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CALORIMETRIC DIAGNOSTIC OF CONVERGENCE OF SOLUTE PARTICLES DURING A HEATING OF FROZEN AQUEOUS SOLUTIONS

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Differential scanning calorimetry and electron spin resonance (ESR) have been applied to study the processes which take place during a heating of frozen salt aqueous solutions containing organic molecules. Such combination of investigation methods has allowed to determine some correlations between the nature of heat release and heat absorption occuring during the heating of rigid system and the change of distances both between different spin-labelled organic molecules and between paramagnetic cations of salts. Heat release and heat absorption have been detected with the use of differential diathermic calorimeter (the sensitivity 10^{-5} J/s and the time constant 50 s), the distances between the paramagnetic centers have been determined on the basis of ESR spectra analysis.

The main attention has been paid to the study of rigid systems formed by cooling solutions with the rate 10 °C/s, the heating has been performed with the rate 10^{-2} °C/s. Solute concentrations in the systems studied haven't exceeded 10 wt. %. Three types of solutions have been investigated. (I) Aqueous solutions of paramagnetic salts ($CuSO_4$, $Cu(NO_3)_2$, $CuCl_2$, $MnSO_4$, $Mn(NO_3)_2$, $MnCl_2$, $VOSO_4$, $Cr_2(SO_4)_3$).(II) Aqueous solutions of diamagnetic salts (LiCl, NaCl, $MgSO_4$, CH_3COONa) containing relatively low amounts of spin probes (low-molecular organics). (III) Aqueous solutions of salts (LiCl, NaCl, $CuSO_4$, $MnSO_4$, $Cr_2(SO_4)_3$, $VOSO_4$) containing various synthetic polymers of pharmacological interest, salt to polymer concentration ratio has been widely ranged. Some of the type (III) systems have contained negligible amounts of low-molecular probes, others have included spin-labelled macromolecules.

In general, the following picture of heat release and heat absorption occuring during the heating of systems which have been preliminary cooled with the rate 10 °C/s can be drawn: glass transition step (at -120 – -90 °C), one or more crystallization peaks (at -90 – -40 °C), the peak corresponding to the melting of solute-rich microphases (at -40 – 0 °C), melting peak of pure ice (at 0 °C).

For all system types, the general regularities have been established. (1) A heating of frozen solutions may lead to convergence of solute particles. The distances on which solute particles may be replaced during such kind of process are 30 – 40 Å (even in the case of polymer molecules convergence). (2) Temperature at which convergence starts is the temperature of the beginning of crystallization. (3) The convergence is much more pronounced in systems where there is intense crystallization and two melting peaks occur, convergence of solute particles is absent in frozen solutions with weak crystallization peaks and nondetected peak corresponding to the melting of regions where solute molecules are localized.

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For the systems of types (I) and (II), the possibility of prediction of low-temperature convergence of solute particles has been shown. This prediction is based on the knowledge of salt ions characteristics in liquid solution. The stronger the binding of water molecules to ions in liquid solution the less complete are crystallization processes occuring both during a cooling of solution and during the subsequent heating of the latter. Convergence of solute particles occurs during a heating of such systems in which, on the one hand, water crystallization in the ion environment is not completed during cooling and, on the other hand, salt ions are not bound with water molecules strongly so that the heating of frozen system leads to the crystallization of these bound water molecules.

When aqueous polymer solutions (type (III) systems) contain salt in relatively high concentrations, the analogous prediction which is based on the knowledge of ion-water bond strength in liquid system is possible too. As has been shown, during a freezing of the solution in which more than approximately six polymer units correspond to one salt molecule, all salt ions bind with polymer fragments and water in complexes so that water molecules contained therein can neither crystallize nor leave complexes to crystallize with free water molecules.