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Hydration and Intermolecular Interactions in Carboxylic Acids

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Abstract

At the moment, the most accurate and reliable information about intermolecular interactions in low-molecular compounds and their polymer analogues can be obtained by means of combined UV, visible, and IR spectroscopy. However, this combination is not always used when interpreting the results of intermolecular interactions in carboxylic acids. Therefore, the aim of our study was to investigate the intermolecular interactions in carboxylic acids and their hydration properties using the UV, visible, and IR spectroscopy.

The article presents the results of the investigation of intermolecular interactions and hydration in carboxylic acids by means of UV, visible, and IR spectroscopy, and the microscopic study of the swelling/contraction curves of the beads of the sorbents with slightly acidic –COOH groups in exchange reactions of $R-COOH + NaOH \leftrightarrow R-COO^-Na^+ + H_2O$. The study revealed that in water dimers, the total energy of hydrogen bonds is determined by the Coulomb, exchange, charge transfer, polarization, and dispersion components. In our study we also tested the formulas for the calculation of the energy of the H-bond, enthalpy, the force constants of the H-bond, and the elongation of the covalent bond. The article suggests a formula for estimation of the distance $RCH_2...O$. The calculations of the length of H-bonds between the donor and the acceptor of the proton based on the information about stretching vibrations in the IR spectra of carboxylic acids. The article demonstrates the possibility of the formation of five- and six-membered cycles, resulting from the formation of H-bonds between CH_2 groups of the chain and –COOH end groups of carboxylic acids.

The characteristic electron and vibrational frequencies in the UV and IR spectra were used to determine the intermolecular interactions in ion exchangers CB-2 and CB-4. The microscopic and microphotographic study of the swelling of certain beads of carboxylic cationites help us to register the presence of the external shell $R-COO^-...Me^+$ and the internal shell $R-COOH$ during the exchange reactions: $R-COOH + Me^+ + OH^- \leftrightarrow R-COO^-...Me^+ + H_2O$.

Keywords: UV-vis spectroscopy, IR spectroscopy, visible spectroscopy, carboxylic acids, intermolecular interactions.

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1. Introduction

When assessing an analytical method, we should take into account the three most important parameters: its accuracy, sensitivity, and cost. Unfortunately, in the modern industrial world there are few people who realise that without analytical chemistry it is difficult to combine these criteria when assessing industrial technological solutions. Indeed, analytics, being just a supplementary discipline at first, is now becoming a popular interdisciplinary branch. This indicates the restoration of analytical chemistry as an independent scientific field.

Most of the information about the structure of the initial components and the physicochemical properties of target products can be obtained by means of spectroscopy. Therefore, spectroscopy is the study of the interaction between matter and light. The electromagnetic spectrum covers electromagnetic waves ranging from high-energy cosmic radiation to X-rays, ultraviolet, visible light, infrared, and low-energy radio waves [1–4]. γ -rays, with the wavelength of just 10^{-11} cm, are emitted during nuclear reactions. X-rays (with the wavelengths of 10^{-8} cm) are formed as a result of electronic transitions between the inner shells of the so-called core electrons (Table 1).

The electronic excitation of molecules, atom vibrations, and excitation of molecular rotation are possible within a single spectrum region (a relatively small one) with the wavelengths ranging from 10^{-1} to 10^{-6} cm. This region of the UV, visible light, and IR radiation is referred to as the “optical spectrum”. When wavelengths are

shorter than 800 nm (i.e. the UV and visible light), the radiation energy is high enough to interact with the electrons in molecules [1–3]. In this case, only the valence electrons of compounds are excited. The strongly bonded σ electrons (Table 1) of simple (single) bonds absorb radiation of shorter wavelengths than weakly bonded π electrons of multiple bonds and n (nonbonding) electrons of heteroatoms.

The vibrations of molecules are excited by lower energy as compared to the ultraviolet and visible light regions of the spectrum, i.e. at longer waves. The molecular rotations are also excited, and therefore we can call these spectra rotational-vibrational [1–4]. To rotate a molecule along the three inertial axes x, y, z , minimal radiant energy is required. Therefore, at wavelengths of more than 800 nm, the rotational, vibrational, and electronic spectra are observed.

At the moment, the most accurate and reliable information about intermolecular interactions in low-molecular compounds and their polymer analogues can be obtained by means of combined UV, visible, and IR spectroscopy. However, this combination is not always used when interpreting the results of intermolecular interactions in carboxylic acids. The effect of the solvent (solvation or hydration) as one of the factors determining the character of intermolecular interactions in solutions and polymers is also rarely taken into account. Therefore, the aim of our study was to investigate the intermolecular interactions in carboxylic acids and their hydration properties using UV, visible, and IR spectroscopy.

Table 1. Classification of the spectral regions

Spectrum	Interaction	Spectral region	Wavelength
X-ray spectrum	Inner electrons	X-rays	0.01–1.0 nm
Electron spectrum	Electrons of the σ -bonds (sp^3 -orbitals)	UV in vacuum	10–190 nm
	Electrons of the π -bonds (sp^2 -orbitals)	UV	190–380 nm
	n electrons (sp -orbitals)	Visible region	380–800 nm
Vibration spectrum	Higher harmonic vibrations	Near IR	0.8–2.5 μ m
	Molecular vibrations	Mid-IR	2.5–50 μ m
Rotation spectrum	Rotation of the molecules	Far IR	50–500 μ m
		Microwaves	0.5–3.0 mm

σ, σ^* bonding and antibonding orbitals;
 π, π^* bonding and antibonding orbitals

2. Experimental

The objectives of the study determined the use of the spectroscopy methods commonly applied for detecting various structures in solutions of target substances. The UV spectra were registered using the Shimadzu 2401 spectrophotometer. Each spectrum was interpreted based on a single wavelength. The absorbance was measured at the maximum peak of the spectrum, followed by the calculation of the concentration [3–7].

The character of the swelling kinetic curves $f = V_\tau / V_n$ (V_τ , V_n is the volume of the bead at the moment τ and the initial volume in the H shape) of the sorbents with slightly acidic –COOH groups was used as a criterion for the transitions taking place in the ion exchanger phase. Therefore, we used the microscopic methodology [8, 9] to study the interaction between the sorbent and the –COOH groups. The character of the swelling kinetic curves (concentrations of separate beads of the sorbent) was studied in special plexiglass cuvettes using the MIR-12 and MBI-6 microscopes. The size of the beads was registered with a precision of up to ± 0.002 mm.

The IR spectra of liquids were recorded during the analysis of either a pure substance or its mixtures with solvents. Solid samples were prepared in the form of oil suspensions, thin films on the surface of NaCl, KBr, and CaF₂ wafers, and pressed tablets with alkali metals halides. The samples were ground in an agate mortar so that the size of the particles was no more than 0.5 μm . The samples were prepared for the analysis using the methodology described in [5]. The spectra were registered by means of the Bruker Vertex 70v vacuum FTIR spectrometer using a “Platina” single-pass ATR adapter. The preparation of samples for the IR spectroscopy most commonly involves pressing them together with KBr [6–9]. To produce the tablets, the press die described in [6] was used until the KBr crystals formed a translucent matrix with the powder of the studied substance regularly distributed within it.

The dependence of the energy of the H-bond (E_{int}) and its components on the distance $R(\text{O}\dots\text{O})$ is demonstrated in Fig. 1. The curves were calculated for the water dimer [10] and they demonstrate that, when the distance is large, the Coulomb energy (E_{coul}) of two

neighbouring molecules with intact electron shells is predominant [2, 4].

Near the equilibrium, the energy of the H-bond is determined by the Coulomb (E_{coul}) and exchange (E_{ex}) contributions [2, 4, 10], where E_{ex} is bonded taking into account the equality of the electrons of the interacting molecules, when their wave functions overlap.

Besides the Coulomb E_{coul} and exchange E_{ex} contributions, the energy of the H-bond (E_{int}) is also contributed to by the following components: the polarisation interaction energy (E_{ind}); the charge transfer energy (E_{cht}) reducing the H-bond energy as a result of the redistribution of the electron density within the subsystem (polarisation) and between the subsystems (charge transfer) [2,4,10]; and the dispersion energy (E_{disp}), which takes into account the correlation in the transmission of electrons of different molecules. Therefore,

$$E_{\text{int}} = E_{\text{coul}} + E_{\text{ex}} + E_{\text{ind}} + E_{\text{cht}} + E_{\text{disp}} + E^{(n \geq 3)}. \quad (1)$$

Depending on the value, the energies of the H-bond are classified as weak, medium, and strong [7]. The formation of the hydrogen bond significantly alters the properties of the molecules

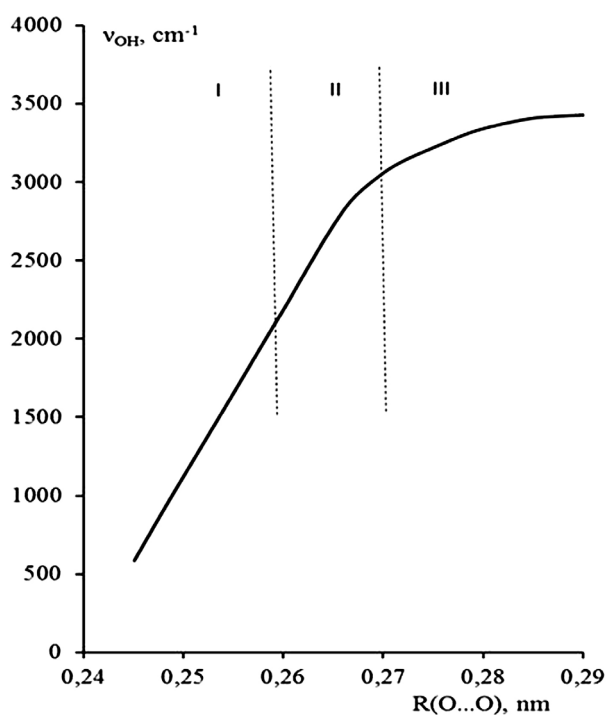


Fig. 1. The dependence of the total H-bond energy E_{int} and its individual components in the H₂O dimer on $R(\text{O}\dots\text{O})$ [7, 8]

of the associates $R_1A-H...BR_2$ (particularly of the $A...H$ group). Our experiment demonstrated (Fig. 2, Table 2) the reduction in the frequency of stretching vibrations of the A-H ($R_1O...OR_2$) bond in the 10-2600 cm^{-1} range depending on the strength of the H-bond.

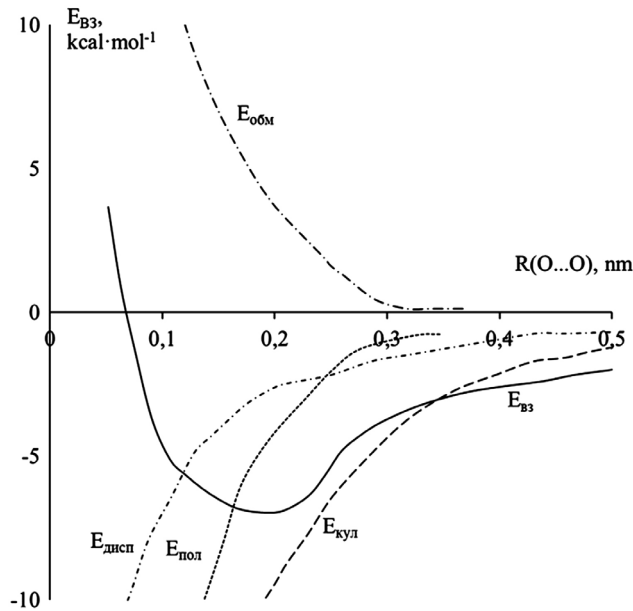


Fig. 2. The correlation between O-H-bond vibration frequency and the equilibrium distance $R_0(O...O)$ in crystals [8]

It should be noted that the characteristic frequencies of absorption of the groups of atoms in carboxylic acids obtained in [11] (Table 3) are similar to those presented in this article (Table 4, Figs. 3 and 4).

However, the results shown in Table 4 and Figs. 3 and 4 allowed us to determine the stretching vibrations and deformation vibrations to be certain functional groups and suggest a new description of the formation mechanisms of cyclic structures with H-bonds in carboxylic acids.

It is somewhat difficult to interpret the IR spectra of carboxylic acids, when the absorption bands of $-COOH$ and $-CH_2$ groups overlap (Table 5). Therefore, we performed a preliminary comparison of the UV spectra (Fig. 3a and 4c) demonstrating the electronic transitions (scheme 1) with the characteristic vibrations of the groups in the IR spectra (Fig. 3a, 3b, 3c).

Scheme (1) demonstrates that the peaks at 2962 and 2834 cm^{-1} are characteristic for $-OH$ -bonds in associates with carboxylic groups and for $-CH_2-$ in "hydrophobic" chains of carboxylic acids [2-6]. For $-CH_2$, C-O, and $-OH$ in COOH groups the peaks at 1525, 1379, 1300, 1245, 960-944, and 737 cm^{-1} appeared to be joint absorption bands. This, although making

Table 2. Formulas used to calculate the parameters of the hydrogen bridge using the values of the shift in the IR spectra

No.	Parameter	Symbol	Unit of measurement	Formula	Source
1	Energy of the H-bond	E_H	kJ/mol	$-\Delta\nu / \nu_{OH}^0 = E_H \cdot 1.6 \cdot 10^{-2}$	[1]*
2	Enthalpy	ΔH	kJ/mol	$-\Delta H = 2.9 \cdot \Delta A^{1/2}$; $\Delta\nu = [\Delta A^{1/2}]^2 \cdot 80$	[2]
3	Force constant of the H-bond	K_H	cm^{-2}	$K_H = (5.5 \pm 1.2) \cdot 10^4 \cdot E_H$	
4	Force constant of the OH-bond	K_{OH}	cm^{-2}	$-K_{OH} = 8.63(5.5 \pm 1.2) \cdot 10^4 \cdot E_H - 12.879 \cdot 10^6$	[3, 4]
5	Length of the hydrogen bridge	$R_{OH...O}$	Å	$\Delta\nu = 4.4 \cdot 10^3 (2.84 - R_{O...O})$	
		$R_{OH...N}$	Å	$\Delta\nu = 6.92 \cdot 10^2 (3.04 - R_{O...N})$	
		$R_{NH...O}$	Å	$\Delta\nu = 5.48 \cdot 10^2 (3.21 - R_{N...O})$	
		$R_{NH...H}$	Å	$\Delta\nu = 1.05 \cdot 10^3 (3.38 - R_{N...H})$	
		$R_{CH_2...O}$	Å	$\Delta\nu = 0.89 \cdot 10^2 (3.42 - R_{CH_2...O})$	
6	Elongation of the covalent bond	Δr_{OH}	Å	$\Delta r_{OH} = 5.3 \cdot 10^2 \cdot \Delta\nu$	

* ν^0 for $R_{OH...O} = 3700 \text{ cm}^{-1}$; ν^0 for $R_{OH...N} = 3400 \text{ cm}^{-1}$ [2, 6]; ν^0 for $R_{NH...O} = 3550 \text{ cm}^{-1}$; ν^0 for $R_{NH...H} = 3300 \text{ cm}^{-1}$ [1, 2, 5, 6]; ν^0 for $R_{CH_2...O} = 3200 \text{ cm}^{-1}$ [1, 2, 5, 6].

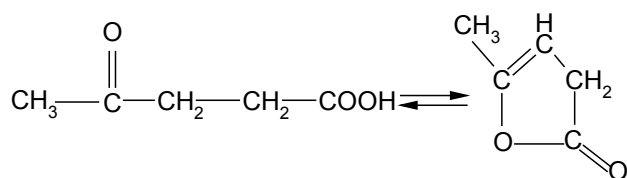
Table 3. Characteristic frequencies of absorption of the groups of atoms of fatty acids [2–8]

Vibrational frequency ν , cm^{-1}			$\Delta\nu^*$, cm^{-1}	Assignment of vibrations
[7, 9, 13]	Stearic acid	Oleic acid		
3010	–	3008	–2;	$\nu = \text{CH}$ – in $\text{RCH}=\text{CHR}'(\text{trans})$; $\text{CH}_3(\nu_{\text{as}})$
2962	2956	–	–6	
2925	–	2918	–7;	$\nu_{\text{as}}^* \text{CH}_2$
	2911	–	–14	
2853	–	2844	–9;	$\nu_s^{**} \text{CH}_3$; $\nu_s \text{CH}_2$
	2843	–	–10	
2726	2686	2883	–40;	–OH in COOH (bonded)
			–43	
1720	1698	1705	–22;	$\nu \text{C}=\text{O}$ in COOH
			–12	
1467	1471	1472	4; 5;	$\delta_{\text{as}}^* \text{CH}_3$; sciss. CH_2 in the chain $\delta_{\text{as}} \text{CH}_2$ (scissoring); δ_{as} , if CH_2 is with $\text{C}=\text{O}$; CH in $-\text{C}=\text{CH}$
1421	1431	1433	10; 12;	
1400	1413	1413	13	
			4;	
1375	1379	1382	7	$\delta_s \text{CH}_3$; $\delta -\text{O}-\text{H}$
1300	1312	1316	12;	CH_2 wagging; –COOH in dimers
			16	
1245–1180	1252–1182	1266–1192	Group of bands	CH_3 ; CH_2 rocking stretching with an unbranched chain; with COOH end groups
1125–1120	1104	1104	–21;	νOH in C–O groups with five or six-membered cycles
			–21	
935	944; 886	953; 895	9;	Wide bands nonplanar δ vibrations of OH in COOH
			18	
750; 720	817; 737	817; 744	67; 67	$(\text{CH}_2)_n$ rocking stretching
–	608	612		δCH in cycles

* ν , δ are stretching and deformation vibrations respectively;

** as, s are asymmetrical and symmetrical stretching vibrations respectively.

the interpretation of the spectra difficult, has a positive effect. For example, it allows determining the form (open or lactone) of levulinic acid, if the spectrum includes the bands 3260, 2970, 2930, 2870, 2850, 1720, 1705, and 900 cm^{-1} [7].



$\text{C}=\text{O}$ peaks are characteristic for the open structure in ketonic (1720 cm^{-1}) and carboxylic (1705 cm^{-1}) acid; 3260 cm^{-1} (νOH), and 900 cm^{-1} (δOH). Frequencies 2970, 2930 cm^{-1} and 2870, 2850 cm^{-1} are determined to be stretching vibrations of methyl CH_3 and methylene CH_2 groups. The cyclic structure should be demonstrated by

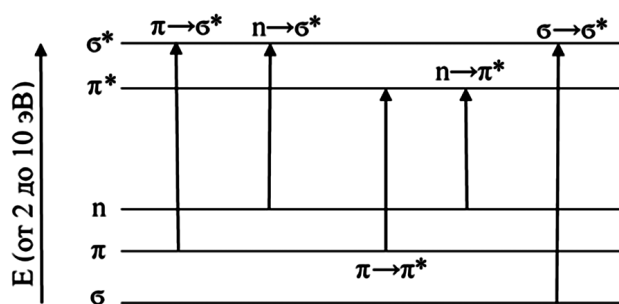
the bands $\text{C}=\text{C}$ and lactone $\text{C}=\text{O}$ (1800–1785 cm^{-1} and 1735 cm^{-1} respectively) [2–5].

It is interesting that there are clear groups of absorption bands at 1433–1104 cm^{-1} (Table 4, scheme 1). This characterises the transition from planar conformation (scissoring – and rocking γ_r stretching) in hydrophobic tails to the nonplanar conformation (wagging γ_w and twisting γ_t stretching) caused by the mixture of the stretching vibrations ν_s and ν_{as} of OH polar groups with γ_r and γ_t deformation vibrations of CH_2 groups of the methylene chain [3, 5, 8]. Each of these transitions is accompanied by the absorption of a photon of a certain value. The $\sigma \rightarrow \sigma^*$ transition requires the most energy (scheme 1). The corresponding absorption bands are observed in the vacuum UV region ($\lambda < 200 \text{ nm}$).

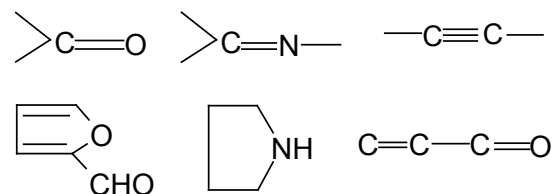
Table 4. Characteristic frequencies of absorption of the groups of atoms of carboxylic acids [2–8]

[2–8]	Vibrational frequency ν , cm^{-1}						Assignment of vibrations
	Acetic acid	$\Delta\nu$, cm^{-1}	Stearic acid	$\Delta\nu$, cm^{-1}	Oleic acid	$\Delta\nu$, cm^{-1}	
3550			3583	-33			Free OH group bonded by 2 H-bonds (νCH_2); bonded by 3 H-bonds (νCH_3); bonded by OH in dimers (νCH_2); OH-bonded in dimers
3005	3028	-23	3125	-120	3052	-47	
2925	2925	0	2927	-2	2918	+7	
2853	2857	+4	2843	-10	2844	-9	
2726	2686	-40	2726	0	2683	-43	
1720	1700	-20	1680	-40	1692	-28	$\nu \text{C=O}$ in COOH; $\nu_{as} \text{COO}^-$; $\nu_{as} \text{COO}^-$
-	-	-	1600	-	1606	-	
1525	-	-	1525	0	1551	+26	
1430	1466	+33	1480	+50	1472	+42	$\nu_s \text{COO}^-$, ΔCH_2 scissoring scissoring in chains, if CH_2 is next to C=O or C-CH=CH_2
	1438	+8	1400	-30	1435	+5	
1375*	1350	+25	1379	-4	1380	-5	δCH_3 in the dimeric ring; γ_w wagging; -COOH in dimers; $Q = \nu \text{C-O}$; δCH_2 twisting in the dimeric ring $\gamma_r \text{CH}_2$ with an unbranched chain with end COOH
1300	1300	0	1320	-20	1305	-5	
1245	1266	-21	1263	-18	1238	+7	
1192	1192	0	1195	-3	1192	0	νOH in C-OH groups with five or six-membered cycles
1125	1104	-21	1104	-21	1104	-21	
940	940	0	926	+14	953	-13	Any OH group; γ_t twisting in the dimeric ring; planar stretching vibrations $Q(\text{C-C}) = \nu_s$ rocking; $\gamma_r \text{CH}_2$ of the methylene chain
750	744	+6	728	+22	756	-6	γOCO ; γCCC ; γOCC in dimeric rings of carboxylic acids
646	642	+4	636	+10	638	+8	

Designations for the vibrations:

 $Q = \nu_s$; ν_{as} – symmetric and asymmetric deformation vibrations; δ_s ; δ_{as} – deformation scissoring, symmetric and asymmetric stretching; γ_w ; γ_t ; γ_r – wagging, twisting, and rocking deformation vibrations; Δ – deformation vibrations of the skeleton of the chain; $\nu \text{C=O} = q = Q = \gamma \text{OCO}$; γOCC ; γCCC – vibrations in the dimeric ring; γOCC ; γCCC – nonplanar vibrations in the stretched chain*transition from the planar to the nonplanar conformation due to the shift of νOH polar vibration with γ_t and γ_r in the methylene chain of the $-\text{CH}_2-$ groups

Scheme 1

region indicate the π and n electronic states. The following functional groups

The absorption of light in the visible region and absorption of the UV light in the near UV

are called chromophoric and cause the absorption in the UV region [2–6].

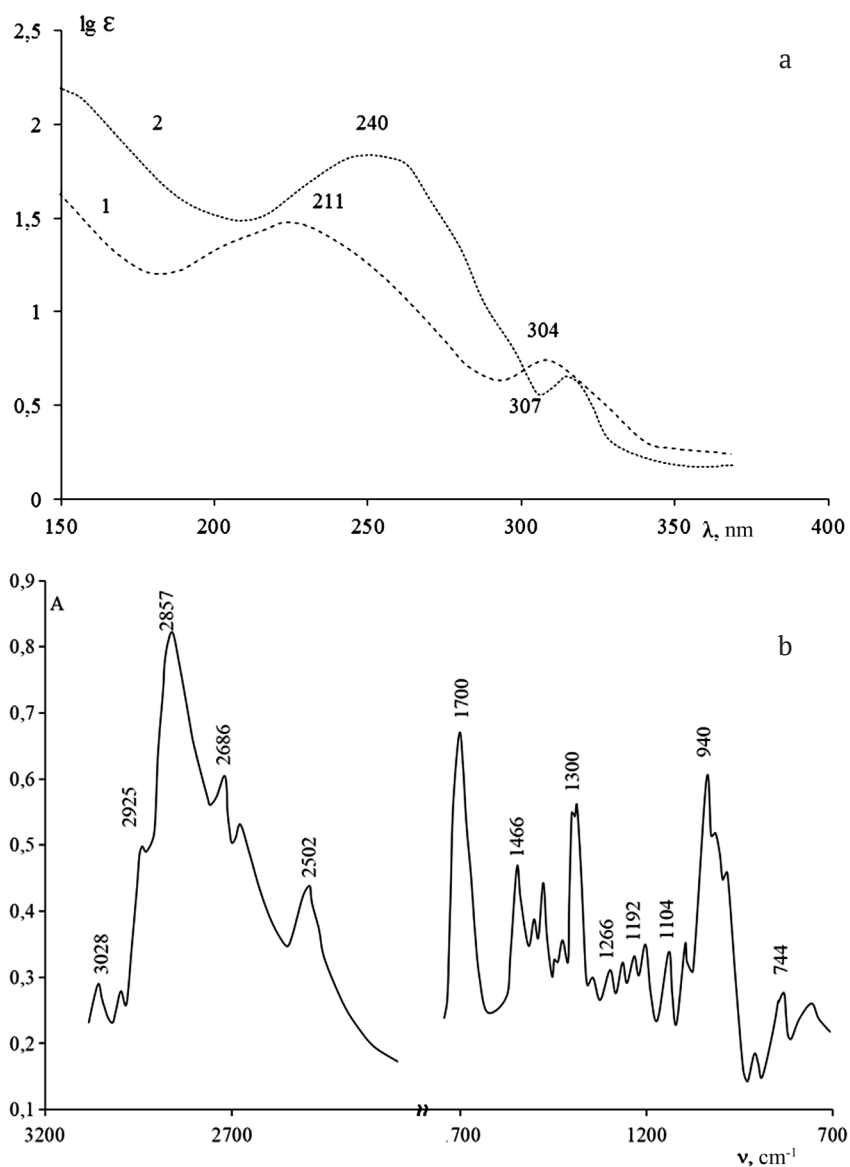
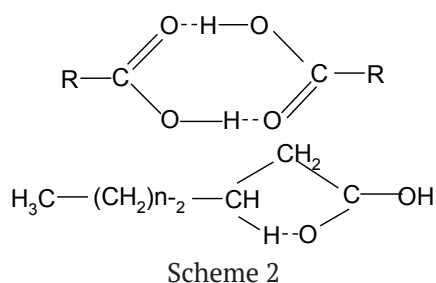
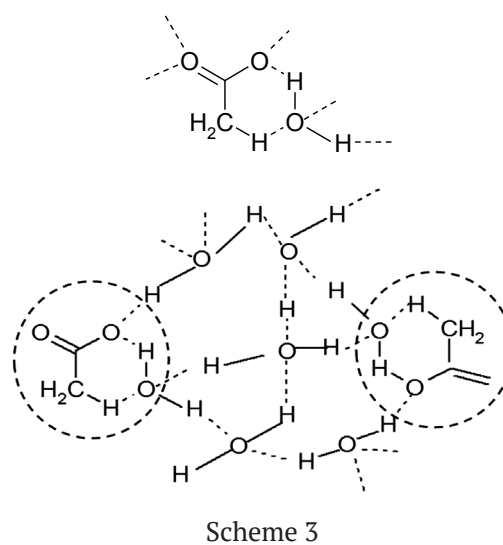


Fig. 3. UV (a) and IR spectra (b) of acetic (1) and oleic acid (2)

It should be noted that such transitions are one of the causes of the formation of dimers by $-\text{COOH}$ end groups:



as well as the formation of five-membered cycles due to the appearance of hydrogen bonds between CH_2 methyl groups of hydrophobic chains and oxygen in carboxylic groups [2, 3, 11]:



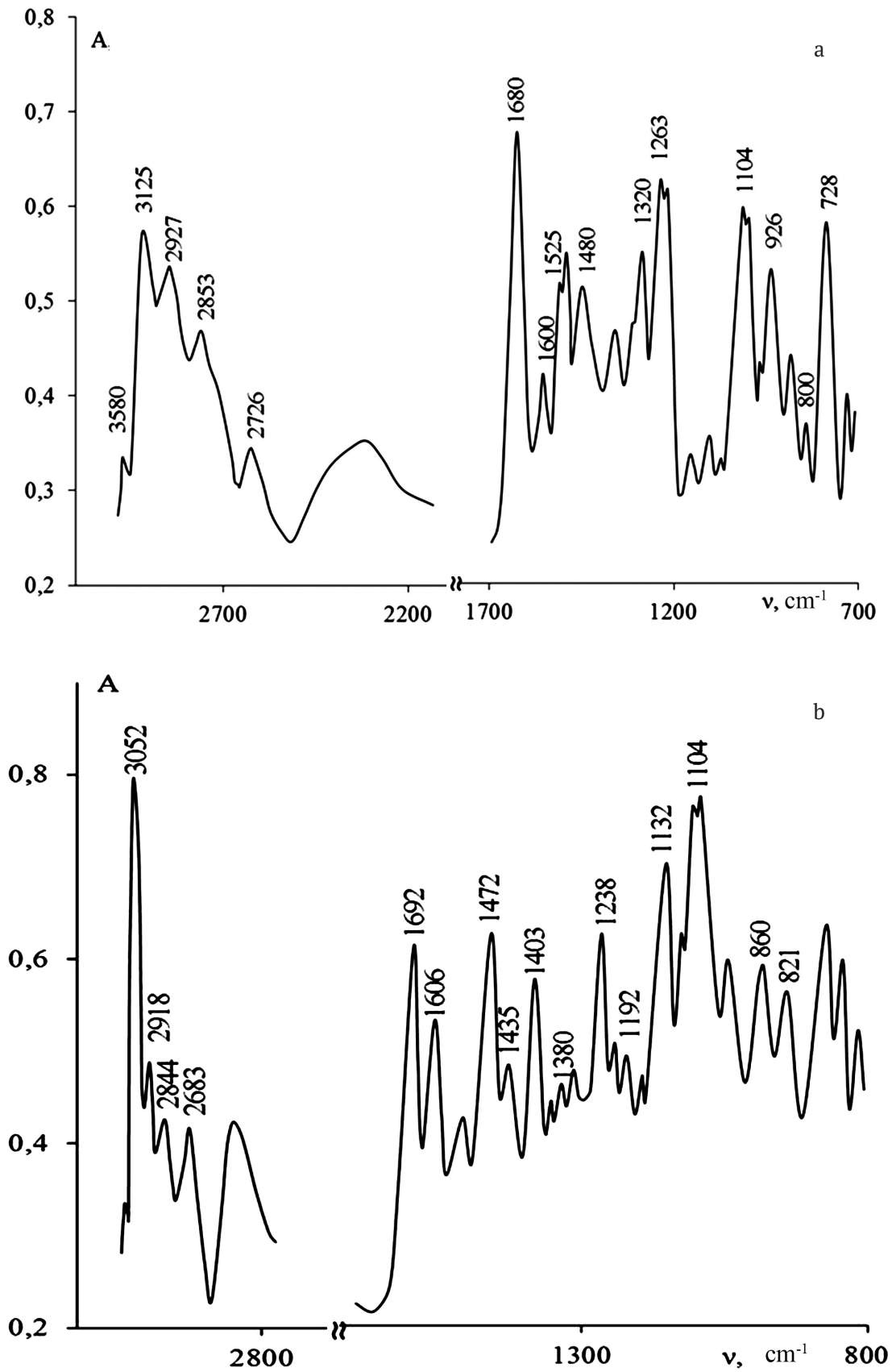
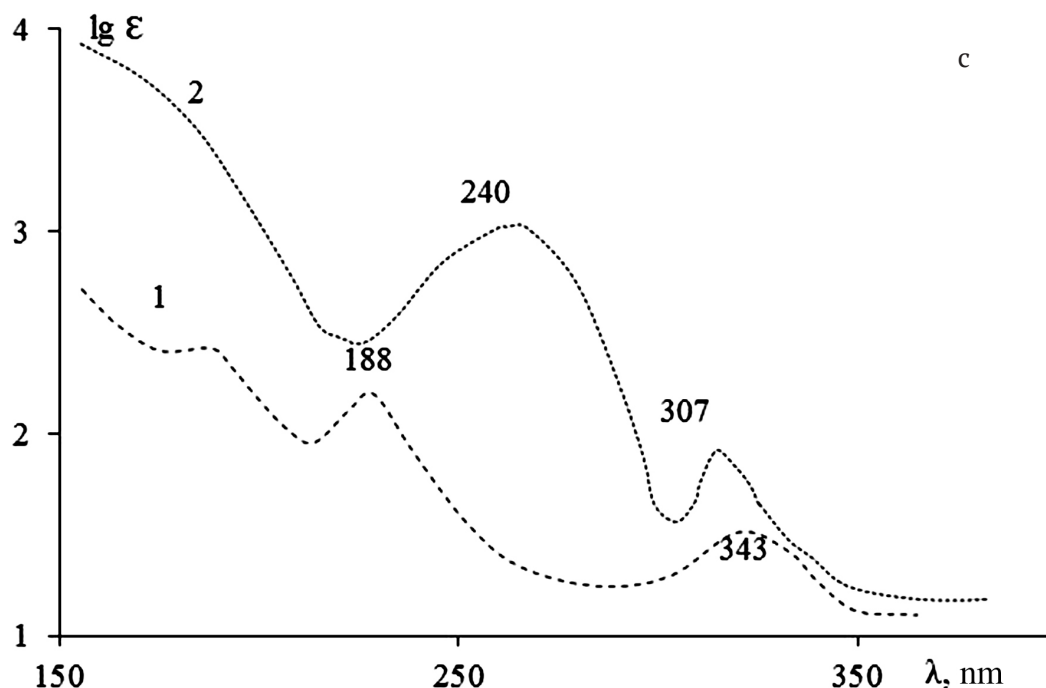


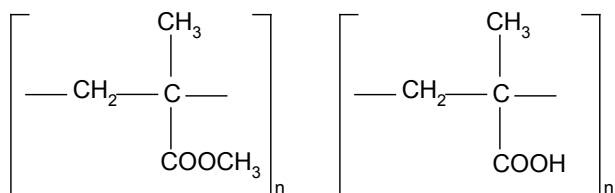
Fig. 4. UV and IR spectra of stearic (a) and oleic (b) acids. UV spectra of stearic (1) and oleic (2) acids (c)



End of Fig. 4

This is demonstrated by the peaks 1192, 1104, 940, 744, and 638 cm^{-1} . Intense bands at 182 nm ($n \rightarrow \sigma^*$ transitions), 240 nm ($\pi \rightarrow \pi^*$ transitions), and 305–343 ($n \rightarrow \pi$ transitions) in the UV spectra of carboxylic acids (Fig. 3a, 4b) indicate the possibility of the formation of cyclic structures in the solutions and the mentioned bands prove the accuracy of the description of their structure (scheme 2 and 3) based on the results of the IR spectroscopy.

Besides experiments with monomers, UV and IR spectroscopy can be used in experiments with polymers containing carboxylic groups [3–6]. The most interesting examples of this group of polymers are poly(methyl methacrylate) and poly(methacrylic acid):



In the IR spectra of poly(methacrylic acid), the bands at 1750 and 1700 cm^{-1} are assigned to the vibrations of carbonyl in monomer and dimer groups, and the bands at 3540 and

2650 cm^{-1} are assigned to the vibrations of free and bonded hydroxyl groups [3, 5, 6]. Peaks 1490 and 1460 cm^{-1} indicate the presence of σ_s and σ_{as} (deformation vibrations) of the methyl group $=\text{CH}_2$. In the spectra of copolymers of methacrylic acid with acrylonitrile, a shift in the location of the bands is observed at 1263 and 1167 cm^{-1} , caused by the vibrations of the C–O-bond [4, 5, 11].

The IR spectra of syndiotactic poly(methyl methacrylate) reveal a group of bands in the 3460–2835 cm^{-1} region, caused by the vibrations of free and bonded hydroxyl groups [3, 5, 6, 9]. It should be noted that the peaks 2948–2835 cm^{-1} also characterise the vibrations of methyl and methylene groups [3, 6, 7] (Table 6). The variability of the bands at 1270, 1240, 1190, 1172, and 1163 cm^{-1} is accounted for by intramolecular interactions, since the multiplet is also observed in the spectrum of diluted solutions, i.e. without intermolecular interaction.

Similar to the monomers of carboxylic acids, poly(methyl methacrylate) demonstrates clear peaks at 1430–910 cm^{-1} , indicating the transition from planar conformation (scissoring ρ_s and rocking γ_r) in hydrophobic tails to the nonplanar conformation (wagging γ_w and twisting γ_t) caused by the mixture of the stretching vibrations

Table 5. Assignment of close absorption bands of -COOH- and -CH₂ groups in the IR spectra of carboxylic acids

Vibrations of COOH groups ν , cm ⁻¹	Vibrations of CH ₂ groups ν , cm ⁻¹
3580 – free OH	
3028 – OH with two H-bonds	3008 =CH in RCH=CHR' (trans)*
2962 – OH with three H-bonds	2962 ν_{as} CH ₂
2843 – OH in dimers	2843 ν_s CH ₂
1700 – C=O in COOH ⁻ groups	
1525 – C=O in COO ⁻ groups	1480 Δ CH ₂ next to C=O
1379 – C-O in dimers	1375 σ C ⁺ H ₃ in the dimeric ring
1300 – COOH in dimers	1300 γ_w CH ₂ wagging stretching in the ring
1245 – C-OH in the dimeric ring	1245 γ_t twisting in the ring
1104 – C-OH in five-membered cycles	1122 γ_r rocking next to COOH
944 – OH groups in COOH	960 $\gamma_w; \gamma_t; \gamma_r$ in the dimeric ring
737 – OCC in the dimeric ring	638 γ OCO; γ CCO in dimers with COOH

Assignment of vibrations:

$Q = \nu_s; \nu_{as}$ – symmetric and asymmetric stretching;

$\phi = \rho = \sigma_s; \sigma_{as}$ – deformation scissoring, symmetric and asymmetric stretching;

$\gamma_w; \gamma_t; \gamma_r$ – wagging, twisting, and rocking stretching;

Δ – deformation vibrations of the skeleton of the chain;

ν C=O= q =QC=O; γ OCO; γ OCC; γ CCC –vibrations in the dimeric ring; nonplanar vibrations in the completely stretched chain.

ν_s and ν_{as} of the polar groups with γ_r - and γ_t deformation vibrations of CH₂ groups of the methylene chain (Fig 5, Table 6) [3, 5, 8, 9]. Thus, dimeric rings are formed in polyacrylates and poly(methyl methacrylates) due to intramolecular interactions. The transition from the planar to the nonplanar conformation is also observed in the polymer chain.

Microscopic and microphotographic methods of studying polymers with carboxyl functional groups are supplementary methods used to visualise the process of swelling and contraction of carboxyl sorbents during their contact with aqueous solutions [13, 14]. The objects of our study were carboxylic cationites CB-2×2 and CB-4 (scheme 7):

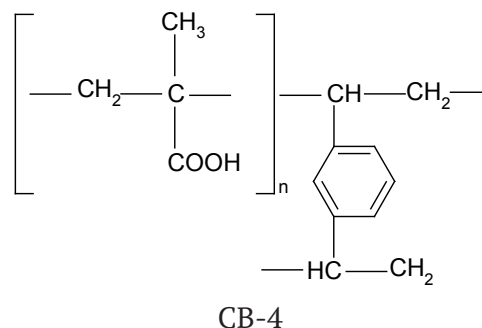
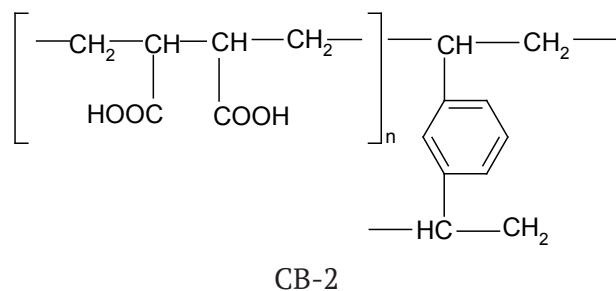


Fig. 5b demonstrates that the IR spectra of the sorbents are close to the IR spectra of poly(methyl methacrylates) (Fig. 5a), namely in the vibration areas of the carboxylic groups, formation of dimers, and intramolecular H-bonds. There is a difference in the vibration areas characterising the presence of divinyl benzene: 1310, 1053, 922, 896, and 700 cm⁻¹.

The microscopic study of the swelling of certain beads of carboxylic cationites, the kinetic curves of volume change, and the swelling diagrams demonstrated that slightly acidic ion exchangers have the minimal volume in the H form as compared to the salt forms (Fig. 6). This effect is accounted for by the formation of associates presented as dimer cycles with methyl-CH₂ groups

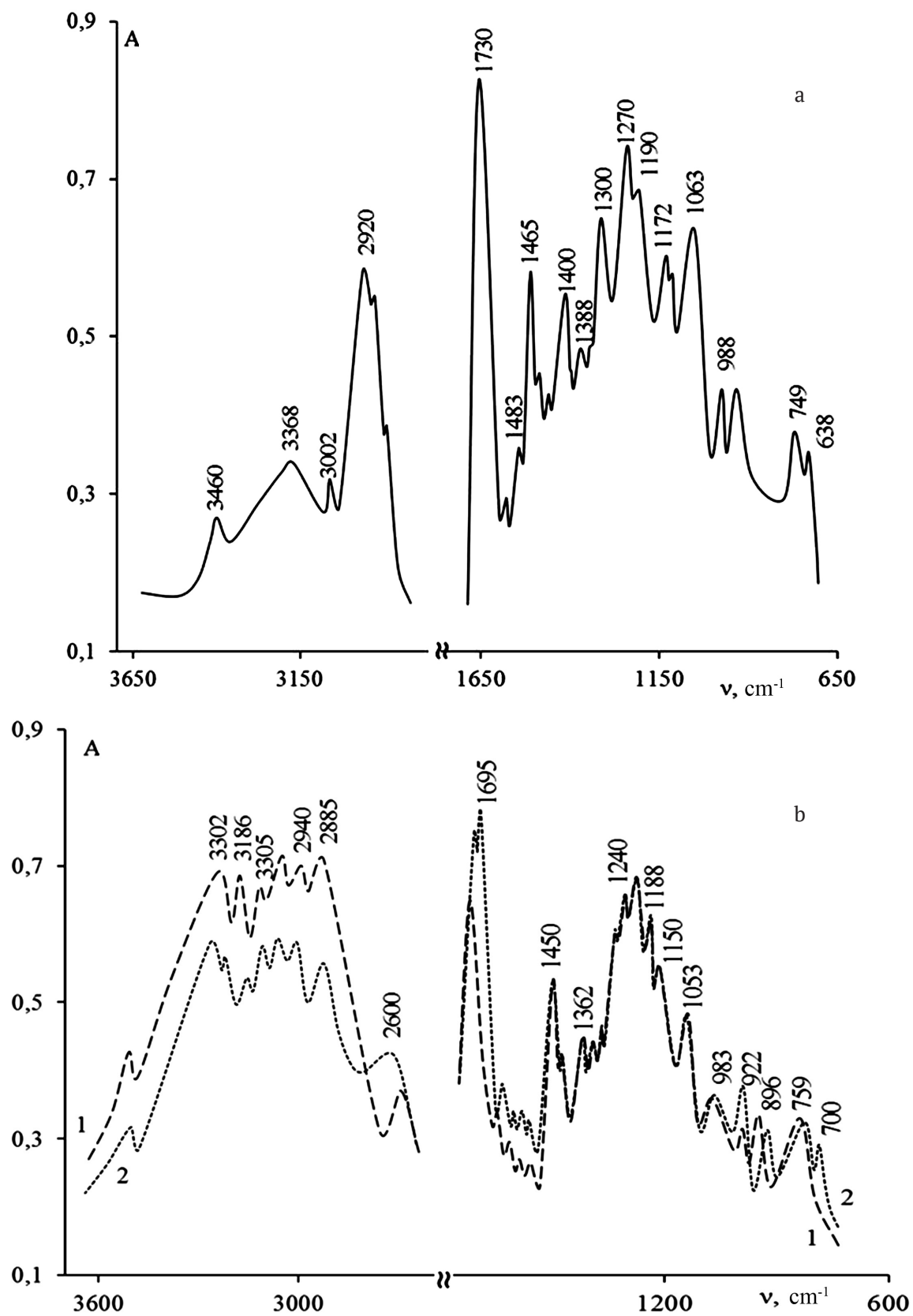


Fig. 5. IR spectra of poly(methyl methacrylate) (5a) CB-2 and CB-4 (5b): 1 – CB-2; 2 – CB-4

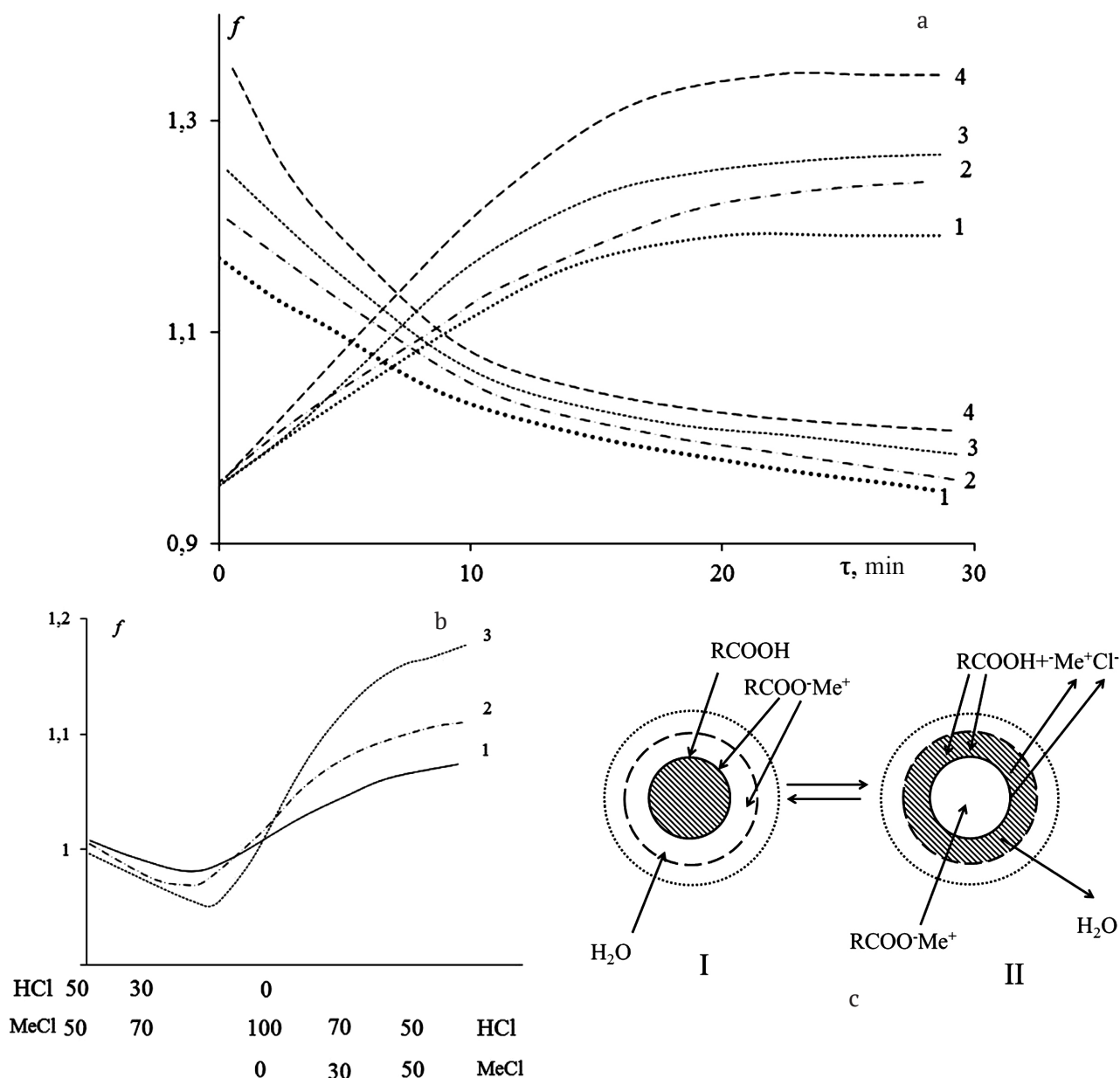
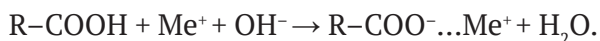


Fig. 6. The swelling curves of the CB-2 cationite (a) and the bead volume change of the cation exchanger CB-4 (b): 1 – R–COOH; 2 – R–COOLi; 3 – R–COONa; 4 – R–COOK $f = V_\tau / V_n$, where V_τ, V_n are the bead volume at the moment τ and initial bead volume in the H form respectively. A scheme of the exchange processes RCOOH+MeOH (I) and RCOOMe+HCl (II) (c)

and as intramolecular H-bonds formed due to the $\pi \rightarrow \pi^*$ transitions in benzol cycles [1–6,15–21].

When the reaction takes place in the surface layers of the cationite bead, the carboxylic groups are ionised through the reaction:



During this reaction, the metal ions neutralise the negative charge R–COO[−]. As a result, two shells are formed in the bead of the carboxylic cationite: the external shell R–COO[−]...Me⁺ and

the internal shell R–COOH (Fig. 6c). The exchange reaction is accompanied by the swelling of the bead. The amount of water transported by the ions during the reaction is not sufficient for the hydration of the cationite in salt form, which results in further introduction of water from the solution into the sorbent (Fig. 6c) [15–19].

During the R–COO[−] + Me⁺ + H⁺ + Cl[−] → R–COOH...Me⁺ + Cl[−] transition, in the first stages of the exchange process the –COO[−] groups located on the bead’s surface absorb H⁺ ions from the solution

Table 6. Poly(methyl methacrylate) IR spectrum

Wave number, cm ⁻¹	Vibrations
3460	Free OH groups; 2 (ν C=O)
3368	Bonded OH groups; ν _{as} CH ₂ + ν _s (CH ₃ -O)
3002	ν _s (CH ₃ -O)+ ν _{as} (L-CH ₃)+ ν _s (L-CH ₃) + ν _{as} (CH ₂)
2920	Combination tone bonded with CH ₃ in an ester group
2835	Id.
1730	ν C=O in COO ⁻ groups
1483	δ _{as} (CH ₃ -O); Δ CH ₂ next to C=O
1465*	σ _{as} (CH ₃ -O); Δ CH ₂ scissoring stretching next to C-CH=CH ₂
1452 1438	δ (CH ₂); σ _s (CH ₃ -O);
1388	σ _s (CH ₃ -O); σ ⁺ (CH ₂) in the dimeric ring
1300	γ _w wagging; -COOH in dimers
1270 1260	ν _{as} (C-C-O); Q = ν(C-O); σCH ₂ = γ _t (CH ₂) in the dimeric ring
1190	γ _r (CH ₂) rocking; νC-C)+ σ(CH) groups
1172	σ _s in esters (intramolecular)
1150	ν(C-C) mixed with deformation vibrations σCH
1063	To же
988 967	ν _s (C-O-C)= γ _r (CH ₃ -O)+ γ _r (L-CH ₃)+γ _t in the ring; γ _r (L-CH ₃) mixed with γ _t in the dimeric ring;
749 638	γ _r (CH ₂) mixed with ν(C-C)+ σ (OCO)+ ν(OCC) in the dimeric rings with COOH groups

* ρ, γ_w; γ_t; γ_r – scissoring, wagging, rocking, and twisting vibrations;
Δ – deformation vibrations of the skeleton of the chain.

and become non-dissociated RCOOH groups. Thus, the bead is once more divided into two zones (Fig. 6c). Then the H⁺ ions diffuse through the outer shell towards the boundary and replace the metal ions which are, in turn, eliminated from the cationite bead. The process can be described as interdiffusion between the hydroxonium ions and metal ions through the layer of the cationite in the H form. Processes (II) and (I) are accompanied by contraction and swelling respectively (Fig. 6c) as well as by the migration of the solvent either from or to the sorbent phase. Both processes have a clear boundary visible through a microscope. Processes I and II are indirectly proved by the calculation of the elongation of covalent bonds r (A–H) as the function of $R(A...B)$ for bonds $R(O...O)$ $R(O...N)$; $R(N...O)$; $R(N...N)$, and $R(CH_2...O)$, according to the results of the IR spectroscopy (Fig. 7). Each curve was obtained by shifting curve 1 (Fig. 7) horizontally according to the van der Waals radii

$$[R_{eq}(O...O) = R_{exp}(A...B) + 2r_v(O) - r_v(A) - r_v(B)]; \quad (2)$$

$$[r_{substr}(A-H) = r_{eq}(O-H) + r_c(A) - r_c(O)],$$

where r_v is the van der Waals radius, r_c is the covalent radius.

The vertical shift is performed taking into account the covalent radii. Taking into account the processes in (2), we obtained an equation for calculating $R(CH_2...O)$, based on the value of the band shift $\Delta\nu$:

$$\Delta\nu^\circ \text{ for } R(CH_2...O) = 3200 \text{ cm}^{-1};$$

$$\Delta\nu = 0.89 \cdot 10^3 (3.42 - R_{CH_2...O}).$$

Similar interactions accompanied by the formation of H-bonds between hydrophobic CH groups and hydrophilic C=O, N–H, C≡H (in acetylene), and S–H groups were described earlier in [2, 4], which makes it necessary to explain the term “hydrophobic interactions”. The term “hydrophobic interactions” was introduced to describe the joint effect of the London dispersion

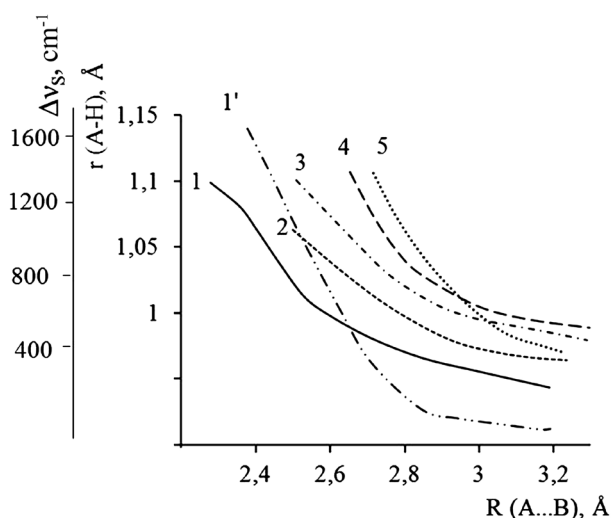


Fig. 7. The values of the covalent bonds $r(\text{A-H})$ calculated as a function of $R(\text{A...B})$ for the associates 1 – $R(\text{O...O})$; 2 – $R(\text{O...N})$; 3 – $R(\text{N...O})$; 4 – $R(\text{N...N})$; 5 – $R(\text{CH}_2\text{...O})$. Curves 1' represent the dependence between $R(\text{O...O})$ and $\Delta\nu_s$

forces (forces resulting from the formation of the instantaneous dipoles), the van der Waals forces (orientation, induction, and steric repulsion), and hydrogen bonds on the processes taking place in aqueous solutions [1, 2, 8]. The nature of these interactions is similar to that of other intermolecular (noncovalent) interactions, although in some cases they are characterised by small enthalpy changes [1, 2, 4], calculated based on the values of $\Delta\nu$ (curve 1' in Fig. 7). It is noteworthy that the shape of the curves showing the dependencies for $[R(\text{O...O}) - r(\text{A-H})]$ and $[R(\text{O...O}) - \Delta\nu_s]$, are symbatic. This proves the correctness of the methods used and accuracy of the calculations presented in this article.

4. Conclusions

The article described the method and analysed the results of the combined use of UV-vis and IR spectroscopy, as well as the microscopic and microphotographic studies of intermolecular interactions and hydration properties of acetic, stearic, and oleic acids, and carboxylated cationites CB-2 and CB-4 in the exchange reactions $R\text{-COOH} + \text{NaOH} \leftrightarrow R\text{-COO}^- + \text{Na}^+ + \text{H}_2\text{O}$. The energy of the hydrogen bond (E_{H}), the enthalpy (ΔH), the force constant of the H-bond (K_{H}) and OH-bond (K_{OH}), and the elongation of the covalent bond (Δr_{OH}) were calculated based on the results of the IR spectroscopy for intermolecular interactions of

carboxylic acids in solutions. The article suggested a method for calculating the length of the H-bond and $R_{\text{CH}_2\text{...O}}$ between the donor (CH_2 group) of the non-polar chains of fatty acids and the acceptor (O- in COOH groups) resulting from the formation of cyclic structures in carboxylic acids.

The microscopic method was used to obtain the swelling/contraction curves for the beads of the cationites CB-2 and CB-4. The first description of the formation of two boundaries (shells) in the beads of carboxylic cationites during the ion exchange reaction $R\text{-COOH} + \text{NaOH} \leftrightarrow R\text{-COO}^- + \text{Na}^+ + \text{H}_2\text{O}$ was provided.

The study demonstrated that the combined use of the UV, IR, and visible spectroscopy is the most effective for studying the intermolecular bonds and hydration properties in solutions and polymers.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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