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DIFFERENTIAL THERMOANALYTICAL STUDIES OF FROZEN FERROUS PERCHLORATE SOLUTIONS

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It is inferred from the thermoanalytical data obtained on 0.2-4.0 *M* solutions of $Fe(ClO_4)_2$ which are frozen under non-equilibrium conditions that the phase containing the solute ions turns into a glassy state below −95°. On the warming of these solutions exothermic and endothermic processes are observed which can be related to the effects observed by the nuclear gamma resonance method.

Introduction

Recent Mössbauer studies of frozen aqueous solutions of Fe(II), particularly of $Fe(ClO_4)_2$ and $FeCl_2$ [1–5], have furnished new information about the structures of these solutions. For the better understanding of some new data, it seemed necessary to study the phase transitions in these systems under non-equilibrium conditions by the use of other methods. For this reason thermoanalytical studies were performed on aqueous solutions of $Fe(ClO_4)_2$.

Experimental

For the differential thermoanalytical (DTA) measurements an apparatus[1] was used which consisted of a brass cell of controlled temperature, housing a glass ampoule containing the sample, and copper constantan thermocouples connected to two compensographs covering the range from 0.1 to 5 mV (Laboratorni Pristroje N. P. Type EZ–3). One of the compensographs recorded the difference Δt between the temperatures of the sample and the brass cell, the other the temperature of the brass cell vs. time $t(\tau)$. Purity grade reagents were used throughout. The volume of the samples was either 1.2 or 2.5 ml.

Experiment 1. The samples were immersed in liquid nitrogen, then left to warm spontaneously in the brass cell at a rate of about 1.0°/min. During this period the DTA curve was measured.

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[1] The apparatus used for the thermoanalytical measurement will be described in another paper.

The DTA curve in Fig. 1 was obtained for a sample of 1 *M* $Fe(ClO_4)_2 \cdot 6\,H_2O$. This pattern is typical for a fairly wide [0.2–4.0 *M* $Fe(ClO_4)_2 \cdot 6\,H_2O$] range of concentrations. For easier reference the three peaks apparent at temperatures below 0° are numbered. Peaks 1 and 2 are characteristic of endothermic, peak 3 of exothermic processes.

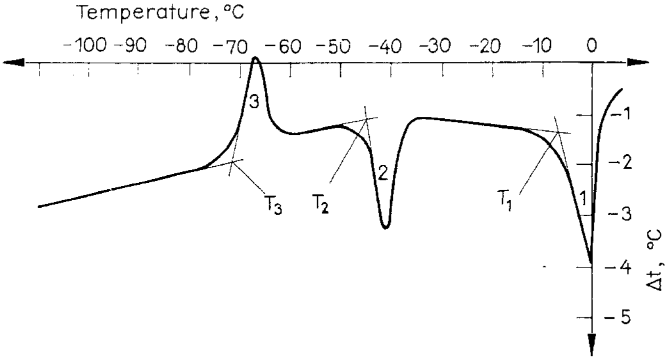

Fig. 1. DTA curve measured on 1 *M* $Fe(ClO_4)_2 \cdot 6\,H_2O$ solution frozen in liquid nitrogen. Rate of warming over the total range of measurement ~1.0°/min

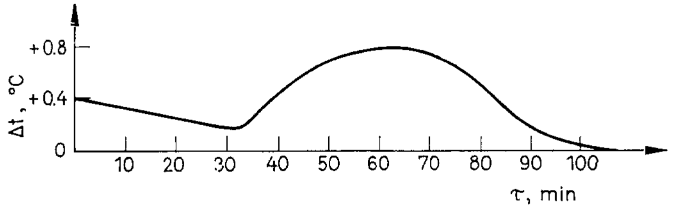

Fig. 2. DTA vs. time curve measured on 1 *M* $Fe(ClO_4)_2$ solution frozen to −196°, then thermostated at 94°

Experiment 2. The sample was cooled to −78°, then kept at this temperature for a few minutes before the gradual warming. The DTA curve in this case exhibits a single peak having the same characteristic temperature[2] and shape as peak 1 in Fig. 1.

Experiment 3. The sample was cooled to liquid nitrogen temperature and thermostated at −94° while the $\Delta t - \tau$ curve was being measured. After an incubation period of about 30 min the onset of an exothermic process taking about 60 min was observed (Fig. 2). When this sample was re-cooled to −120° and warmed again, the DTA curve displayed only the two endothermic peaks of Fig. 1.

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[2] The characteristic temperature is determined by the point of intersection of the nearly linear section of the ascendant section of the peak with the base line.

In further experiments it was observed that only peak 3 has a characteristic temperature dependence on the rate of warming. If the rate of warming is considerably slower, the characteristic temperature tends to a limit value of about −95°.

In the same manner as used for the first experiment, the DTA curves were studied as a function of concentration. For dilute solutions (≥ 0.2 *M*) the characteristic temperature of peak 1 increasingly tends to 0° and the area below this peak becomes approximately equal to that observed below the single peak in the DTA curve of pure water measured under the same conditions. At higher concentrations (above 4 *M*) the difference between the characteristic temperatures of peaks 1 and 2 decreases with a parallel decrease in the area below peak 1; this gradually merges into peak 2. The characteristic temperatures of peaks 2 and 3 do not vary with the concentration, but the areas below the peaks are proportional to the $Fe(ClO_4)_2$ concentration as may be seen in Fig. 3.

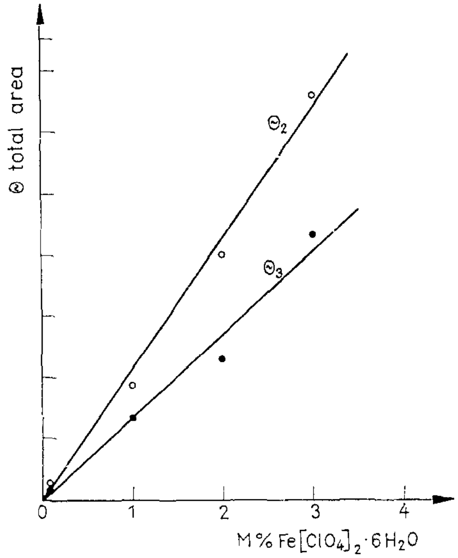

Fig. 3. Concentration dependence of the areas (Θ) below the peaks 2 and 3

Discussion

The thermoanalytical data can be interpreted as follows.

1) Peak 1, appearing in each of the measured DTA curves irrespective of the cooling rate, can be attributed to a change in enthalpy caused by the melting of the ice crystals formed from the solute + solvent system.

2) Peak 2 reflects the change in enthalpy caused by the melting of the crystals formed from the solution of locally eutectic composition. The melting temperature

of the eutectic mixture was evaluated from the characteristic temperature of peak 2, as −46 ± 1°, in good agreement with the observed disappearance of the Mössbauer lines above this temperature, indicating that the Fe(II) ions pass into the liquid phase [2].

3) The opposite signs and the insensitivity of the ratio of the peak areas 2 to 3 to concentration suggest a relationship between the endothermic and exothermic processes. As a possible explanation it is thought that the ice crystallizes out from the solutions even during a fast cooling down while the solute ions remain in a solution of eutectic or nearly eutectic composition and become supercooled. If the solution is supercooled below a given temperature [this seems to be −95° for $Fe(ClO_4)_2$] the mobility of both the solute ions and the water molecules will decrease to an extent that the solution solidifies to a glassy state and maintains the structure of the liquid phase. On the warming of the thus solidified sample the glassy solution turns first into a high viscosity liquid which completely crystallizes out with eutectic structure. The heat released by the second crystallization produces peak 3 in the DTA curve.

It is of interest to note that the sudden change in the Mössbauer parameters and the decrease in the intensity of the effect were also observed at about −95°. If the solidified glassy solution is warmed, the probability of the Mössbauer effect goes to zero at about −95° due to the melting of the glassy solution, but it reappears at higher temperatures at which the eutecticum crystallizes and the ion mobility decreases. The melting of solidified systems containing solute ions at about −95° or higher temperatures seems to be a fairly general phenomenon. A markedly accelerated motion of the solute ions has been observed too in the frozen solutions of Fe(III) [5], Eu(II) [4] and Sn(IV) [6] by Mössbauer effect measurements, and in the frozen solution of Ta ions by perturbed gamma angular correlation measurements [7].

It has been found that the observed changes in the Mössbauer parameters can be well connected with the thermal effects due to the phase transitions of the system. The changes observed in the solidified solutions in both the Mössbauer and the thermoanalytical studies at about −95° in the range of concentrations covered can be attributed to a melting process and a crystallization of the eutectic mixture.

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Résumé — L'étude thermoanalytique de solutions congelées de $Fe(ClO_4)_2$ montre que pour les solutions dont la concentration du soluté varie de 0.2 à 4.0 *M*, et qui sont congelées sous des conditions de non-équilibre, la phase contenant les ions dissous se transforme en un état vitreux au-dessous de $-95°$. En chauffant ces solutions, on a observé des processus endothermiques et exothermiques qui peuvent être reliés aux effets mis en évidence par la méthode de résonance nucléaire gamma.

Zusammenfassung — Es wurde über thermoanalytische Versuche mit gefrorenen Lösungen von $Fe(ClO_4)_2$ von 0.2 bis 4.0 *M* Konzentration berichtet, die unter Nichtgleichgewichtsverhältnissen zum Einfrieren gebracht worden waren. Es zeigte sich aus den thermoanalytischen Daten, daß die gelöste Ionen enthaltende Phase in einen glasartigen Zustand unter $-95°$ übergeht. Beim Erwärmen dieser Lösungen beobachtete man exothermische und endothermische Vorgänge, die mit den durch Nukleargamma-Resonanz gefundenen Effekten in Einklang gebracht werden konnten.

Резюме — Термоаналитическим методом исследованы вымороженные растворы $Fe(ClO_4)_2$ с концентрацией 0,2—4,0 *M*. На основании экспериментальных данных сделан вывод, что в растворах, вымороженных при неравновесных условиях, фаза, содержащая ионы, переходит в стекловидное состояние при температуре ниже -95 °C. При нагревании этих растворов наблюдаются экзотермический и эндотермический процессы, имеющие отношение к эффектам, установленным методом γ-резонанса ядра (эффект Мэсбауера).