$ (1 g/liter Hg^{2+}), and 1 ml bidistilled water.

To evaluate the effects of potentiated $Hg(NO_3)_2$ we mixed 1 ml 1 M LiCL, 0.1 ml potentiated $Hg(NO_3)_2$, and 1 ml bidistilled water.

RESULTS

Potentiated water produced various effects on IVA signals of mercury. CH6 activated mercury. However, increasing the dose was accompanied by the decrease in mercury activity up to the inhibition of signals (mixed sample, Table 1). It should be emphasized that mercury signals increased (CH6, CH24, and mixed sample) or decreased in time (CH12). Taking into account the time dependence, reproducibility of signals for various samples corresponded to the relative standard deviation s_r (0.03-0.07). The shape of signals (peak half-width, δ, mV) indicated that mercury underwent reversible electrochemical dissolution: δ was practically equal to the theoretical value (90/2=45 mV for CH12, CH24, and mixed sample). Only sample CH6 was characterized by a lower reversibility (δ=70 mV). The maximum peak potential for various samples approached the control level and differed by 0.05 V. Mercury adsorbed on the electrode was more active in the mixed sample, but less active in CH6. Different behavior of potentiated water samples suggests that the structure of test solutions undergoes complex reconstruction and depends on the degree of potentiation and time of action. Thermodynamic (*E* peak) and kinetic characteristics (δ) of IVA mercury signals changed, which produced statistically significant differences between average IVA mercury signals in test samples.

The effect of PS-LiCl on IVA mercury signals was similar to that produced by potentiated water samples (Table 2). Initially the signal of CH6 was greater than that of the control sample. Increasing the potency (CH12 and CH24) was accompanied by the inhibition of signals. The only exception was the mixed sample (CH6+CH12+CH24) that increased mercury signals. Taking into account the time dependence for mercury signals, our results indicate that their dispersions were homogenous and characterized by reproducibility at a level of the blank sample (s_r=0.04-0.06).

Mercury signals increased in time during exposure to CH6 and mixed sample (CH6+CH12+CH24). The decrease in mercury signals (CH12 and CH24) was followed by relaxation to a level of the control sample. Similarly to experiments with potentiated water, dissolution of mercury was characterized by electrochemical reproducibility (δ=37-52 mV) and small shift of the peak potential toward negative values (by 0.02-0.05 V). These data indicate that the activity of mercury was high in CH24 and mixed sample (CH6+CH12+CH24).

These characteristics of potentiated water and 1 M LiCl reflect the solvation effect of potentiation, which is probably related to structural changes in the solution.

Potentiation of $Hg(NO_3)_2$ produced other effect (Table 3).

TABLE 1. IVA Mercury Signals in the Presence of Potentiated Water

Solution	Signal amplitude (h), rel. U	Area (ρ), rel. U	Peak half-width (δ), mV	Peak current potential (E_p), V
Blank	89.43±2.99	235.00±11.53	46.14±2.48	-0.33±0.00
CH6	101.57±8.24	395.86±48.32	68.00±3.42	-0.28±0.00
CH12	89.00±2.00	255.57±20.13	49.86±3.67	-0.30±0.00
CH24	84.00±6.00	231.57±39.97	48.00±5.16	-0.38±0.00
Mixed sample, CH6+CH12+CH24	72.00±6.45	181.43±16.56	44.00±0.00	-0.38±0.00

Note. Here and in Tables 2 and 3: peak current potential (E_p) in relation to a reference GC electrode.

TABLE 2. IVA Mercury Signals in the Presence of Potentiated 1 M LiCl

Solution	h, rel. U	ρ, rel. U	δ, mV	E_p, V
Blank	89.43±2.99	235.00±11.53	46.14±2.48	-0.33±0.00
CH6	89.50±7.31	251.00±42.01	48.43±4.50	-0.33±0.00
CH12	85.14±7.86	205.29±29.03	42.14±2.48	-0.33±0.00
CH24	93.93±7.66	199.57±33.59	37±3.61	-0.35±0.00
Mixed sample, CH6+CH12+CH24	89.86±5.52	261.14±25.37	50.29±2.36	-0.38±0.00

TABLE 3. IVA Mercury Signals in the Presence of Potentiated 1 M $Hg(NO_3)_2$ (1 g/liter Hg^{2+})

Solution	h, rel. U	ρ, rel. U	δ, mV	E_p, V
Blank	89.43±2.99	235.00±11.53	46.14±2.48	-0.33±0.00
CH6	107.14±5.52	354.14±71.28	57.14±8.78	-0.36±0.01
CH12	104.14±7.95	359.57±70.69	59.71±8.10	-0.33±0.00
CH24	109.86±2.73	411.29±34.13	65.43±5.09	-0.33±0.00
Mixed sample, CH6+CH12+CH24	110.86±1.95	463.00±55.74	72.71±7.65	-0.33±0.00

The activity of mercury increased more significantly. Mercury signals were less reproducible. However, dispersions for CH12 and mixed sample (CH6+CH12+CH24) remained homogenous (compared to the control). Greater amplitudes of mercury signals and widening of peaks (δ=52-87 mV) reflect more intensive accumulation of Hg on the electrode surface. These changes characterize intensification of stage I (Hg(II) reduction) and decrease in electrochemical reproducibility of stage II (Hg^0 dissolution). Therefore, potentiation of Hg(II) solutions increases the effective concentration (activity) of mercury ions.

Our results indicate that potentiated preparations may increase or decrease the activity of mercury ions and atoms in the solution. Inactivation of mercury reflects a higher-energy solvation (temporal effect). The increase in mercury activity may result from its intensive accumulation on the electrode and rapid electrochemically reversible dissolution.

Therefore, potentiated substances modify kinetic and thermodynamic characteristics of solutions. As regards Hg(II), this effect was unlimited in time and polymodal.

Due to peculiarities of potentiation and physicochemical effects of potentiated substances, the mechanism of their action should be evaluated taking into account kinetic and thermodynamic characteristics and dual nature of gravitation [4].

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