SHOCK POLARIZATION OF SOLUTIONS OF STRONG ELECTROLYTES

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It is shown that the main cause of shock emf in shock compression of a metal–electrolyte–metal system is shock polarization of the electrolyte solution. The emf is linearly dependent on ion mass and is an additive function of the ion composition of the electrolyte solution. The relaxation time for the nonequilibrium processes produced by shock polarization of the metal–electrolyte boundary does not exceed $5 \cdot 10^{-7}$ sec for single-time compression.

1. Under dynamic compression by a shock wave with amplitude of the order of tens or hundreds of kbar, matter simultaneously experiences the effects of deformations and rapidly propagating high pressures and temperatures. The study of shock-wave compression (pressure duration of the order of 10^{-5} sec) requires inertialess methods. Information on the behavior of matter directly at the shock-wave front can be obtained through study of electrical signals produced by shock polarization. At the present time shock polarization in dielectrics [1] and ionic crystals [2] has been studied sufficiently. It follows from the majority of experimental results that the electrical signal in shock compression of plastics is related to orientation of dipole molecules in the shock-wave front. In the majority of cases the signal polarity corresponds to motion of the lighter and larger portion of the dipole molecule in the direction of propagation of the shock wave [1, 3].

In shock compression of solutions of strong electrolytes one might expect a process analogous to shock polarization in dielectrics, i.e., separation of ions in the shock-wave front because of differences in their mass and volume.

The experimental studies performed with electrical signals developed in shock compression of a metal–water–metal system indicate that it is necessary to consider not only the material studied (water), but the entire system as a whole, since a significant contribution from the metal–water boundary to shock polarization was observed. This is indicated by the dependence of the emf which remains constant during shock compression on the nature of the metal used [4] and addition of small amounts of surface-active agents [5]. Using the data presented in [4, 5], in studying shock polarization of solutions of strong electrolytes special attention must be given to selection of experimental conditions which reduce the contribution of boundary processes occurring at high temperatures and pressures.

It should be noted that shock polarization of strong electrolytes is of interest because it is a source of information on the behavior of such systems in the process of shock compression. It is convenient to use aqueous solutions in such studies because electrical signals in metal–water–metal systems and conductivity of aqueous electrolyte solutions at high pressures and temperatures have been studied thoroughly. Moreover, the simplicity of changing the ionic composition of the solution makes it possible to study the effects of concentration, mass, and other physicochemical properties of the charged particles on emf.

2. The experimental apparatus shown in Fig. 1 was used to record the electrical signals. The side walls of cell 1 were made of materials which do not produce polarization signals and also have an acoustic impedance close to that of the electrolyte solution (paraffin, Teflon). The wall thickness was chosen so that the time for recording the electrical signal was less than the time needed for lateral decompression waves to reach the interior portion of the cell (D-d = 15 mm).

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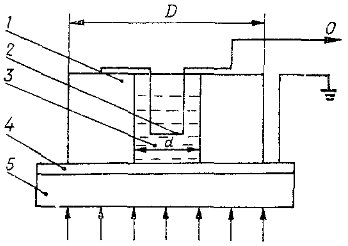

Fig. 1

Electrodes 2, 4 are made of copper, since this metal produces the the smallest boundary-effect contribution when water is used as a solvent [4]. The electrode surfaces were polished and cleaned of surface-active substances. Special experiments indicated that more complex electrochemical processing of the electrode surfaces was not needed for reproducibility of the results. The geometric area of the electrode surfaces was 1 cm^2 with a separation of 1 cm. These values were changed in special experiments with lower electrolyte concentrations.

In the majority of experiments equimolar solutions of sodium or nitric acid salts were employed as the electrolyte 3. These electrolytes were chosen for a number of reasons: first, the cation Na^+ and the anion NO_3^- are not surface active; secondly, the electrical signal in shock compression of the system Cu – $1MNaNO_3$ – Cu differed only slightly (by 0.08 V) from the electrical signal in a Cu–water–Cu system: thirdly, the high solubility of these salts allowed wide variation of cation and anion concentrations in the solution. The solutions were prepared in the following manner: the salt was recrystallized from doubly distilled water, baked, and dissolved in doubly distilled water.

The metal–electrolyte–metal system was shock compressed by dynamic screen 5, made of 6-mm-thick copper, with a shock wave 50 kbar in amplitude of 15 μsec duration. The pressure used (50 kbar) was chosen for the following reasons: for many of the unimolar solutions used the shock emf at such a pressure reached a significant value in the range ±2 V. At lower pressures the emf value drops rapidly, while at higher pressures a peak at the start of the signal is observed. The shock-wave duration (15 μsec) allowed development of a practically constant pressure in the working electrode region during the signal recording time (2-3 μsec).

Signals were recorded by high-speed oscilloscopes, types C1-11 and OK-33 (O in Fig. 1 indicates the oscilloscope connection) with 100-Ω input impedance. The internal impedance of the cell before shock compression did not exceed 10 Ω. Experimental error in amplitude measurement was 20-10% of the signal value. Thus, from the commencement of working electrode shock compression the change in shock emf over the signal recording time was measured within experimental accuracy.

Characteristic oscillograms for the systems Cu – $1MRbNO_3$ – Cu; Cu – $1MRbNO_3$ – Cu; Cu – $1MNi(NO_3)_2$ – Cu; Cu – $0.5NH_2SO_4$ – Cu are shown in Fig. 2. For systems 1-3 shock compression was performed by a shock wave in the form of an ascending step; for the fourth system a long-duration shock wave was used. The working electrode was installed perpendicular to the shock-wave front (t_1, moment of shock compression of the working electrode; t_2, moment of shock compression of comparison electrode; t', commencement of working electrode compression; t'_1, moment when second step of shock wave exists onto working electrode surface). The electrical signals may be divided into two groups: those produced by a constant emf, and signals with a rapidly decaying peak at the moment of shock compression of the working electrode. These peaks were observed most often with increased shock-wave pressure (Fig. 2b) or with twofold compression of the working electrode surface (Fig. 2c). The drop in the leading edge of the signal (0.1-0.2μsec) is related to variation in the time at which various points of the electrode surface are compressed. This can be demonstrated simply by changing the angle between shock-wave direction and the plane of the working electrode. In the case of shock compression of a thin working electrode oriented parallel to the movement of the shock-wave front (Fig. 2d), the time for development of maximum emf also corresponds to the time for shock compression of the working electrode over its entire surface. As was shown by experiments with a series of systems, the time for development of a shock emf with instantaneous compression of the entire working electrode surface does not exceed 10^{-8} sec.

Figure 3 shows the dependence of shock emf in the systems Cu – $1MNa_*A$ – Cu on anion A weight [1) OH^-, 2) F^-, 3) Cl^-, 4) CH_3COO^-, 5) NO_3^-, 6) Br^-, 7) BrO_3^-, 8) S^{--}, 9) CO_3^{--}, 10) SO_3^{--}, 11) HPO_4^{--}, 12) SO_4^{--}, 13) $S_2O_3^{--}$, 14) CrO_4^{--}, 15) SeO_4^{--}], while Fig. 4 shows shock emf in the systems Cu – $1MCa(NO_3)_*$ – Cu as a function of cation Ca weight [1) Li^+, 2) H_2O^+, 3) Na^+, 4) K^+, 5) Rb^+, 6) Cs^+, 7) Mg^{++}, 8) CO^{++}, 9) Ni^{++}, 10) Sr^{++}, 11) Cd^{++}, 12) Ba^{++}, 13) Al^{+++}, 14) Fe^{+++}, 15) La^{+++}]. The experimental results are presented in the coordinates ion mass–shock emf, since these functions are of special interest from the viewpoint of shock polarization of an electrolyte solution. As follows from Figs. 3 and 4, under the experimental conditions chosen these functions have a linear character. Somewhat exceptional are the ions I^- and CNS^-. In the case of anions, within experimental accuracy one linear dependence was observed for univalent and bivalent

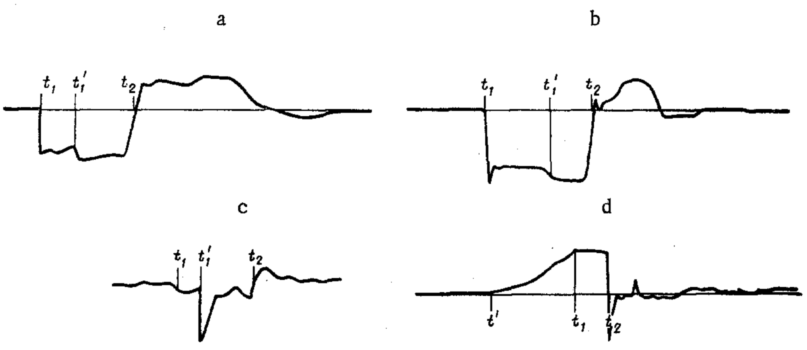

Fig. 2

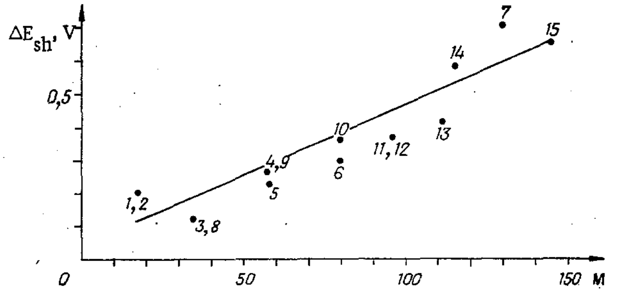

Fig. 3

ions, while for cations the valence exerts a significant effect. Thus with growth of valence the slope of the function decreases.

It should be noted that both with change of the cation and, especially with charge of anion, the structure of the near-electrode region can change significantly. In order to eliminate the dependence of the shock emf on the structure of the electric double layer, a small addition (0.1 M) of sulfide ion was made to solutions with a univalent cation. The sulfide ion has significant specific adsorptivity on metal surfaces. The original electrode potential in this case shifted to the negative region and was equal to 1.5 V as compared to the normal calomel electrode. This addition produced no observable effect on the shock emf values. This fact, together with the linear dependence of emf on ion mass, indicates the volume origin of the electrical signal.

Figure 5 shows the shock emf as a function of the ion concentration in the solution for the systems: 1) Cu–1 M(NaI + $NaNO_3$) – Cu; 2) Cu – 1M($CsNO_3$ + NaI) – Cu; 3) Cu – 1M($CsNO_3$ + $NaNo_3$ – Cu; 4) Cu – $CsNO_3$ – Cu. The ions I^- and Cs^+, which produced a large electrical signal at unimolar concentration, were chosen for study. Decrease in salt concentration can produce a significant increase in internal impedance of the measurement apparatus. In order to prevent this the salt $NaNO_3$ (background) was added, up to unimolar concentration. However, the introduction of a large amount of the background salt can affect the value of the electrical signal. The absence of an $NaNO_3$ effect was demonstrated for the system Cu–$CsNO_3$–Cu, where a series of points at different concentrations were obtained without use of the background. In this case the electrode surface was increased and interelectrode distance reduced to preserve the apparatus conductivity. The absence of a background effect may be explained by the fact that the difference between shock emf in the systems Cu–1 M $NaNO_3$–Cu and Cu–water–Cu (0.08 V) is less than the error in signal measurement in the complex solution.

It should be noted that the ions chosen (Cs^+ and I^-) differ significantly in their specific adsorptivity on a metal surface. The linear dependence of shock emf on electrolyte concentration is incontravertible evidence of the volume origin of the electrical signal. As follows from Fig. 5, the shock emf is an additive function of the concentration and the ionic composition of the electrolyte solution.

3. We will evaluate the experimental results. In recording the electrical signal in the metal–electrolyte–metal system we observed the appearance of two new boundaries, across which a potential difference may exist. One of these boundaries occurs between the metal and the shock-compressed metal, the other, between the electrolyte and the shock-compressed electrolyte, i.e., at the shock-wave front. The electrical circuit in which the shock wave appears may be written in the form

$$\mathrm{Me} - \mathrm{Me}^* - \mathrm{El}^* - \mathrm{El} - \mathrm{Me},$$

where Me–Me* is the metal–shock-compressed metal boundary; Me*–El* and El–Me are the boundaries of working electrode and comparison electrode; El*–El is the shock-wave front. The emf of such a circuit may be written in the following manner:

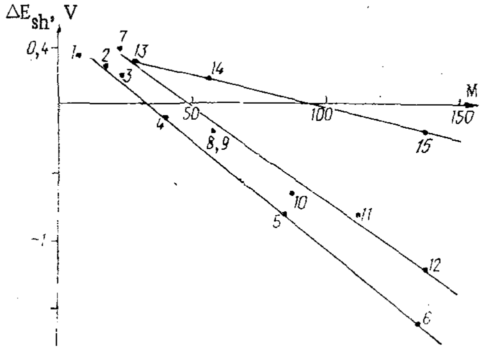

Fig. 4

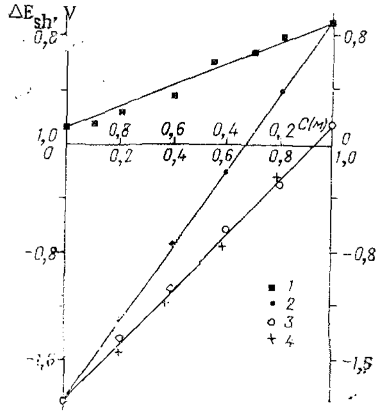

Fig. 5

$$\Delta E_{sh}(\tau) = \varphi_{Me-Me*}(\tau) + \Delta\varphi_{Me-El}(\tau) + \varphi_{swf}(\tau),$$

where $\Delta E_{sh}(\tau)$ is the shock emf; $\varphi_{Me-Me*}(\tau)$ is the potential difference across the metal–shock-compressed metal boundary; $\Delta\varphi_{Me-El}(\tau)$ is the change in working electrode potential in comparison with the original state; $\varphi_{swf}(\tau)$ is the potential change at the shock-wave front. The symbol (τ) indicates that all these quantities may be time-dependent.

The potential change at the metal–shock-compressed metal boundary may be neglected, since its change upon replacement of one metal by another, as follows from [6, 7] and the experiments of [8], does not exceed the error in shock-wave emf measurement (100 mV). Moreover, in performing experiments with identical metallic electrodes and shock-wave amplitudes the change $\varphi_{Me-Me*}(\tau)$ will produce a constant component in the signal.

Both of the other components of the shock emf can depend significantly on the nature of the electrolyte. To clarify this, we will consider a number of processes which may produce the appearance of $\Delta\varphi_{Me-El}(\tau)$ and $\varphi_{swf}(\tau)$; $\Delta\varphi_{Me-El}(\tau)$ may occur, for example, because of deformation of the electric double layer by processes which can occur at the working electrode boundary at high pressures and temperatures, and also by shock polarization of molecules at the boundary. The change $\varphi_{swf}(\tau)$ can appear because of differences in ion concentration in the shock-compressed and uncompressed electrolyte, as well as because of shock polarization of the solution.

We will consider how φ_{swf} and $\Delta\varphi_{Me-El}$ should depend on the signal recording time ($t_2 - t_1 = \tau_{rec}$). To do this we will use the time for establishment of the nonequilibrium process (τ_e) and the relaxation time to some equilibrium state (τ_r). In studying shock polarization of metal–water–metal systems it was established that the shock emf in such systems is constant over time and insignificant in magnitude. Its value was significantly dependent on the nature of the metal, and for copper–coppr electrodes did not exceed 0.15 V at a shock-wave pressure of 90 kbar [4]. It follows from this experimental data that τ_e and τ_r are significantly smaller than τ_{rec}, while τ_e for shock polarization of an electrolyte solution at the shock-wave front will be composed of τ_e for shock polarization of the solvent and τ_e for the ion-displacement process due to difference in their masses: τ_e for the ion-displacement process will be determined by the time over which a stationary regime of ion motion through the shock-wave front is established; i.e., a regime in which the number of entering and existing particles is the same. If we assume that such a stable ion-separation process sets in after the shock-wave front traverses 10 times its own width, we may make an approximate estimate of τ_e. The front width in condensed homogeneous systems does not exceed 10^3 Å [9]; consequently, $\tau_e \sim 10^{-9}$ sec. Such an estimate for τ_e agrees well with the minimum time for development of the electrical signal (10^{-8} sec). The φ_{swf} relaxation processes should occur in the same manner as in water [3, 10]. Thus if a constant pressure change is maintained in the shock-wave front, φ_{swf} should not depend on time in the interval τ_{rec}; $\Delta\varphi_{Me-El}$ may be produced by nonequilibrium processes of boundary shock polarization having τ_r comparable to τ_{rec}. Thus, for example, the time τ_r determined by charged-particle diffusion near the working electrode surface under usual temperatures and pressures comprises 10^{-6}-10^{-5} sec [11]. The times τ_e and τ_r for processes which occur upon shock compression of the working electrode surface may vary over a very wide interval. It may be seen from the above that the change in shock emf upon recording of an electrical signal not related to pressure change in the working electrode region indicates the presence of processes occurring at the metal–electrolyte boundary.

In this study conditions were chosen specially (electrode material, shock-wave pressure, electrolyte concentration) to reduce the effect of boundary processes on the electrical signal and to produce the clearest picture of the principles connected with shock polarization of the electrolyte solution. The experimental results obtained (independence of the shock emf of the original state of the electric field, and its linear dependence on concentration and ion mass) indicate the origin of the shock emf in the shock-wave front.

In reality, in the case of a large difference between ion and solvent molecule masses immediately at the shock-wave front the ion motion velocity should differ from the mean mass flow velocity. The sign of the signal should correspond to motion of the heavy particles toward the working electrode surface. The charged-particle shift and, correspondingly, the shock emf should depend not only on mass, but also the interaction energy of these ions with the solvent, i.e., the hydration energy. This may explain the decrease in angle between the linear shock emf-cation weight function and the molecular weight axis. In actuality, the cation hydration energy increases much more rapidly than the valence, for example, in the series Cs^+, Ba^{++}, La^{+++} the hydration energy is 63, 320, 805 kcal/mole, respectively. On the other hand, with anions the hydration energy increases at a significantly lower rate with increase in valence, for example, for BrO_3^- and CrO_4^{--} the values are 68 and 220 kcal/mole, respectively.

It must be noted that because of charged-particle separation at the shock-wave front not only can the voltage φ_{swf} develop, but also $\Delta\varphi_{Me-El}$; $\Delta\varphi_{Me-El}$ may appear at the moment when the shock-wave front exists onto the surface of the working electrode. A flux of heavy particles falls on this surface, changing its potential. After the shock-wave front traverses the metal–electrolyte boundary resorption of excess charge should be observed. These two processes may explain the rapidly decaying peaks at the start of the signal when solution concentration or shock-wave pressure is increased (see Fig. 2b).

Thus the experimental results indicate that in the absence of processes at the working electrode caused by high temperature and pressure, the main cause of the appearance of shock emf is ion separation in the shock-wave front.

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