

It is known that knowledge of thermodynamic coordinates (changes of Gibbs energy ( $\Delta_r G^0$ ), an enthalpy ( $\Delta_r H^0$ ) and an entropy ( $\Delta_r S^0$ )) of studied processes is necessary for the scientifically based choice of optimum conditions of their carrying out in practice [22]. At the same time many researchers assume that for systems with participation of macromolecules the fundamental laws of thermodynamics established for the systems consisting of low-molecular weight compounds [23, 24] are used.

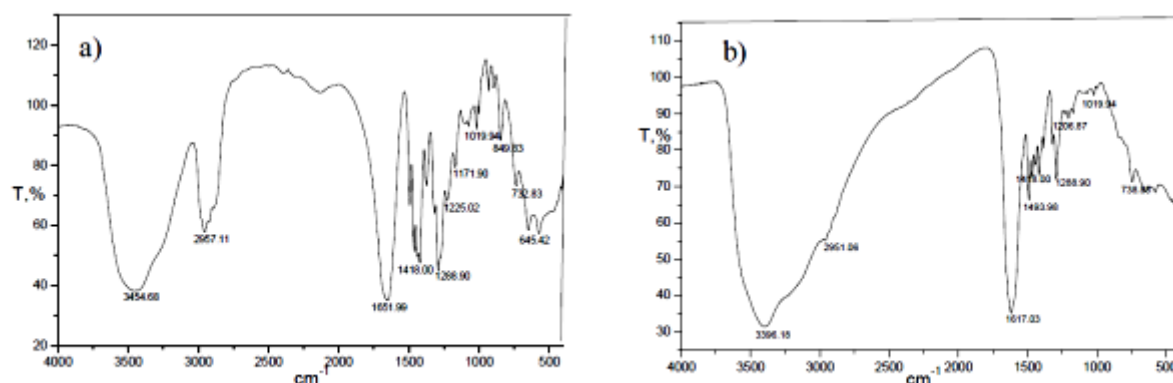
On the basis of thermodynamic constants of stability, using isotherm equations and isobars of Vant Hoff and Gibbs, changes of energy of Gibbs ( $\Delta_r G^0$ ), an enthalpy ( $\Delta_r H^0$ ) and an entropy ( $\Delta_r S^0$ ) were calculated and presented in Table 3. As confirmation of a possibility of course of a complexing reaction in these systems in a forward direction serve the negative sizes of Gibbs' energy on the sign of the studied processes. Apparently from Table 3, interactions of iron ions with PVP are followed by exo-effects that point the negative values of change of an enthalpy during a reaction. Processes of formation of iron complexes with polyvinylpyrrolidone are characterized by the negative values of an entropy change. The negative values of change of an entropy  $\Delta S$  at the negative change of an enthalpy  $\Delta H$  says that the studied reaction is possible at rather low temperatures.

Table 3

Thermodynamic characteristics of complexing processes of PVP with  $\text{Fe}^{3+}$  ions

$T, K$	$\lg \beta^0$	$-\Delta_r G^0, \text{kJ/mol}$	$-\Delta_r H^0, \text{kJ/mol}$	$-\Delta_r S^0, \text{J/mol} \times K$
298	31.00	176.849	725.653	1841.620
318	23.00	140.016	174.334	5041.910
333	10.10	64.397	1134.375	3213.150

The nature of the modifying effect of PVP on ions Fe (III) and a possible molecular structure of the PVP- $\text{FeCl}_3$  complex were studied by IR-spectroscopy (Fig. 5). The IR spectra of PVP and PVP- $\text{FeCl}_3$  complex are given in Figure 5. The characteristic peak of C=O bond in PVP becomes asymmetric after addition of the  $\text{FeCl}_3$  complex that testifies to the strong coupling between PVP and Fe (III) in the PVP- $\text{FeCl}_3$  complex. IR spectra and PVP and the PVP- $\text{FeCl}_3$  complexes contain bands at 3454 and 3396  $\text{cm}^{-1}$  characteristic for PVP. The carbonyl group in PVP is characterized by peak at 1652  $\text{cm}^{-1}$ , widened because of double bond C=N in a lactam ring. This band is shifted to 1617  $\text{cm}^{-1}$  in the PVP- $\text{FeCl}_3$  complex. Differences between the IR spectra of PVP and the PVP- $\text{FeCl}_3$  complex suggest strong donor-acceptor interaction between the oxygen atoms of the PVP ligand and the Fe (III) ions [25–27].

Figure 5. IR spectra of PVP (a) and complex  $[\text{Fe}(\text{PVP})_4(\text{H}_2\text{O})_2]\text{Cl}_3$  (b)

The PVP ligand contains iminic bond C=N and demonstrates the polybasic behavior in aqueous solutions because of protonation/deprotonation of an oxygen atom, as shown in the Figure 6. The partially negative oxygen promotes interaction with the metals ions in solutions showing the strong ability to coordination with the transitional metals [28].