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Thermodynamics of Nitrophenols Sorption from Aqueous Media with *N*-Vinylpyrrolidone-Based Polymer

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Abstract—Nitrophenols sorption with polymer material based on *N*-vinylpyrrolidone has been studied in the static conditions. The sorption constant and the basic thermodynamic parameters of sorption have been determined. The sorption occurs via non-specific physical interactions, it is so called "extraction sorption." The prepared polymer material has been more efficient in nitrophenols sorption than silica.

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The nitrophenols, common water pollutants, are widely used in production of plastics, plastifiers, drugs, dyes, explosives, pesticides, cleaning agents, stabilizers, and antioxidants [1]. The industrial wastewater is the major source of surface water pollution with nitrophenols. Thus, the extraction and concentration of nitrophenols from diluted aqueous solutions is a topical issue; the commonly applied procedures to do so are liquid extraction, freezing, electrochemical methods, chromatography, and sorption [2–4].

Concentration via sorption has been among the most efficient and widely used methods in analytical chemistry. Polymers based on *N*-vinylpyrrolidone (VP), efficiently extracting hydrophilic and hydrophobic phenols from aqueous media, are of practical and fundamental importance [5]. Commercial VP-based sorbents Oasis and Strata-X have revealed higher recovery degree than that of styrene-based polymers [6]. Development of new VP-based sorbents with special properties will further extend their application area.

In this work we studied nitrophenols sorption with polymer sorbent based on VP and ethyleneglycol dimethacrylate (EGDMA). We aimed to determine of the basic thermodynamic parameters of the sorption and to figure out its mechanism.

The crosslinked poly(VP-co-EGDMA) was applied for static sorption of mono-, di-, and trinitrophenols from aqueous solutions. In order to investigate the sorption process in detail, we studied the effect of pH, temperature, and presence of salting out agents on the system behavior.

Nitrophenols are weak acids, and their sorption efficiency is a function of pH. Following the previously reported results on the extraction of the acids with $K_a \leq 10^{-5}$ [7], we hereafter studied di- and trinitrophenols sorption at pH 5, without additional acidification. In the case of 4-nitrophenol, the highest extraction degree was found at pH of 2–3 (Fig. 1). The revealed pH effect was in line with that reported in the case of phenols liquid extraction with polyVP solutions [5].

Nitrophenols sorption isotherms in the concentration range of 0–8 mmol L^{-1} are reported in Fig. 2.

From the data collected, we determined the sorption capacity of the polymer towards the nitrophenols and the respective sorption equilibrium constants at different temperatures (Table 1). The sorption isotherms were linear in the concentration range of 0–1.5 mmol L^{-1}). Thermodynamic sorption parameters, enthalpy and Gibbs free energy, were calculated using the Henry equation [8], the results are reported in Table 1 as well. In the cases of all nitrophenols studied, K_h decreased with increasing temperature, and the equilibrium was shifted towards desorption.

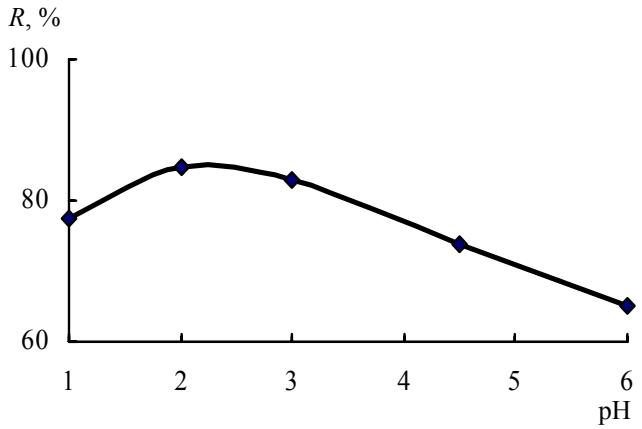

Fig. 1. Degree of 4-nitrophenol extraction as function of pH ($V_{solution}$ 10 mL, $m_{sorbent}$ 0.05 g).

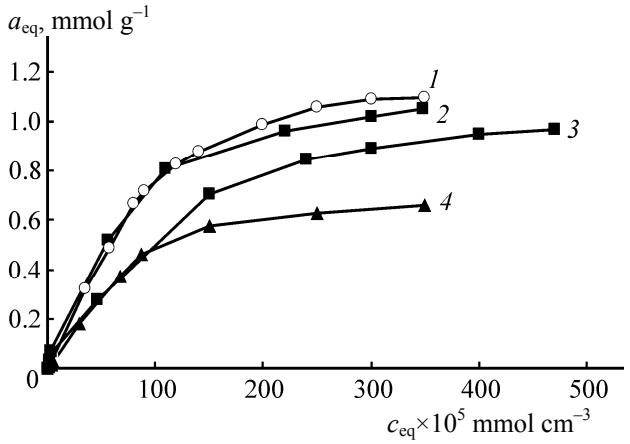

Fig. 2. Sorption isotherms of (*1*) 2,5-dinitrophenol, (*2*) 2,6-dinitrophenol, (*3*) 4-nitrophenol, and (*4*) 2,4,6-trinitrophenol from aqueous solution at 298 K.

The profiles of equilibrium sorbate concentration versus reciprocal temperature at constant loadings a_{eq} are shown in Fig. 3. From the slopes of the plots, the isosterical heat of sorption q was determined. It was independent of a_{eq} for all nitrophenols studied (Fig. 4), which is typical or primary surface filling (without the condensed phase formation) and of even distribution of the active binding sites over the surface. The active sites in the studied case were seemingly the polar groups of polymer, capable of hydrogen bonding.

As the values of a_{eq} were relatively low, and $\Delta G^0 \approx$ 3–6 kJ mol^{-1}, the sorption seemed to occur via the physical mechanism, majorly due to hydrophobic and hydrogen bonding interactions. Such sorption is referred to as extraction sorption [9]; the phenols are adsorbed via so called dissolution in the polymer scaffold.

The extraction type of sorption was further confirmed by increasing the sorption efficiency with addition of inorganic salt. The distribution coefficient of 4-nitrophenol in the cases of aqueous and saline (0.1 mol L^{-1} of ammonium sulfate) solutions was of 1220 mL g^{-1} and 2130 mL g^{-1}, respectively.

The effect of electrolyte addition on the nitrophenols extraction was analyzed using the equation similar to the Sechenov equation [10]:

$$\log (D_0/D_S) = k_S c_S,$$

where D_0 and D_S being distribution coefficient of the nitrophenol in the aqueous and in the saline solutions, respectively; k_S, salting out coefficient; c_S, electrolyte concentration.

The k_S value is a measure of free water before and after addition of the electrolyte [11]. The salting out effect is determined by both anion and cation, being dependent on their charges and radii [12].

According to the salting out effect, the salts were arranged in the series: $(NH_4)_2SO_4 > NH_4Cl > Na_2SO_4 > K_2SO_4 > NaCl > KCl$.

Table 1. Henry's constants and other thermodynamic parameters of nitrophenols sorption

Sorbate	Henry's constant $K_h\times10^{-2}$				$-\Delta H^0$, kJ mol^{-1}	$-\Delta G^0$, kJ mol^{-1}	$a_{eq\,max}$, mmol g^{-1} (298 K)
	288 K	303 K	328 K	343 K			
4-Nitrophenol	12.5	11.1	10.5	10.0	3.1	18.4	1.08
2,4-Dinitrophenol	12.4	11.6	10.0	9.3	4.2	18.3	1.07
2,5-Dinitrophenol	23.7	20.7	17.5	16.2	5.5	19.8	1.10
2,6– Dinitrophenol	7.3	7.0	6.1	5.9	3.2	17.0	1.11
2,4,6– Trinitrophenol	4.4	4.1	3.3	2.9	6.2	15.4	0.68

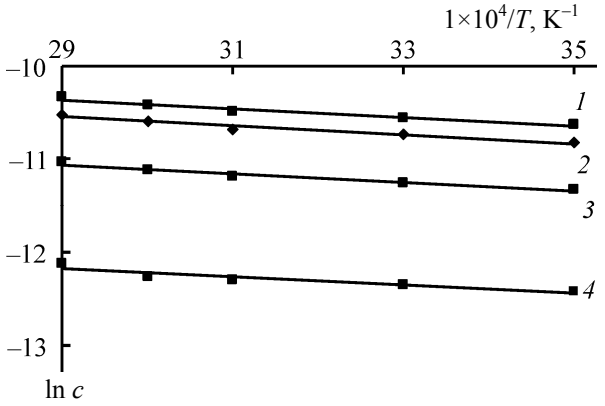

Fig. 3. Determination of 2,4-dinitrophenol isosterical heat of sorption at various equilibrium loadings $a_{eq}\times10^6$, mol g^{-1}: (*1*) 30, (*2*) 25, (*3*) 15, and (*4*) 5. See details in the text.

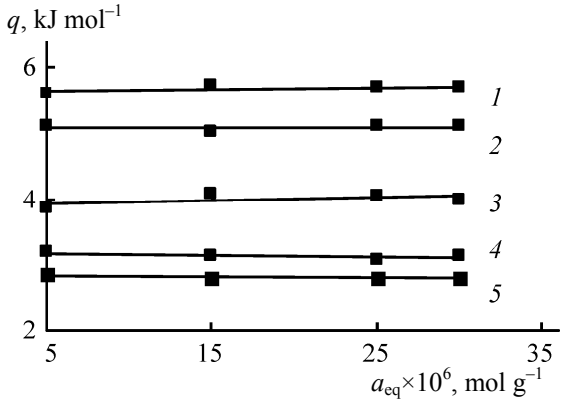

Fig. 4. Isosterical heat of sorption of (*1*) 2,4,6-trinitrophenol, (*2*) 2,5-dinitrophenol, (*3*) 2,4-dinitrophenol, (*4*) 2,6-dinitrophenol, and (*5*) 4-nitrophenol from aqueous solution as function of the loading.

In the two series, $(NH_4)_2SO_4 > Na_2SO_4 > K_2SO_4$ and $NH_4Cl > NaCl > KCl$, the order of the salting out effect change was in line with the ordering-disordering effect of the ions on water structure [13].

With increasing hydration of the cation (anion), its interaction with water was enhanced, the amount of free water in the sorption system decreased, and the sorbate dehydration occurred. The degree of nitrophenols recovery increased as compared to the salt-free sorption. The effect was especially pronounced in the case of ammonium sulfate: the recovery enhancement reached 20–30%. In that system water almost completely entered the hydration sphere of ammonium ions, whereas Na^+ and K^+ were less hydrated.

In the cases of different nitrophenols, the salting out coefficient was dependent on the nature, number, and position of the substituents in the aromatic ring (Table 2). Additional NO_2 group capable of hydrogen bonding with water and inducing association processes increased k_S. The highest salting out coefficient was found in the case of 2,6-dinitrophenol, likely due to formation of the intramolecular hydrogen bonds and less hydration of the molecules.

Chemically modified silica is a popular sorbent for phenols concentration [14]. Its application is due to rapid equilibration during sorption, negligible swelling in water, and easy desorption of the organic compounds. Other conditions being the same, the distribu-

Table 2. Distribution coefficients D (extraction degree R) and salting out constants of nitrophenols at 0.1 mol L^{-1} of the salting out additive (pH = 3, n = 3, p = 0.95, $V_{solution}$ = 10 mL, $m_{sorbent}$ = 0.01 g)

Salting out additive	4-Nitrophenol		2,4-Dinitrophenol		2,5-Dinitrophenol		2,6-Dinitrophenol		2,4,6-Trinitrophenol	
	$D\times10^{-2}$	k_S	$D\times10^{-2}$	k_S	$D\times10^{-2}$	k_S	$D\times10^{-2}$	k_S	$D\times10^{-2}$	k_S
$(NH_4)_2SO_4$	21.3±1.7 (68%)	2.5	15.0±1.2 (60%)	5.4	16.3±1.3 (62%)	4.3	27.7±2.2 (74%)	7.5	13.3±1.1 (57%)	5.4
NH_4Cl	16.3±1.3	1.3	12.6±1.0	4.8	12.7±1.0	3.2	19.2±1.5	6.2	12.2±1.0	5.0
Na_2SO_4	18.0±1.4	2.0	11.1±0.9	4.2	11.6±0.9	2.8	16.3±1.3	5.5	13.8±1.1	5.9
K_2SO_4	17.0±1.4	1.5	10.2±0.8	3.8	10.0±0.8	2.1	14.4±1.1	4.9	12.1±1.0	5.0
NaCl	13.8±1.1	0.6	5.4±0.4	1.0	7.5±0.6	0.9	10.6±0.8	3.5	9.3±0.7	3.9
KCl	13.3±1.1	0.4	4.7±0.4	0.4	6.7±0.5	0.4	9.9±0.8	3.1	8.5±0.7	3.5
None	12.2±1.0 (55%)	–	4.3±0.3 (30%)	–	6.1±0.5 (38%)	–	6.9±0.3 (41%)	–	3.9±0.3 (28%)	–

tion coefficients in the case of poly(VP-*co*-EGDMA) sorbent were 280 (4-nitrophenol) and more than 4 (2,4-dinitrophenol) times higher than those in the case of silica [15].

To conclude, the studied sorbents based on *N*-vinylpyrrolidone can be recommended to concentrate and separate micro amounts of nitrophenols from the aqueous media under static and dynamic conditions.

EXPERIMENTAL

4-nitrophenol, 2,4-dinitrophenol, 2,5-dinitrophenol, 2,6-dinitrophenol, and 2,4,6-trinitrophenol were purified by recrystallization [16] and identified according to the melting point of absorption coefficient. The studied solutions were prepared by dissolving the sample in twice distilled water.

The salts used in the salting out experiments (sodium, potassium, and ammonium chlorides and sulfates) of the chemical pure grade were twice recrystallized from bidistilled water. The salt concentration was in the range of 0.1–0.5 mol L^{-1}.

The polymer sorbent was prepared via radical copolymerization of *N*-vinylpyrrolidone VP and ethyleneglycol dimethacrylate EGDMA in anhydrous methanol during 16 h at 65°C. AIBN was used as initiator, VP : EFDMA ratio was of 1 : 15. The so prepared polymer was washed with methanol several times, dried in vacuum oven at 50–55°C, and finally crushed in the agate mortar. The fraction of 250 μm particles was separated with sieve.

In the sorption experiments, 10 mL of aqueous or saline solution of nitrophenol (up to 8 mmol L^{-1}) at known pH value was put into the thermostatted flasks. (0.0100±0.0002) g of the polymer was then added, and the system was treated with vibromixer during 1 h (preliminary studies showed that it was enough to reach the equilibrium [17]). The sorbent was centrifuged from the solution. The concentration of nitrophenol was determined in the equilibrium liquid as follows. 5 mL of the analyzed solution was mixed with 1 mL of 5 wt % ammonia, and the absorption was measured after 5 min (KFK-2MP or UV 1240 Shimadzu) at λ_{max} = 400 nm.

The sorption isotherms were derived as described in [18]. Sorption equilibrium constant, the limiting sorption, standard enthalpy (ΔH^0), and free energy (ΔG^0) of sorption were determined [8]. The heat of sorption (q, J mol^{-1}) was determined by isosterical method [19]: the equilibrium sorbate concentration was plotted as function of temperature at constant surface filling. The results were fitted to Eq. (1).

$$\ln c = -\frac{q}{R}\cdot\frac{1}{T} + J, \quad (1)$$

where c, equilibrium sorbate concentration (mol L^{-1}); R, gas constant [J/(mol·K)]; T, temperature, K; J, integration constant.

Degree of recovery (R, %), distribution coefficient (D, mL g^{-1}), and sorption (a_{eq}, mmol g^{-1}) were calculated according to Eqs. (2)–(4).

$$P = \frac{c_0 - c}{c_0}\times 100, \quad (2)$$

$$D = \frac{P}{100 - P}\frac{V}{m}, \quad (3)$$

$$a_{eq} = \frac{(c_0 - c)V}{m}, \quad (4)$$

where c_0, initial sorbate concentration (mol L^{-1}); V, solution volume (mL); m, sorbent mass (g).

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