Intercalation compounds of phenols and poly-*N*-vinylcaprolactam

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Intercalation compounds of phenols and poly-*N*-vinylcaprolactam (PVC) form when their aqueous solutions are mixed. Using ^{13}C NMR and IR spectroscopy complexation was shown to proceed through the formation of hydrogen bonds between the carbonyl groups of the caprolactam moieties and phenolic hydroxyls as well as through displacement of water from the polymer structure and its compaction. The processes of the formation of intercalation compounds of PVC with phenol and *tert*-butyl alcohol were compared.

Key words: poly-*N*-vinylcaprolactam, phenol, chlorophenols, complexes; hydrogen bond.

Poly-*N*-vinylcaprolactam (PVC) is a promising reagent for the production of various supramolecular structures. PVC-based complexes are of interest not only from a scientific but also from a practical viewpoint (intercalation of enzymes and of microorganism cells).[1—3] The formation of complexes of poly-*N*-vinylpyrrolidone with phenols and polyphenols of vegetable origin and with medicines has been studied in sufficient detail.[4,5] In this work, the formation of intercalation compounds of different phenols with PVC and their structures were studied by ^{13}C NMR and IR spectroscopy.

Experimental

The complexes of phenols with PVC were obtained by the addition of an aqueous PVC solution to a phenol solution. The precipitate that formed was filtered off and washed with distilled water until tests for phenol in washing water were negative (monitored by a SF-46 spectrometer at λ = 510 nm). The degree of the phenol intercalation (η) was estimated from the difference in its content in the initial solution and in solutions obtained after separation of the precipitate. The phenol concentration was determined according to a procedure described previously.[6]

The $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AM-250 spectrometer (62.896 MHz) in the Fourier transformation regime with broadband decoupling of the spin-spin interaction of protons. Spectra of solutions of PVC, phenol, *tert*-butyl alcohol (for comparison), and of intercalation compounds (20% solutions in $CDCl_3$) were recorded in ampules (10 mm) at 303 K. Chemical shifts were measured relative to the signal of $CDCl_3$ and recalculated to $SiMe_4$. The temperature of the spectrometer sample unit was established with ±0.5 K accuracy.

The spin-lattice relaxation times (t_1) of the ^{13}C nuclei were measured by the inversion—reduction method, using the pulse sequence t—180°—τ—90°. The τ values were varied from 0.01 s to t, which was chosen to be equal to (4—5)t_1 for complete relaxation of nuclei. The t_1 values were calculated according to the equation $A_\infty/A = 2A_\infty\exp(-\tau/t_1)$, where A_∞ is the limiting value of A_τ at the longest interval between the 180- and 90-degree pulses, A_τ is the amplitude of the induced signal after the 90-degree pulse. Calculations were performed on an Aspect 3000 processor of the spectrometer; the relative error in the t_1 measurement did not exceed 5%.

The IR spectra were taken on a Specord IR 75 spectrometer in $CHCl_3$ solutions in the range of concentrations 0.36—0.0012 mol L^{-1} with successive dilution with a solvent.

Results and Discussion

As follows from the data presented below, phenols form complexes with PVC of various compositions:

Phenol	The degree of intercalation in PVC, η (%)
o-Cresol	80
p-Cresol	80
Resorcinol	70
Benzoic acid	60
Salicylic acid	66
Salicylaldehyde	39
2,4-Dinitrophenol	20
2,4-Dinitro-*o*-cresol	20

Concentration and time dependences, the effect of pH, and the temperature of complexation are considered by the example of chlorophenols.

The highest degree of intercalation (%) of chlorophenols into a complex for all compounds studied is observed at high concentrations (>0.5 g L^{-1}), and the degree of the intercalation of *o*-chlorophenol is less than that of *m*- and *p*-isomers (Fig. 1). This is likely to be due to the presence of the intramolecular hydrogen bond in the *o*-chlorophenol molecule.

The η value also depends on the chlorophenol/PVC weight ratio (Table 1). The degree of intercalation for

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Table 1. Dependence of the degree of intercalation (η) of chlorophenols in PVC on the chlorophenol/PVC weight ratio (the concentration of chlorophenols is 1 g L^{-1}, that of pentachlorophenol is 0.5 g L^{-1})

Chlorophenol/PVC	η (% of initial)					
	o-ClC$_6$H$_4$OH	m-ClC$_6$H$_4$OH	p-ClC$_6$H$_4$OH	2,4-Cl$_2$C$_6$H$_3$OH	2,4,6-Cl$_3$C$_6$H$_2$OH	C$_6$Cl$_5$OH
1 : 1	22.2	29.4	30.2	27.9	41.2	17.3
1 : 3	25.6	42.0	36.8	55.4	63.7	38.6
1 : 5	35.0	45.9	48.5	76.5	70.1	44.0
1 : 7	37.8	55.1	54.1	80.7	76.3	57.3
1 : 10	45.2	65.5	59.6	91.3	80.1	60.1
1 : 14	47.6	70.1	62.3	84.0	81.3	64.5

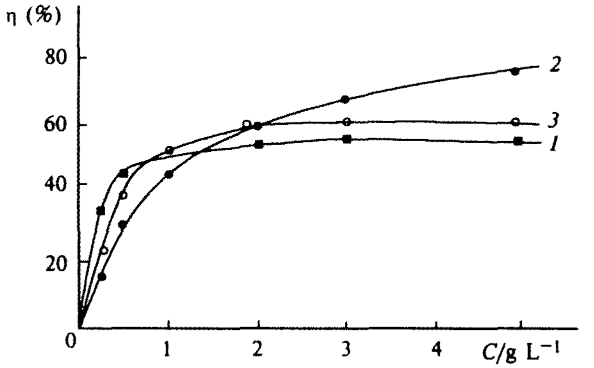

Fig. 1. Dependence of the degree of intercalation (η) of phenols in PVC on concentration for o-chlorophenol (*1*), m-chlorophenol (*2*), and p-chlorophenol (*3*).

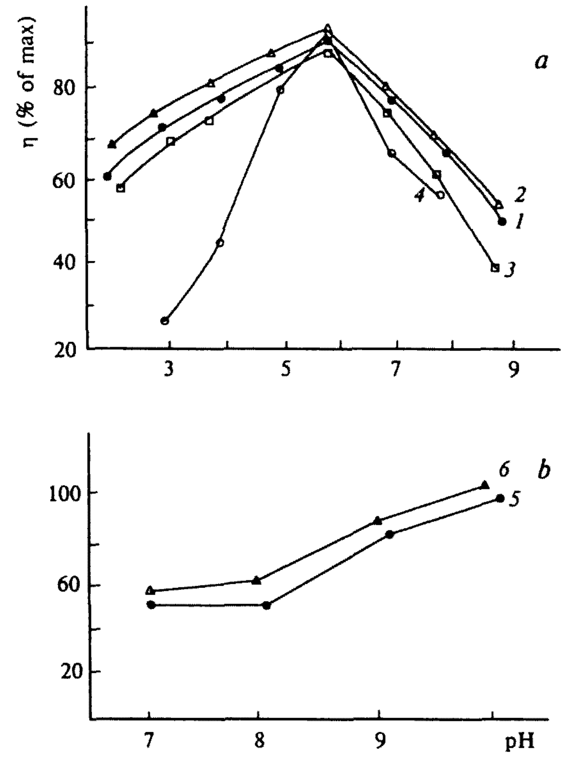

Fig. 2. Dependence of the degree of intercalation (η) of phenols in PVC on pH: *a*, for o-chlorophenol (*1*), m-chlorophenol (*2*), p-chlorophenol (*3*), and 2,4-dichlorophenol (*4*); *b*, for 2,4,6-trichlorophenol (*5*) and pentachlorophenol (*6*).

all chlorophenols considered with the exception of 2,4,6-trichlorophenol (41.2%), is low at the chlorophenol/PVC = 1 : 1 weight ratio. The optimum ratio is 1 : (5—7), and it is 1 : (3—5) for 2,4-dichloro- and 2,4,6-trichlorophenols. At the higher phenol/PVC ratios, the degree of intercalation does not change substantially.

The intercalation of monochlorophenols and 2.4-dichlorophenol in PVC was studied at pH 2.0—9.0 and that of 2,4,6-trichlorophenol (with allowance of its solubility) at pH 7.0—10.0 (Fig. 2). In the first case, the maximum intercalation was observed at pH 6.0, whereas in the latter case, the degree of intercalation of phenols in PVC was independent of pH.

It follows from the data presented in Table 2 that the maximum intercalation of chlorophenols in PVC takes place in the temperature range 25—35 °C. At lower temperatures, no easily separated granules form. As temperature increases further (>40 °C), the degree of intercalation begins to decrease. The hydrogen bonds that stabilize the complex seem to break.

The maximum degree of the intercalation of all chlorophenols studied in PVC is achieved in 8—10 min (Fig. 3).

It is noteworthy that the use of the NaCl—NaOH (1 : 10) system as a desorbing solution allows one to regenerate PVC with separation of phenols. Thus, the successive reuse (up to 10 times) of the regenerated PVC is possible.

On this basis, the suggestion was made that the intercalation of phenols in PVC might be useful for extracting phenols from waste water in which they are present in high concentrations. To verify this method, p-chlorophenol and 2,4-dichlorophenol were introduced into sea water (1 g L^{-1}) to simulate the contamination with phenol. The addition of PVC at ambient temperatures (27—28 °C) made it possible to extract 60—80% of the chlorophenols.

By using ^{13}C NMR and IR spectroscopy techniques, we found that the intercalation of phenols in PVC

Table 2. Dependence of the degree of intercalation (η) of chlorophenols in PVC on temperature (*T*)

T/°C	η (% of initial)					
	o-ClC_6H_4OH	*m*-ClC_6H_4OH	*p*-ClC_6H_4OH	2,4-$Cl_2C_6H_3OH$	2,4,6-$Cl_3C_6H_2OH$	C_6Cl_5OH
10	Precipitate is not filtered off					
20	78.1	73.7	72.7	79.3	76.4	96.9
25	92.3	94.1	87.3	94.0	92.6	97.6
30	100.0	100.0	100.0	100.0	100.0	100.0
35	87.5	89.0	93.4	96.5	95.3	94.2
40	74.4	72.0	76.4	84.6	85.2	87.0
50	69.7	70.3	70.1	73.1	71.3	72.3
60	57.8	65.3	66.8	67.4	66.4	65.7

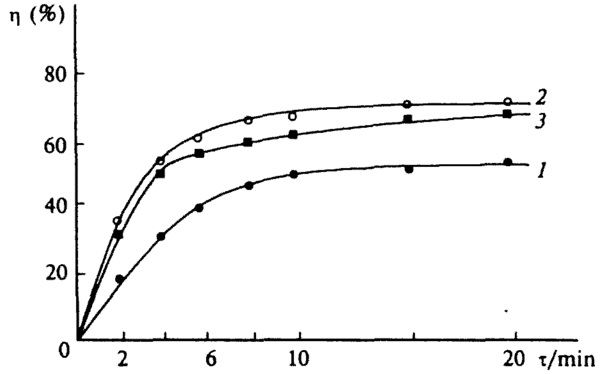

Fig. 3. Dependence of the degree of intercalation (η) of phenols in PVC on the duration of the process for *o*-chlorophenol (*1*), *m*-chlorophenol (*2*), and *p*-chlorophenol (*3*).

occurs through the formation of hydrogen bonds between the carbonyl groups of the caprolactam moieties and the phenol hydroxyls as well as through the displacement of water from the polymer structure, which is accompanied by compaction of the polymer. The latter is confirmed by the absence of the band of bound water in the 3400 cm^{-1} region in the spectrum of PVC—phenol complexes. This band is clearly pronounced in the spectrum of the individual PVC.

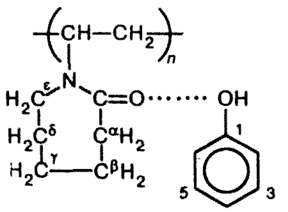

Table 3 presents the values of the chemical shifts and the spin-lattice relaxation times of the ^{13}C nuclei in the NMR spectra of individual PVC, phenol, and the

Table 3. Effects of the intercalation of phenol and *tert*-butyl alcohol in the PVC matrix according to the ^{13}C NMR spectroscopy data

Atom	Individual compound		PVC—phenol				PVC—*tert*-butyl alcohol			
	δ	Nt_1/s	δ	Δδ	Nt_1^c/s*	$t_1^c : t_1$	δ	Δδ	Nt_1^c/s*	$t_1^c : t_1$
					PVC					
CO	177.50	3.29	177.05	−0.45	3.180	1.18	175.82	−1.23	1.870	0.568
CH	46.09	0.228	46.48	0.39	0.253	1.11	46.78	0.30	0.203	0.809
CH_2	34.08	0.109	34.11	0.03	—**	—**	34.08	0.00	—**	—**
C(ε)	42.47	0.129	42.39	−0.08	0.163	1.26	42.04	−0.35	0.131	1.020
C(α)	37.08	0.126	36.95	−0.13	0.142	1.13	37.29	0.34	0.132	1.050
C(γ)	22.92	0.153	22.86	−0.06	0.161	1.05	22.78	−0.08	0.143	0.935
C(β, δ)	29.42	0.154	29.11	−0.31	0.181	1.18	29.38	0.27	0.159	1.030
					Phenol					
C(1)	155.25	21.48	156.89	1.64	3.520	0.164				
C(2, 6)	115.10	12.13	115.18	0.08	0.555	0.046				
C(3, 5)	129.50	12.14	129.13	−0.37	0.545	0.045				
C(4)	120.63	9.97	119.18	−1.45	0.508	0.051				
					tert-Butyl alcohol					
$-\overset{\vert}{\underset{\vert}{C}}-$	66.35						68.39	2.04	15.59	
CH_3	32.78						30.87	−1.91	2.70	

* t_1^c is the time of spin-lattice relaxation of the ^{13}C nuclei in the complex; *N* is the extent of protonation of the C atoms. ** Broadening of the signal does not allow one to estimate t_1 on inversion.

intercalation compounds. The assignments of the signals of the ^{13}C nuclei were based on literature data[7] and on calculations according to the Lindeman—Adams method.[8]

In the intercalation of phenol into PVC, shielding of the carbon nuclei of all groups of PVC except CH occurs (see Table 3). The C atoms of the carbonyl group are the most shielded as well as C(β) and C(δ), whose chemical shifts are the same. It is of interest that the intercalation of *tert*-butyl alcohol is accompanied by significant shielding of the C nuclei of the carbonyl group and much less shielding of C(ε). The signals of the CH groups of the main PVC chain are shifted downfield, as in phenol intercalation.

The shielding of the C nuclei of the carbonyl groups of the caprolactam fragment is accompanied by the deshielding of the C(1) nuclei of phenol and the quaternary C atom of *tert*-butyl alcohol. Similar changes give evidence for the formation of hydrogen bonds between the phenolic and alcoholic OH groups and the O atom of the carbonyl group. The fact that the change in the chemical shift of the quaternary C atom of *tert*-butyl alcohol is greater than that of the C(1) atom of phenol indicates that a stronger hydrogen bond is formed upon the intercalation of alcohols into PVC.

As can be seen from the data of Table 3, the effect of deshielding decreases sharply on going from C(1) to C(2, 6), whereas shielding increases from C(3, 5) to C(4). The nuclei of the C atoms of the methyl groups of *tert*-butyl alcohol are also shielded more in the intercalation compounds than in a solution in $CDCl_3$. These changes in chemical shifts can be explained by the dispersion interaction between the phenyl ring and the methyl groups of *tert*-butyl alcohol when these molecules are introduced into lipophilic zones formed in PVC.[9] The differences in the chemical shifts of the C(α) and C(β, δ) signals after the intercalation of phenol and *tert*-butyl alcohol are due to the different electronic and spatial structure of their molecules.

A comparison of the spin-lattice relaxation times t_1 of the ^{13}C nuclei of the phenyl ring (see Table 3) shows that after intercalation of phenol, the value of t_1 of the C(1) nucleus decreases by a factor of 6.8 and those of the C(2)—C(6) nuclei decrease by a factor of 20. As t_1 is determined by the time of rotational correlation τ_c, which describes the fragmentary mobility of a molecule, a decrease in t_1 is due to hampering of the inner rotation relative to the bonds and to a limitation in the movement of the molecule as a whole. Thus, the intercalation of phenol molecules in PVC restricts their mobility.

The effects of the intercalation of phenol and *tert*-butyl alcohol on the fragmentary mobility of PVC are different. The intercalation of phenol causes some increase in the mobility of the side caprolactamic moiety, especially in C(ε), in the CO group (in spite of the formation of the hydrogen bond), and in C(β, δ). At the same time, the intercalation of *tert*-butyl alcohol causes the fragmentary mobility of the carbonyl group and the main chain of the polymer to decrease. The t_1 values for the CO and CH groups decrease by factors of 1.76 and 1.12, respectively, and those for other groups remain in fact unchanged.

The vibrational spectra confirm the data of ^{13}C NMR spectroscopy on the formation of intercalation compounds of phenol and PVC. The concentration dependences are measured in a chloroform solution at the molar ratio phenol/PVC = 1 : 1 (per one monomeric unit); the range of the concentration of phenol is from 0.36 to 0.0012 mol L^{-1}.

A significant fraction of the bands of phenol in the IR spectrum of the complex is masked by the bands of PVC (Fig. 4). However, in the short-wave region, one can see intense bands of O—H stretching vibrations of the unbound phenol hydroxyl group at 3580 cm^{-1} and a broad O—H absorption band in the 3150—3400 cm^{-1} region due to intermolecular hydrogen bonds. The position and shape of the narrow absorption band of the unbound OH group is independent of the phenol concentration. However, a comparison with the spectra of individual phenol at different concentrations in chloroform gives evidence for a 15 cm^{-1} shift of this band to the short-wave region. This shift can be explained by the increasing rotational mobility of the free phenol molecules in the cavities formed by the packing of the PVC chain. Thus, the regions of the PVC chains bound with phenol can include unbound phenol.

The singlet band at 1610 cm^{-1} in the IR spectrum that is due to the stretching vibrations of the C=O group is the most intense. This band is shifted 70 cm^{-1} farther to the long-wave region than in the IR spectra of lactams with large cycles. This band also indicates the participation of the carbonyl groups of caprolactam in the formation of the intermolecular hydrogen bonds.

The other bands of the IR spectrum are less informative. There are bands at 2890 and 2835 cm^{-1}, which are due to asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of the CH groups of PVC, and a band at 2925 cm^{-1} due to the C—H stretching vibrations of the

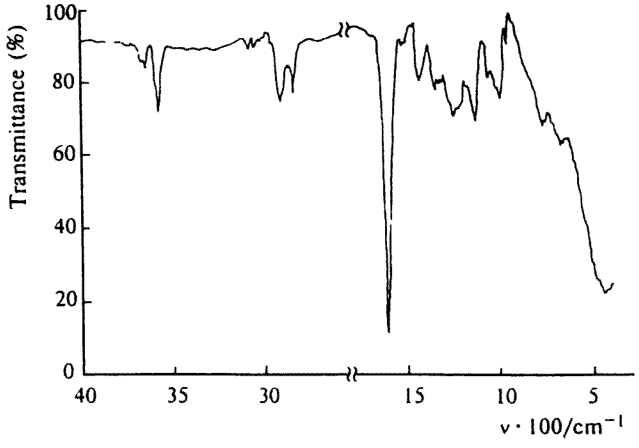

Fig. 4. The IR spectrum of the PVC complex with phenol.

aromatic ring. At high concentrations of the complex, the latter appears as a shoulder on the ν_{as} band, which is less intense than ν_s. With a decrease in the concentration, the total intensity of the ν_s band and the C—H vibrations of the aromatic ring exceeds that of the ν_s band. This can be due to an increase in the contribution of absorption of the CH groups of the aromatic ring when the intercalation compound is destroyed by a nonpolar solvent.

Thus, the results of the studies performed allow one to conclude that the complexation between poly-*N*-vinylcaprolactam and phenols proceeds in a similar way as the same process with the participation of copolymers of *N*-vinylpyrrolidone, *i.e.*, *via* a mechanism involving polymer-polymeric cooperative interaction due to the formation of the hydrogen bonds between the carbonyl groups of the caprolactamic moieties and the phenolic hydroxyls.

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