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Intermolecular Interactions in the Extraction System Nicotinic Acid–Water–Poly(*N*-vinylpyrrolidone)

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Abstract—Computer simulation of molecular structures in the nicotinic acid–water and nicotinic acid–water–poly(*N*-vinylpyrrolidone) systems was performed, and the IR spectra of these systems were calculated. The theoretical and experimental IR spectra were compared. Parameters of hydrogen bonds in the studied systems were calculated.

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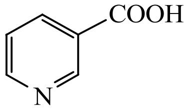
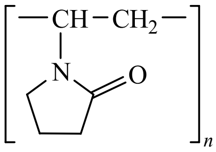
Nicotinic acid is one of the most important water-soluble vitamins involved in redox processes in human body and exhibiting vasodilating activity [1].



Nontoxic water-soluble polymers hold promise as extractants [2, 3]. It is known that extraction systems on the basis of poly(*N*-vinylpyrrolidone) are quite efficient toward vitamins [4].



To explain the high extraction power of poly(*N*-vinylpyrrolidone), in the present work we performed computer simulation of the nicotinic acid–water and nicotinic acid–water–poly(*N*-vinylpyrrolidone) systems formed in extraction systems and calculated their IR spectra. Figure 1 shows the experimental IR spectrum of an aqueous solution of nicotinic acid which is present primarily as a dipolar ion. The latter suggestion is evidenced by the observation of absorption bands with maxima at 1590 and 1440 cm^{-1}, which are characteristic of, respectively, asymmetric and symmetric stretching vibrations of the COO^{-} group [8, 9]. The band with a maximum at 1380 cm^{-1} corresponds to symmetric stretching vibrations of the R_3N^+H group in dipolar ions. Moreover, the spectrum of an aqueous solution of nicotinic acid shows a band at 3550 cm^{-1} which corresponds to stretching vibrations of water OH groups involved in three hydrogen bonds (Table 1). The maximum at 3450 cm^{-1} relates to stretching vibrations of water OH groups involved in four hydrogen bonds. The band with a maximum at 3264 cm^{-1} is characteristic of water OH groups involved in $COO^{-}\cdots H_2O$ hydrogen bonding [10].

The IR spectra of the nicotinic acid after extraction (Fig. 2) shows absorption bands with maxima at 2700 and 1620 cm^{-1} corresponding to the $C{=}O\cdots H–N$ bond. The absorption maximum at 3335 cm^{-1} corresponds to a $C{=}O\cdots H_2O$ hydrogen bond. The decrease on the carbonyl stretching vibration frequency of the polymer from 1655 (before extraction) to 1620 cm^{-1} (after extraction) points to hydrogen bonding between the C=O group of poly(*N*-vinylpyrrolidone) and the NH group of nicotinic acid.

For quantitative characterization of hydrogen bonds we calculated their enthalpies, energies, and lengths. The formulas for hydrogen-bond parameters from the shifts of the IR absorption maxima of the analyzed samples are presented in Table 1 [11]. The calculated parameters of hydrogen bonds in the systems water–nicotinic acid and water–nicotinic acid–polymer are listed in Table 2.

The length of the hydrogen bond between the C=O group of poly(*N*-vinylpyrrolidone) and the NH group of nicotinic acid is 2.6 Å (Table 2), which is smaller than the length of the hydrogen bond between two

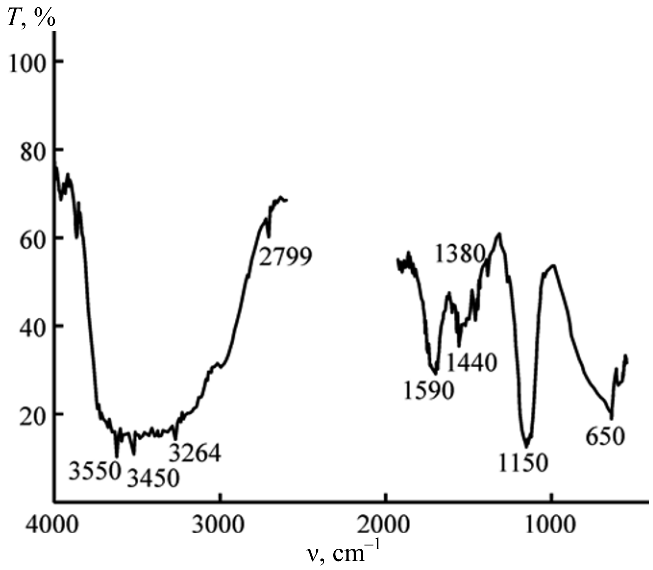


Fig. 1. IR spectrum of nicotinic acid in aqueous solution.

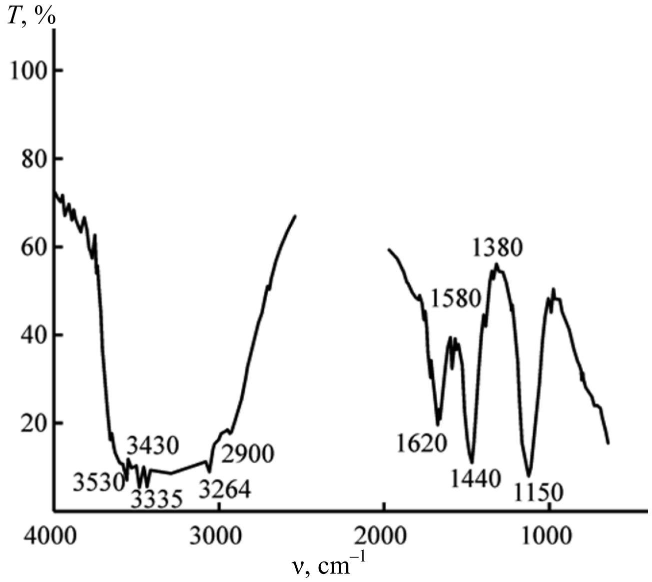


Fig. 2. IR spectrum of nicotinic acid after extraction with poly(*N*-vinylpyrrolidone).

water molecules (2.8 Å). This fact suggests association between the polymer and nicotinic acid during extraction. The vibration frequencies obtained by quantum-chemical calculations of the interaction between nicotinic acid and poly(*N*-vinylpyrrolidone) in water (Table 3) are consistent with those in the experimental IR spectrum.

The calculation results listed in Table 3 show that extraction will shift the stretching absorption maxima of the N–H group of nicotinic acid to lower frequencies from 2700 to 2625 cm^{-1} and of the polymer C=O group from 1620 to 1614 cm^{-1}. This fact suggests hydrogen bonding between the C=O group of the polymer and the NH group of nicotinic acid and is consistent with experimental data. Figure 3 shows an optimized structure of nicotinic acid with 18 water molecules. The results of computer simulation provide evidence showing that the NH groups of nicotinic acid form hydrogen bonds with two water molecules, and water molecules, in their turn, form hydrogen bonds with each other. Poly(*N*-vinylpyrrolidone), when introduced into the system (Fig. 4), destroys hydrogen bonds between water and nicotinic acid due to formation of a stronger polymer– nicotinic acid hydrogen bond.

Thus, the transfer of nicotinic acid to the polymer phase is accompanied by hydrogen bonding between poly(*N*-vinylpyrrolidone), nicotinic acid, and water, as well as strengthening of intermolecular hydrogen bonds in the water–nicotinic acid–polymer system compared to hydrogen bonds in the water–nicotinic acid system, which results in selective extraction of nicotinic acid with the polymer.

EXPERIMENTAL

The IR spectra of aqueous solutions of nicotinic acid, poly(*N*-vinylpyrrolidone), and the nicotinic acid–

Table 1. Formulas for calculation of the energies (E_H), enthalpies (ΔH), and lengths ($r_{OH\cdots O}$, $r_{O\cdots O}$) of hydrogen bonds in the water–nicotinic acid and water–nicotinic acid–polymer systems before and after extraction with poly(*N*-vinylpyrrolidone)

Parameter	Formula
E_H, kJ mol^{-1}	$\Delta\nu/\nu^0_{OH} = E_H \cdot 1.6\times10^{-2}$
ΔH, kJ mol^{-1}	$\Delta H = 2.9\Delta A^{1/2}$; $\Delta\nu = [\Delta A^{1/2}]^2 80$
$r_{OH\cdots O}$, Å	$\Delta\nu = 4.43\times10^3(2.84 - r_{OH\cdots O})$
$r_{OH\cdots O}$, Å	$\Delta\nu = 5.48\times10^2(3.21 - r_{NH\cdots O})$

Table 2. Parameters of hydrogen bonds in the water–nicotinic acid–polymer system before and after extraction with poly(*N*-vinylpyrrolidone)[a]

$R_{OH\cdots O}$, ν, cm^{-1}	E_H, kJ mol^{-1}	ΔH, kJ mol^{-1}	$r_{OH\cdots O}$, Å	$r_{NH\cdots O}$, Å
3335	25.8	25.9	2.7	–
3264 (3264)	30.8 (30.8)	28.5 (28.5)	2.7 (2.7)	–
2700	70.7	42.5	–	1.4

[a] Values in parentheses are those before extraction.

Table 3. Parameters (ν, cm^{-1}) of the experimental IR spectra of nicotinic acid before and after extraction with poly(*N*-vinylpyrrolidone) and obtained by quantum-chemical calculations including water molecules

Experiment		Nicotinic acid–water	Nicotinic acid–water–polymer	Band assignment
before extraction	after extraction			
3550	3530	3560	3509	ν(OH), water molecules associated by 3 hydrogen bonds
3450	3430	3463	3390	ν(OH), water molecules associated by 4 hydrogen bonds
–	3335	–	3339	ν(OH), $C{=}O\cdots H_2O$
3264	3264	3342 3236	3328 3273	OH stretching vibrations of water in the $COO^{-}\cdots H_2O$ system
2900	2900	2904	2827	Stretching vibrations of the polyelectrolyte chains and the pyrrolidone ring
–	2700	–	2625	$C{=}O\cdots H{-}N$
–	1620	–	1614	Polymer C=O
1590	1580	1547	1599	$\nu_{as}(COO^{-})$
1440	1440	1513	1456	$\nu_{s}(COO^{-})$
1386	1380	1369	1359	$\nu_{s}(R_3N^{+}H)$

water–poly(*N*-vinylpyrrolidone) system were obtained on a InfraLYuM FTIR spectrometer at 400–4000 cm^{-1}. The quantum-chemical calculation of nicotinic acid was performed by the DFT method using GAUSSIAN-03 [5, 6]. Initially, to optimize the structure of nicotinic acid in aqueous solution, we added to it, one by one, water molecules, beginning with their addition to the most active centers of the vitamin molecule [7, 8]. Water molecules were added until they no longer affected the N–H and COO^{-} stretching vibration frequencies of nicotinic acid, which relate to the hydrogen bond energy. A total of 18 water molecule were

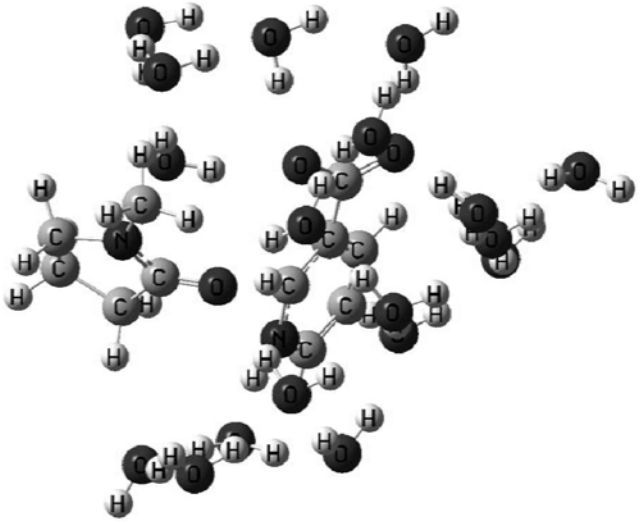


Fig. 3. Optimized structure of a molecule of nicotinic acid with 18 water molecules.

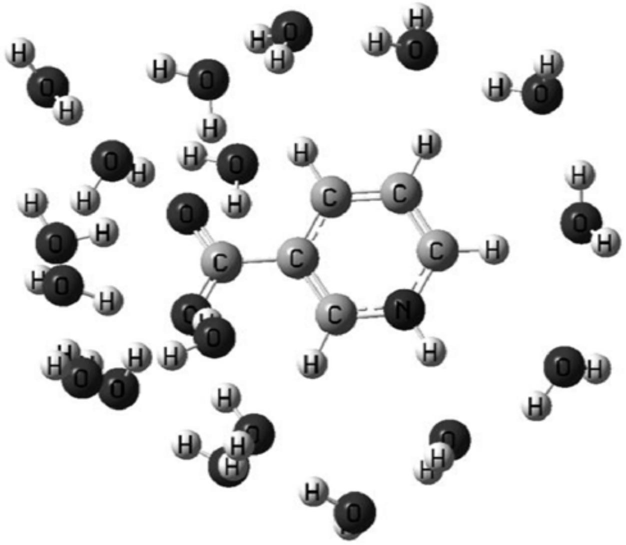


Fig. 4. Optimized structure of a molecule of nicotinic acid with 18 water molecules in the presence of poly(*N*-vinylpyrrolidone).

added. The next stage was extraction simulation, specifically, replacement of several water molecules by a poly(*N*-vinylpyrrolidone) structural unit.

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