

Direct Measurement of H⁺ Activity inside Cross-Linked Functional Polymers Using Nitroxide Spin Probes

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Received: August 1, 2002; In Final Form: September 29, 2003

The lack of a direct method for measuring activity inside ion-exchange resins was the main obstacle for strict thermodynamic investigations of such objects during the past decades. This paper proposes a method for the activity determination. The method is based on exploring the ESR response of stable nitroxide radicals introduced as probes into the resin phase. This method allows for the measurement of the hydrogen ion activity inside cross-linked polyelectrolytes. In addition to the method verification, the paper reports its application to the determination of ionization constants of functional groups and to the investigation of the hydrolysis and sorption of copper on different types of sorbents (weak cation and anion-exchange resins, functionalized and nonfunctionalized polymeric films). The applicability of known thermodynamic approaches developed for the investigation of micelles and biomembranes with nitroxide radicals is discussed. The paper also includes a critical analysis of the potentiometric method conventionally used for the investigation of ion-exchange equilibria.

1. Introduction

Ion-exchange resins are widely used in different areas of human activity. However, there is no indisputable thermodynamic procedure for the description of ion-exchange equilibria. One of the main reasons is the lack of direct methods for the investigation of the resin phase; every work on the thermodynamics of ion exchange encounters the problem of determining the inter-resin activity (the activity of ions in the internal solution of the resin). Conventional approaches are based on a measurement of the compound's activity in the solution surrounding the resin and concentrations of the compound in the resin phase. The thermodynamic values are estimated by applying some assumptions and simplifications. Even the simplest equilibrium, such as the ionization of functional groups in the internal solution, cannot be directly monitored in most cases.

1.1. Objectives of the Work. The present work aims to establish a method for the direct measurement of activity in the resin phase. The approach is based on measuring the ESR response of nitroxide radicals introduced into the solution contained in micropores of ion-exchange resins. Thus, the radicals serve as internal probes, providing information that cannot be obtained with other methods. The work targets

- verifying that nitroxide spin probes can provide a direct means to measure activity in phase of different ion-exchange resins;

- a critical analysis of the applicability of the theoretical approaches developed for the application of nitroxide radicals to systems other than ion-exchange resins;

- application of the method to a direct investigation of the acid–base properties of different functional groups bound to different cross-linked polymeric networks;

- comparison of the experimentally obtained results with the tendencies found by the conventional potentiometric studies.

1.2. Conventional Method for the Thermodynamic Investigation of Ion-Exchange Resins. Potentiometric titration performed in batch or column reactors is generally recognized as the only method to estimate the ionization of the resin's functional groups.^{1–5} A titration curve is plotted using pH values measured in the solution in contact with the ion exchanger. An “apparent” ionization constant of functional groups ($p\tilde{K}_a$) is calculated using equation 1

$$pH = p\tilde{K}_a + m \cdot \log \frac{\alpha}{1 - \alpha} \quad (1)$$

where α is the degree of ionization of the functional groups⁴² and m is an empirical coefficient reflecting the redistribution of charge along the polymeric network.⁴³ This simple approach is based on a hypothesis of an equality of pH in the equilibrium solution surrounding the resin and in the internal solution of the resin grains. The obtained values of $p\tilde{K}_a$ are used to characterize the resin acidity (cation exchangers) or basicity (anion exchangers).

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An experimental examination of the model described by eq 1 reveals a high sensitivity of pK_a to pH and to the composition of the solution. Such sensitivity suggests that the physicochemical properties of functional groups depend on the inter-resin environment. The following observations were made by different researchers:^{1,6–9}

(i) An increase in the degree of neutralization⁴⁴ results in a decrease in the functional groups' acidity (cation exchangers) or basicity (anion exchangers).

(ii) A 10-fold increase in the ionic strength results in a 10-fold increase in pK_a values (cation exchangers).

(iii) Increasing the ion exchangers' degree of cross linking decreases the acidity of cation-exchange functional groups and the basicity of anion-exchange groups.

(iv) The introduction of a complexing agent inside the cation exchangers increases the acidity of the protonated functional groups.

Because the apparent constant pK_a depends on the chemical environment, it cannot be considered to be a thermodynamic characteristic, even with a high degree of approximation. Researchers have developed another model considering an ion-exchange reaction between H⁺ and a univalent metal ion instead of the neutralization process.^{10,11} The ion-exchange approach reduces (but does not eliminate) the divergence of experimentally obtainable parameters from the corresponding thermodynamic values. However, the ion-exchange constant must be determined for each pair of ions specifically, and K_a is as an intrinsic characteristic of the ion-exchange resin that describes acid–base properties of functional groups.

The difference between pK_a and the thermodynamic value results from the difference in properties between the inter-resin solution and the solution surrounding the resin grains. This difference can be caused by a structural anomaly of water contained in the polymer phase that was demonstrated in a number of publications.^{12–14} For example, the freezing point of the inter-resin water is significantly lower in comparison with that of free water. This anomaly can be explained by an alteration of the hydrogen bond structure that was confirmed by IR investigations.¹⁵ The high mobility of water molecules and the high rate of proton exchange between H⁺ ions of water and functional groups of the sorbent have been demonstrated by ¹H NMR spectroscopy.¹⁶ Hence, the difference between solution properties inside and outside the resin beads must not be ignored.

1.3. Direct Investigation of the Solution in Porous and Colloid Media. A number of attempts have been made to find molecular-sizes probes, which can help in the investigation of the peculiar properties of solutions contained in porous and colloid media. Fluorescent substances^{17,18} and stable pH-sensitive nitroxide radicals^{19–21} were successfully used to investigate micelles and biomembranes. An efficient approach to apply these probes was proposed by Fromherz¹⁸ and developed by Khramtsov et al.²⁰ According to this approach, the radical-protonation constant (pK_a^*)⁴⁵ is shifted because of the probe's incorporation into the porous medium. The activity of protons near the inter-phase boundary was assumed to be equal to the proton activity in the bulk water ($\overline{pH} = pH$).⁴⁶ The difference between the thermodynamic pK_a^* and its apparent value was described as the sum of two terms:

$$\Delta pK_a^* = \Delta pK_a^{*el} + \Delta pK_a^{*pol} \quad (2)$$

The first term (ΔpK_a^{*el}) depends on the electrostatic surface potential (for instance, the surface potential of the micelle)¹⁷

$$\Delta pK_a^{*el} = -\frac{F\Psi}{2.3RT} \quad (3)$$

where F is Faraday's constant, Ψ is the electrostatic surface potential, R is the general gas constant, and T is the temperature (K). The polarity-dependent term, ΔpK_a^{*pol} , of eq 2 depends on the nature of the probe. For example, if pH probes dissociate according to



then their polarity-induced shift ΔpK_a^{*pol} is described by a linear dependence

$$\Delta pK_a^{*pol} = b(\epsilon - \epsilon_{water}) \quad (5)$$

where b is an empirical coefficient ($b > 0$) and ϵ is the dielectric constant of the medium ($\epsilon \leq \epsilon_{water}$).²⁰ Dependence 5 is valid for the case of relatively small variations of ϵ .

The Fromherz approach is the most commonly used for the investigation of heterogeneous systems nowadays. However, an alternative approach was developed for colloidal systems.²² It is based on the general principle of constant pK_a^* (thermodynamic value) and states that the activity of the hydrogen ions varies in different phases (i.e., $\Delta pK_a^* = 0$ and $\overline{pH} \neq pH$). According to Hartley and Roe,²² the reason for the pH difference between solution and an inter-colloidal medium is an influence of the micelle electrical potential (Ψ), and the pH shift can be calculated using the expression

$$\Delta pH = \overline{pH} - pH = \frac{F\Psi}{2.3RT} \quad (6)$$

2. Experimental Section

2.1. Reagents and Resins. Commercial inorganic reagents ZnSO₄·7H₂O, Cd(NO₃)₂·4H₂O, CuSO₄·5H₂O, NaCl, NaOH, and HCl were of analytical quality and were used as obtained. Double-distilled water was used in all experiments.

The sorbents investigated are listed in Table 1. Their structures are presented in Figure 1. Commercially available granular sorbents were obtained from different manufacturers. Polystyrene carboxylic resins KB-2×3, KB-2×4, KB-2×6, KB-2×7P, and KB-2×20 were obtained from NIIPM, Moscow, Russia. Resin KRF-2p was obtained from NPO Biochemreactive, Olaine, Latvia. Cation exchanger KB-51 and anion exchanger AN-31 were obtained from Polymer, Nizhnij Tagil, Russia. Strong cation-exchange resin KU-2×4 was obtained from NPO Azot, Cherkasy, Ukraine.

The films were synthesized at the Voronezh Agricultural Academy, Russia by a known procedure.²³ A solution of polyamido acid in formamide was heat treated on a glass plate at 353 K for 1 h. The following 30-min heat treatment was performed at different temperatures. A carboxyl-free film (polymeric network only) was obtained at 573 K (film 0). A carboxyl-containing film (film 1) was obtained at 423 K. Different preparation temperatures were essential to obtain films with different chemical properties because the higher temperature initiates the reaction of decarboxylation. Their suggested structures are also presented in Figure 1. The films are chemically resistant. They are stable in acidic solutions (tests down to pH −0.8 were performed). However, they can be slowly dissolved in strong alkaline solutions.

The KB-2 cation exchangers have been studied in H⁺ and mixed H⁺–Na⁺, H⁺–Zn²⁺, H⁺–Cd²⁺, and H⁺–Cu²⁺ forms. Samples containing different amounts of the metal ions were

TABLE 1: Sorbents Investigated

sorbent	national name ^a	cross link	steric shape	synthesis method
KB-2×3	KB-2×3	3	gel,	cross linking of polyacrylic acid with divinylbenzene
KB-2×4	KB-2×4	4	grains with diameter 0.25 mm	
KB-2×6	KB-2×6	6		
KB-2×20	KB-2×20	20		
KB-2×7P	KB-2×7П	7	macroporous, grains with diameter 0.25 mm	cross linking of polyacrylic acid with divinylbenzene
KRF-2p	KPФ-2п	2	gel, grains with diameter 0.25 mm	phosphorylation of styrene-divinylbenzene matrix with phosphorus trichloride
KB-51	KB-51		gel, grains with diameter 0.25 mm	polycondensation of salicylic acid, phenol, and formaldehyde
KU-2×4	KY-2×4	4	gel, grains with diameter 0.25 mm	sulfonation of the styrene-divinylbenzene matrix
AN-31	AH-31		particles, undefined shape	polycondensation of polyethylenepolyamine with epichlorohydrin/ammonia oligomer described in the text
film 0			film, thickness 33 μm	described in the text
film 1			film, thickness 28 μm	

^a We present the national names of the resins to avoid confusion initiated by different spellings.

used. Ion exchangers KB-51 and KRF-2p as well as the film were studied in the H⁺ form. Ion exchangers KU-2×4 and AN-31 were used in H⁺–Na⁺ and OH[–] forms, correspondingly.

Stable pH-sensitive nitroxide radicals of imidazoline (**R1**, **R3**, **R5**) and imidazolidine (**R2**, **R4**, **R6**, **R7**) types (Table 2) were used. The laboratory-synthesized radicals were obtained from the Novosibirsky Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences.

2.2. Preparation of Mixed Ionic Forms of Ion-Exchange Resins. The sorption of Zn²⁺ and Cd²⁺ ions on the KB-2×3 resin was performed in batch experiments. The initial solution contained 0.07 M ZnSO₄ or 0.05 M Cd(NO₃)₂ at pH 6.0. The H⁺ form of the resin was used and is essential in obtaining an even distribution of the metal ions in the resin phase.²⁴ To avoid a pH decrease during the sorption process, the desorbed H⁺ ions were neutralized by the on-line addition of 1 M NaOH.

Cu²⁺ ions were sorbed on the mixed H⁺–Na⁺ form of the KB-2×4 resin. The Na⁺ fraction (\bar{x}_{Na}) in the initial samples varied: 10, 20, 40, and 60%. The value of \bar{x}_{Na} was defined as the ratio between the amount of sodium sorbed and the ion-exchange capacity of the resin. The resin capacity was determined by a method described earlier.²⁵ To obtain the targeted Na⁺ fraction, the samples were equilibrated with NaOH (pH control), rinsed with a small amount of water (to avoid hydrolysis of the sodium form), and air dried. Prior to the sorption experiments, the samples were swollen in an aqueous solution of NaNO₃ of ionic strength $\mu = 0.145$ and pH 3.86 (HCl). The internal pH was measured with the nitroxide radicals to monitor the possible hydrolysis of the sodium form. The initial solution contained different amounts of copper (from 0.0005 to 0.03 M CuSO₄) at pH 3.86. The ratio between the initial solution and the resin was 100 mL per 1 g of air-dried resin. This ratio was the same in all experiments. The sorption was performed at a constant ionic strength, $\mu = 0.145$. No on-line addition was made. Solutions of different concentrations were used to achieve different loading of the resin by the metals. The concentration of metal ions in solutions was determined by EDTA titration. The metal content in the phase of the ion exchanger was calculated from the concentration difference.

2.3. ESR Spectra Recording. The spectra were recorded by an automatic X-band ESR PS 100.X spectrometer (Advanced Analytical Instruments Inc., Belarus) at room temperature.

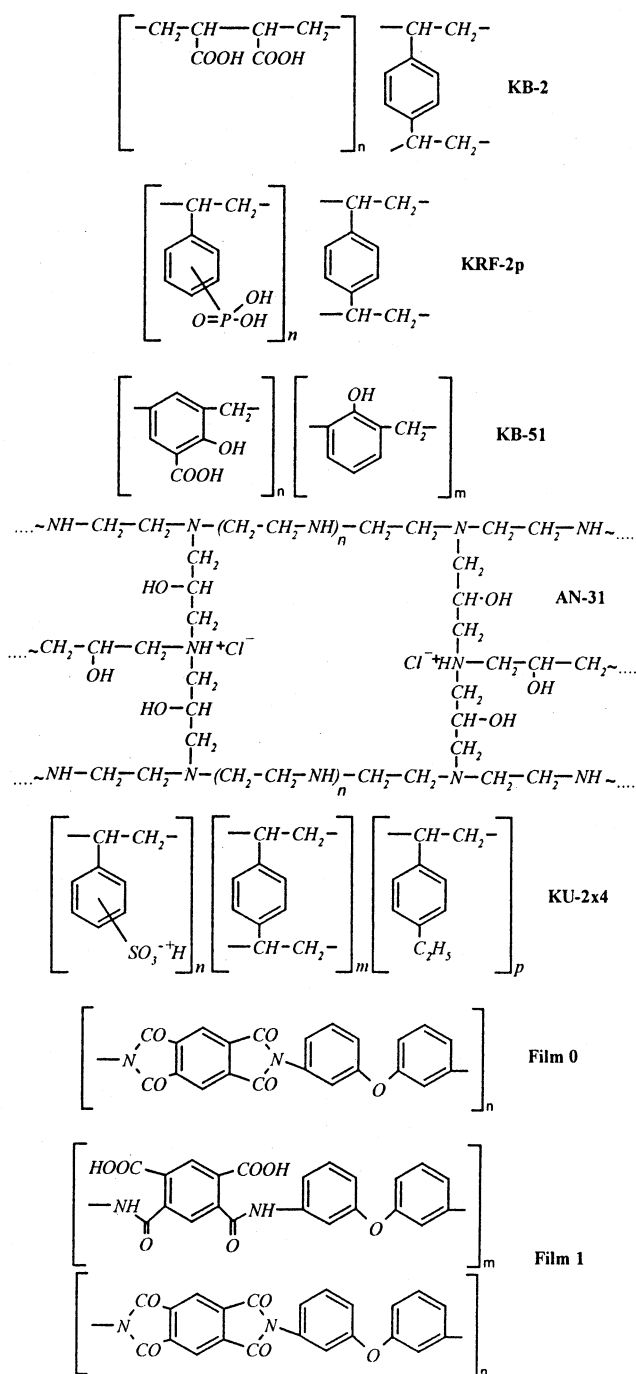


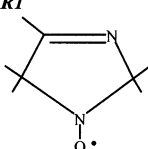
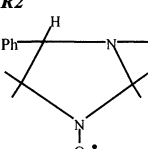
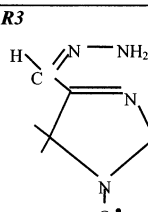
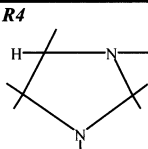
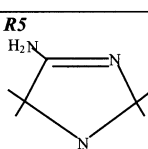
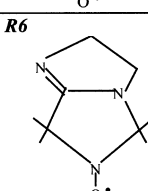
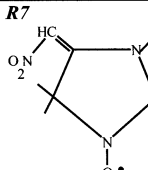
Figure 1. Chemical structures of used resins. The structure denoted as KB-2 is common to the family of resins: KB-2×3, KB-2×4, KB-2×6, KB-2×7P, and KB-2×20.

Quartz sample holders with an internal diameter of 3.5 mm were used for samples of resins. Solution spectra were recorded using quartz capillaries.

ESR spectra of 0.5 mM aqueous solutions of the nitroxide radicals were recorded after pH adjustment by HCl or NaOH. Dependencies of $a = f(\text{pH})$ were investigated for each radical. The values of a were obtained from the ESR spectra recorded for each solution by measuring the distance between the low- and central-field component of the triplet on the ESR spectra (Figure 2). This characteristic is a superposition of hyperfine interaction constants (a_N) characterizing protonated and deprotonated forms of the nitroxide radical.

To record ESR spectra of ion exchangers, the resins were separated from the solution by filtration. The solvent film was

TABLE 2: Used Nitroxide Radicals

radical	$pK_a^* \pm 0.1$	ESR characteristics in water			
		$g \pm 0.0001$		$a_N \pm 0.006 \text{ mT}$	
		R^*H^+	R^*	R^*H^+	R^*
R1 	1.3	2.0051	2.0049	1.505	1.575
R2 	3.0	2.0051	2.0048	1.485	1.610
R3 	3.55	2.0056	2.0054	1.518	1.581
R4 	4.7	2.0051	2.0048	1.485	1.590
R5 	6.1	2.0051	2.0048	1.515	1.595
R6 	7.2	2.0051	2.0049	1.532	1.566
R7 	7.8	2.0056	2.0055	1.529	1.575

removed from the surface by filter paper prior to recording of the spectrum. The spectra were recorded immediately after this procedure (i.e., no time was allowed for the resin to dry). As a result, the spectra reflected interactions in fully swollen (hydrated) ion-exchange resins.

ESR spectra of Cu^{2+} complexes in the resin phase were recorded at room temperature for both swollen (hydrated) and air-dried samples. The air-dried samples were obtained by drying the swollen samples for 3 days under ambient conditions.

2.4. Potentiometric Titration of the Resins. Potentiometric titration of the studied resins was performed by a conventional batch multisample technique.¹ The ratio between the amount of resin and the amount of solution was 1:100 g/mL. The ionic strength (μ) was 0.145, 1.0, and 3.5 in experiments with KB-2 cation exchangers; 0.05 with KB-51; and 0.145 with other sorbents. pH probes (nitroxide radicals) were introduced into the surrounding solution after achievement of equilibrium. The calculated concentration of the probe in the equilibrium solution

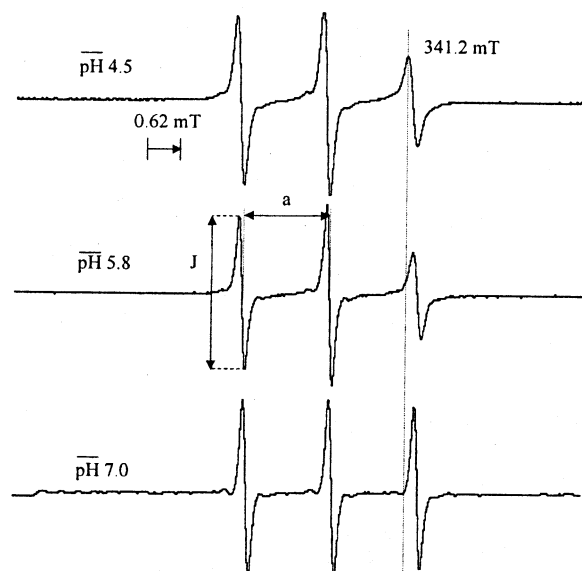


Figure 2. ESR spectra of nitroxide radical **R5** in cation-exchange resin KB-2 \times 4.

was 0.5 mM. ESR spectra of the samples were recorded to obtain a values. Potentiometric determinations of pH were also performed for equilibrium solutions.

2.5. Determination of pH in Solutions. pH was measured by a "1 in 3" combined electrode with a model 340 pH meter (Corning Inc., N. Y.). The accuracy of these measurements was within 0.01.

2.6. Experiments on the Retention of Nitroxide Radicals by Resins. Ten milligrams of the air-dried KB-2 \times 3 resin was swollen in a solution of radical **R5**. The resin was transferred to a quartz tube with an internal diameter of 1 mm. The tube was placed in the ESR spectrometer along the vertical axis of the resonator. A solution of NaNO₃ ($\mu = 1$, pH adjusted with HCl) was passed through the tube in 5-mL portions. Air was quickly blown through the tube after each portion to remove the liquid remaining between the resin beads. ESR spectra were recorded each time, and the height of the low-field component of the radical spectrum (J) was measured as shown in Figure 2.

3. Experimental Results

3.1. Character of the ESR Spectra of Nitroxide Radicals. Figure 2 shows experimental ESR spectra that are typical for nitroxide radicals incorporated in ion-exchange resins. A spectrum consists of three components reflecting an interaction between the unpaired electron and the unit nuclear spin of the nitrogen belonging to the NO group of the radical. The nitrogen included in the heterocycle of radicals used in this study is able to associate a proton.²⁶ The corresponding values of pK_a^* are presented in Table 2. The alteration of the ESR spectra in the pH range between 4.5 and 7 is caused by (i) the reaction of deprotonation that results in an altering of the radical spectral characteristics and (ii) the reduction of the rotation correlation time of the radical (τ_c). The correlation time depends on the mobility of the radical. It reflects interactions with surrounding structures, which result in the mobility being restrained. In some cases, this restraint was so significant that the ESR spectra became anisotropic. The shape of the spectra can be simulated (in most cases) by using a simple model of the diffusion rotation of a spherical nitroxide radical in an isotropic medium.^{27–29} This model was used in the present work for the τ_c determination and for an examination of the radicals' protonation when anisotropic spectra were obtained by direct ESR investigation.

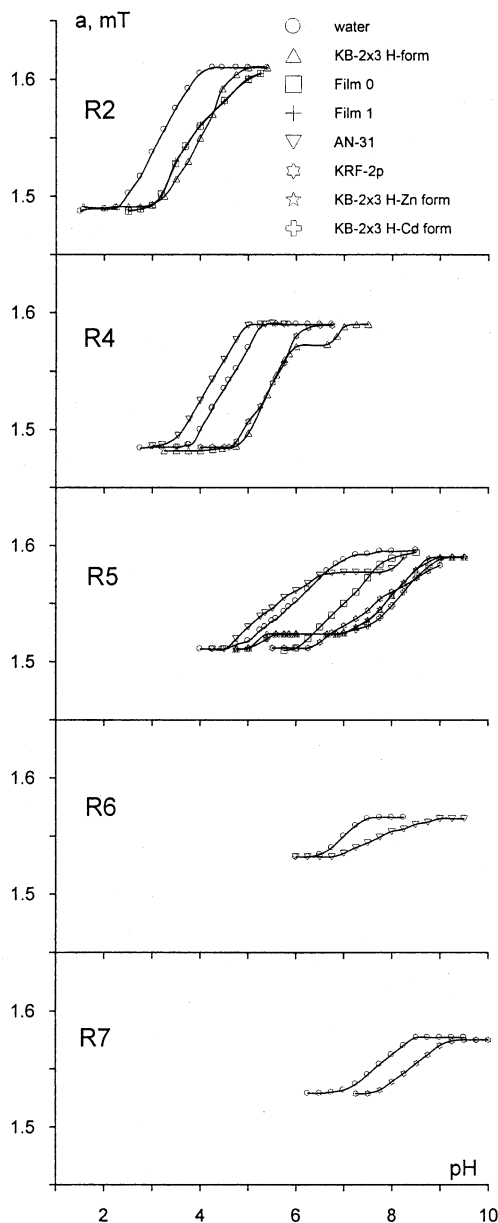


Figure 3. Dependencies of the ESR parameter a on the pH of the external solution for nitroxide radicals introduced into different systems. Partial loading of carboxylic cation-exchange resin KB-2 \times 3 by transition metals was 35% loading by Zn (H-Zn form) and 32% loading by Cd (H-Cd form).

3.2. Titration of Nitroxide Radicals Incorporated into the Resin Phase. Figure 3 shows the primary results of the titration of nitroxide radicals introduced into different ion-exchange resins; pH was measured in the solution surrounding the resin beads. The method of the a determination is illustrated in Figure 2. Titration results for nitroxide radicals dissolved in water are presented in the same plots for reference. All obtained titration curves are S-shaped. They are differently positioned along the pH axis that reflects difference in their pK_a^* values. The bottom and top horizontal parts of each curve correspond to a_N constants of the protonated and deprotonated forms (see Table 2). Figure 3 indicates that the radicals are sensitive to the solution acidity only in a narrow pH range (inclined part of each curve), and this range is specific for each radical. Experiments with different resins and films required different sets of nitroxide radicals because of the narrow sensitivity range of each probe. Between

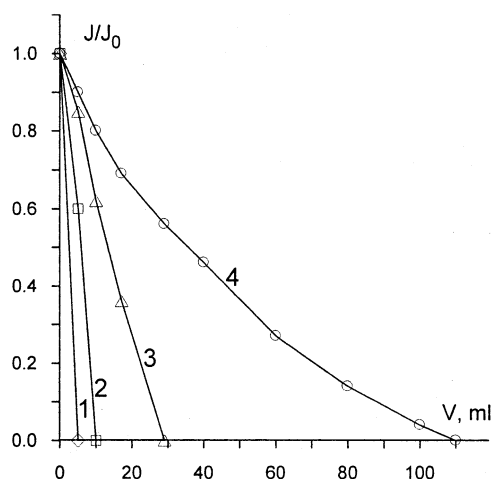


Figure 4. Retention of nitroxide radical **R5** by cation-exchange resin KB-2×3 while washing with an aqueous solution of $NaNO_3$ ($\mu = 1$) with different pH values (adjusted by HCl or NaOH). Dependence of the relative height (J/J_0) of the ESR signal on the volume of the washing solution passed. J is the height of the ESR signal of the resin phase; J_0 is the initial height before washing. 1 – pH 8.65; 2 – pH 7.15; 3 – pH 6.05; 4 – pH 5.3.

five and seven radicals with different pK_a^* values were used to cover the entire span of each titration curve.

3.3. Retention of a Radical by an Ion-Exchange Resin. Dependencies of the ESR signal height (radical **R5**) on the volume of solutions that were passed through the ion-exchange resin (KB-2×3) are shown in Figure 4. The experiments are described in section 2.6. Retention of the radical depends on the pH of the solution. A single 5-mL portion of solution with pH 8.65 removes the radical from the resin phase. Lowering of the pH reduces the mobility of the radical in the resin phase, causing an increase in the retention time.

3.4. Potentiometric Monitoring of pH in External Solutions. The resin titrations with nitroxide radicals were followed by potentiometric monitoring of pH in the external solution. The obtained titration curves were used for comparison. These curves are presented in Figures 6–10 and discussed later. Each titration curve consists of three regions. The first and the last regions (sharp inclines or declines) correspond to completely protonated or completely deprotonated states of functional groups. The middle regions correspond to pH values favorable for the interaction of the titrating reagent and functional groups. The small changes in pH in this region are explained by the sensitivity of the acid–base properties of the functional groups to alterations in the matrix charge. This phenomenon is reflected by presence of the coefficient $m \neq 1$ in eq 1.

3.5. ESR Spectra of Copper Complexes in the Resin Phase. ESR spectra of Cu^{2+} complexes in the KB-2×4 resin are presented in Figure 5. The width of the spectral line reflects the protonation of the samples. Samples with a higher fraction of deprotonated groups (samples 3 and 4)⁴⁷ allow better resolution of the spectra. The spectra are not sensitive to the degree of hydration (swollen and air-dried samples). Polycrystalline (powder) anisotropic spectra of Cu(II) were observed in all cases; these spectra are typical for mononuclear complexes of copper in crystal fields with D_{4h} symmetry. The spectra obtained allowed us to determine ESR characteristics $A_{||}$ and g – that are discussed below.

4. Discussion

Ion-exchange resins are polymeric networks carrying charged functional groups. Conventional theories consider the overall

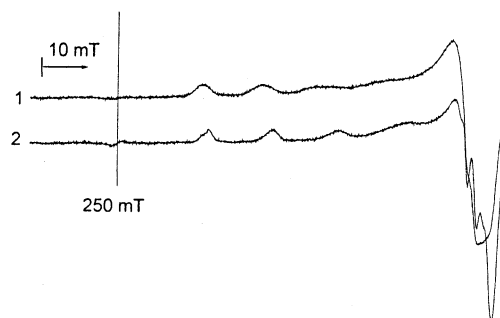


Figure 5. ESR spectra of Cu^{2+} complexes in mixed Na–Cu forms of cation-exchange resin KB-2×4: 1 – sample 1 with $C_{Cu} = 0.054$ mmol/g; 2 – sample 4 with $C_{Cu} = 0.072$ mmol/g.

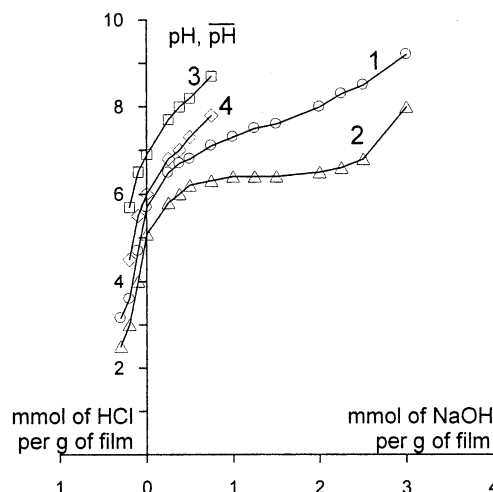


Figure 6. Titration curves of the films investigated. The left-hand direction of the abscissa illustrates titration with HCl. The right-hand direction illustrates titration with NaOH. 1, 2 – film 1; 3, 4 – film 0. 1, 3 – pH of the external solution (potentiometric determination); 2, 4 – inter-resin pH (measured with nitroxide radicals).

charge of the matrix as a result of the uniform redistribution of the functional groups' charge along the polymeric chains. The electroneutrality principle is fulfilled by the presence of counterions in the internal solution of the resin. According to these theories, the association of the functional groups with counterions reduces the overall charge of the matrix. Therefore, the matrix charge can vary between zero and a maximum negative value for cation exchangers and between zero and a maximum positive value for anion exchangers. This change in the matrix charge occurs within a narrow range of pH. According to eqs 3 and 6, the influence of the matrix charge has to be considered when using nitroxide radicals because the matrix charge controls the electrostatic surface potential Ψ . The following two sections discuss the results of an experimental search for such an influence and, therefore, the applicability of the approach proposed by Fromherz. In case of the existence of an such influence, charged and electroneutral matrixes should act in different ways. Hence, we consider these two cases separately.

4.1. Testing the Fromherz Approach for Systems with an Electroneutral Matrix. The influence of an electroneutral matrix on the ESR response of nitroxide radicals was studied at the beginning. As was already mentioned, the Fromherz approach states that $\overline{pH} = pH$. Therefore, the difference between the titration curves of the radicals incorporated into the resin and dissolved in an aqueous solution must be defined by eq 2. Panel R2 of Figure 3 shows a comparison of the $a = f(pH)$ dependencies obtained for nitroxide radical **R2** in the KB-2×3 resin and in the aqueous solution. The dissociation of this

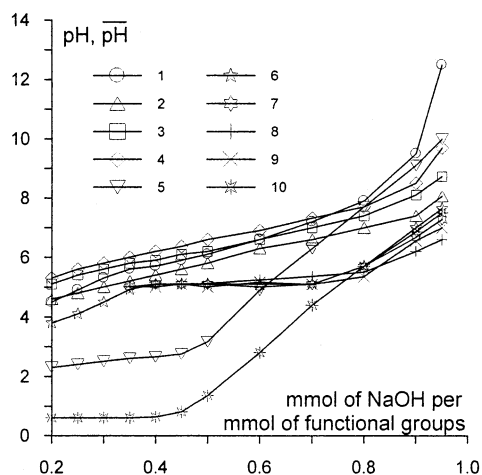


Figure 7. Titration curves of carboxylic cation-exchanger KB-2 \times 3. 1, 6 – H⁺ form; 2, 7 – mixed H⁺–Zn²⁺ form (15% Zn loading); 3, 8 – mixed H⁺–Zn²⁺ form (35% Zn loading); 4, 9 – mixed H⁺–Cd²⁺ form (32% Cd loading); 5, 10 – mixed H⁺–Na⁺ form. 1–5 – pH of the external solution (potentiometric determination); 6–10 – inter-resin $\overline{\text{pH}}$ (measured with nitroxide radicals).

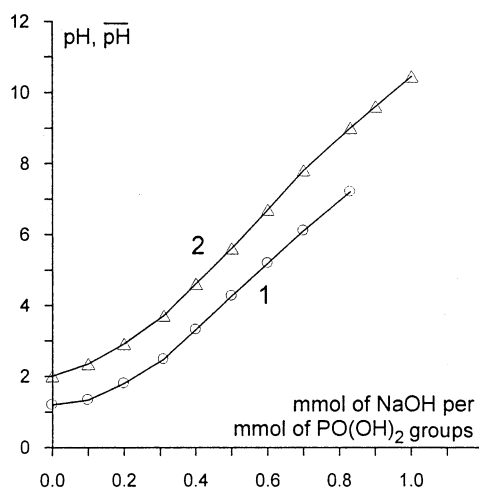


Figure 8. Titration curves of phosphonic cation-exchange resin KRF-2p (H⁺ form). 1 – pH of the external solution (potentiometric determination); 2 – inter-resin $\overline{\text{pH}}$ (measured with nitroxide radicals).

radical takes place in the pH region where the resin matrix remains uncharged (i.e., $\Psi = 0$). Hence, according to eq 3, $\Delta pK_a^{\text{el}} = 0$ and $pK_a^* = 6$. However, the following discrepancies with the Fromherz approach can be observed:

(i) The curve corresponding to the nitroxide radical incorporated into the ion exchanger is shifted to the right side relative to the curve representing the same radical in the aqueous solution. This tendency was found for all investigated pairs of nitroxide radical–ion-exchange resin. In contrast, eq 5 predicts a left-side shift.

(ii) The polarity of the media does not affect the values of the hyperfine coupling constant a_N . This is true for both protonated and deprotonated forms of the nitroxide radicals. Hence, the resin matrix does not cause a reduction in the unpaired electron spin density on the nitrogen atoms of the radicals' NO groups, as predicted by the Fromherz approach.

An investigation of the films (Figure 3, R2) yielded the same observations. No difference was found between the dissociation of radical **R2** in functional (film 1) and nonfunctional (film 0) films. This can be considered to be proof of the absence of any direct interactions between nitroxide radicals and the polymer.

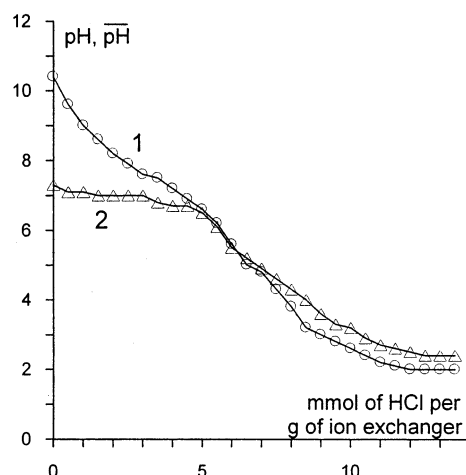


Figure 9. Titration curves of anion-exchange resin AN-31. 1 – pH of the external solution (potentiometric determination); 2 – inter-resin $\overline{\text{pH}}$ (measured with nitroxide radicals).

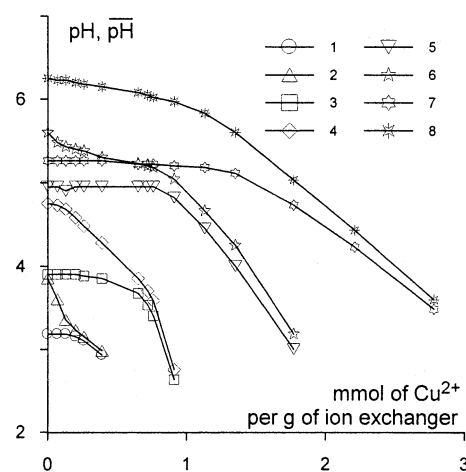


Figure 10. Dependence of $\overline{\text{pH}}$ (curves 1, 3, 5, 7) and pH (curves 2, 4, 6, 8) on copper content in resin KB-2 \times 4 loaded with Na⁺. Curves correspond to the following initial loading by sodium: 1, 2 – 10%; 3, 4 – 20%; 5, 6 – 40%; 7, 8 – 60%.

These observations indicate that the Fromherz approach is not applicable to the investigated systems with an uncharged matrix.

4.2. Testing the Fromherz Approach for Systems with a Charged Matrix. The overall charge of the resin changes during the titration process. Most curves in Figure 3 represent the case when reagent addition results in an increase of the matrix charge. By analyzing experimental data results presented in Figure 3, the following were observed:

(iii) A gradual negative charging of the matrix (cation-exchange resins) results in a gradual right-side shift of the $a = f(\text{pH})$ curves. The positive charge of the matrix (anion-exchange resins) results in a left-side shift.

(iv) The curves corresponding to certain nitroxide radical–resin pairs exhibit intervals of constant a values.

(v) The two-step dissociation of $-\text{PO}(\text{OH})_2$ groups (cation exchanger KRF-2) doubles the charge of the matrix. However, this is not reflected by the $a = f(\text{pH})$ curves.

(vi) The replacement of H⁺ in the resin phase by transition-metal ions affects the matrix charge because of the altering of association between the counterions and functional groups. However, a partial loading of the resins by Zn²⁺ or Cd²⁺ does not affect the $a = f(\text{pH})$ dependence.

The shifts observed upon matrix charging (right side for cation exchangers and left side for anion exchangers) can be qualita-

TABLE 3: Dissociation of Cation Exchange Resin KB-2×4 Containing Different Amounts of Na⁺

sample	initial (air-dried)		equilibrium (swollen in water)		
	α_0 , %	theoretical p <i>H</i> ₀ in initial samples	experimental p <i>H</i> (equilibrium)	buffer capacity, % of exchange capacity	α , % (calculated from p <i>H</i>)
1	10	4.14	3.15	2	1.1
2	20	4.50	3.90	4	6.0
3	40	4.92	4.95	11	41.5
4	60	5.27	5.23	20	57.5

TABLE 4: Acid–Base Characteristics of the Studied Ion Exchangers

ion exchanger	exchange capacity, mmol/g	ionic form	μ	conventional method of determination		determined by proposed method
				<i>m</i>	p <i>K</i> _a	p <i>K</i> _a ± 0.1
KB-2×3	13.5	H ⁺	0.145	2.67	6.2	5.1
KB-2×3	13.5	H ⁺	1	2.25	5.3	5.2
KB-2×3	13.5	H ⁺	3.5	1.93	5.1	5.1
KB-2×6	12.5	H ⁺	0.145	2.18	6.3	5.1
KB-2×7P	10.3	H ⁺	0.145	1.91	6.0	5.2
KB-2×20	8.68	H ⁺	0.145	2.42	7.1	5.0
KB-2×3	11.5	H ⁺ –15% Zn ²⁺	0.145	1.86	5.9	5.1
KB-2×3	8.8	H ⁺ –35% Zn ²⁺	0.145	1.14	6.2	5.1
KB-2×3	9.21	H ⁺ –32% Cd ²⁺	0.145	1.10	6.2	5.1
KB-51	1.12	H ⁺	0.05	2.00	5.1	4.0
film 1	3.03	H ⁺	0.145	1.40	7.4	6.4
KU-2	4.75	H ⁺	0.145	2.08	2.3	0.6
KRF-2p	8.4	H ⁺	0.145	2.15	8.3	6.5 ^a
				2.92	3.6	<i>B</i> = 1.57 2.6 ^a
AN-31	7.19	H ⁺ /OH [−]	0.145	2.16	7.6	<i>B</i> = 2.08 7.2

^a Values obtained through the fitting of eq 11 to the titration data.

tively characterized by eq 3. However, the following considerations show the absence of a quantitative correlation. According to eq 3, the shift in p*K*_a^{*} values initiated by the matrix charge does not depend on the nitroxide radical's nature. Hence, the maximum shift can be expected from radicals changing the *a* value in the p*H* region corresponding to the maximum charge of the matrix. Panels R4 and R5 of Figure 3 show that most significant shifts are observed for the radicals changing their protonation in the same p*H* region as the functional groups of the resin. This result cannot be explained with the Fromherz approach. Observations v and vi indicate a lack of the linear dependence $\Delta pK_a^* = f(\psi)$ that is predicted by eq 3. This is one more discrepancy with the Fromherz approach.

4.3. Concept Proposed. All of the above facts testify to the inapplicability of the Fromherz approach to the systems investigated. We propose the employment of a thermodynamic concept based on the idea of a difference in activity coefficients between the resin phase and the surrounding solution. This approach was widely used for thermodynamic modeling; however, it was never directly confirmed.^{30,31} The authors of the cited works suggest that the resin phase contains two types of differently structured water. One type is identical to the surrounding solution. The other type is reckoned as a solution of the cross-linked polyelectrolyte. Its hydrogen bond structure is disorganized because of neighboring hydrophobic chains. Our experiments reveal only the second kind of water that is different from the surrounding solution.

Contrary to the Fromherz approach, we suggest the following:

- The transfer of nitroxide radicals from the surrounding solution into the resin phase does not affect the ionization constants ($\Delta pK_a^* = 0$).

- The activity of the hydrogen ions inside the resin phase differs from that in the surrounding solution ($pH \neq pH$).

- The p*H* difference is caused by the difference in water structure inside the resin phase and in the aqueous solution.

The second conclusion partially correlates with the approach of Hartley and Roe.²² However, Hartley and Roe explained the changes in the proton activity by the influence of the surface potential (see eq 6). Our experiments do not confirm this explanation. Because the nitroxide radicals are positioned far enough from the charged surface (see section 4.4), they indicate p*H* in the internal water, which can be affected by the changes in the water structure rather than by the surface influence.

4.4. Verification of the Concept. Obviously, molecules located close to the polymeric chains can be exposed to certain interactions with the “surface” of the polymer. Because of such an influence, the location of the radicals near the surface would result in a significant alteration of the ESR spectra.²⁰ To survey the positioning of the probes in the inter-resin solution, we performed experiments on the retention of the nitroxide radicals by the resin when washing with a solution of a certain p*H* (see Figure 4). A reduction of the solution p*H* from 8.65 to 5.3 caused the protonation of the **R5** radical (p*K*_a^{*} = 6.1). Carboxylic groups of the resin are deprotonated at this p*H* value (see section 4.6 and Table 4). The dependence of *J*/*J*₀ on the p*H* of the washing solution reflects the association of the protonated nitroxide radicals with deprotonated carboxylic groups of the resin. Restraining of the radical mobility is also reflected by the shape of the ESR spectra. An illustration of such a spectral response is presented in Figure 2 (the **R5** radical in the KB-2×4 resin). A reduction of the p*H* value from 7.0 to 5.8 results

in an increase of τ_c from 3.5×10^{-11} to 4.5×10^{-10} . Protonation of the carboxylic groups at pH 4.5 does not cause a further change in the radical mobility; τ_c remains constant at 4.5×10^{-10} . The same was observed for systems including resins with different degree of cross linking (KB-2×3, KB-2×4, KB-2×6, and KB-2×7P) and different sized radicals (**R1**, **R2**, **R4**, **R5**, and **R7**). The mobility was restricted only in highly cross-linked sample (KB-2×20) containing large radicals.

Therefore, the following can be concluded:

- The absence of strong interactions between the radical and the matrix indicates that the nitroxide radicals are located in the inter-resin solution. They are well separated from the polymeric chains. The interactions between the radicals and the organic matrix are weak.

- There is an exchange of protons between the nitroxide radicals and the functional groups of the resin until both (the radical and the functional group) are completely deprotonated.

- If the pore size is essentially reduced (experiments with significantly cross-linked samples), then the mobility of the nitroxide radicals is affected.

The proposed method is based on the dependence of the ratio between the deprotonated and protonated forms of the radicals on the hydrogen ion activity. This ratio can be monitored by measuring parameter a of the corresponding ESR spectra or simulating the experimental spectra. Because of the very high mobility of the radicals in most studied systems ($\tau_c < 10^{-9}$), parameter a was used for the measurements. Only the highly cross-linked cation exchanger KB-2×20 was investigated using the spectra simulation because τ_c of some radicals in this resin corresponded to slow radical mobility ($2 \times 10^{-9} < \tau_c < 10^{-8}$), and these anisotropic spectra were unsuitable for the determination of parameter a . The simulation was performed with Freed's program as described in ref 29. ESR spectra of frozen (77 K) water–methanol (1:1) solutions of completely protonated, partially protonated, and completely deprotonated radicals were recorded. Spectra of completely protonated and completely deprotonated radicals were treated (simulated) to obtain the signal characteristics and radical mobilities. Simulated spectra (completely protonated and completely deprotonated radicals) were combined with different weight ratios and used to simulate experimental spectra of partially protonated radicals to obtain the calibrating curve

$$\frac{[R^\bullet]}{[R^\bullet] + [R^\bullet H^+]} = f(\text{pH}) \quad (7)$$

Experimental anisotropic spectra of the radicals incorporated in KB-2×20 were treated with Freed's program, producing values of τ_c and the ratio between amounts of protonated and deprotonated forms of the radical. pH in the resin phase was determined on the basis of this ratio and the calibrating dependence (eq 7).

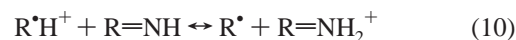
A condition for the applicability of the proposed method is the identity of the proton-exchange mechanism in aqueous solutions and in ion-exchange resins ($\text{p}K_a^* = 0$) for the radicals used. This mechanism is described by the reaction



The only process that can alter the proton-exchange mechanism (for incorporation in the resin phase) is direct acid–base interaction with ion-exchange groups:



or



where R represents the matrix of the resin. The altering of $\text{p}K_a^*$ due to interactions 9 and 10 could be suggested as a possible hindrance for the applicability of the method. However, Khramtsov and Weiner³² have shown that $\text{p}K_a^*$ values are not affected by such interactions. Only the kinetic characteristics of the radicals (lifetimes of R^\bullet and $R^\bullet H^+$ forms) are affected.

4.5. Determination of H^+ Activity in the Resin Phase. As already mentioned, the main limitation for the correct thermodynamic investigations was related to the absence of a method for the direct measurement of activity in the inter-resin solution. We overcame this limitation through monitoring the ionization of nitroxide radicals in the resin phase by ESR.

The values of a were explored to indicate the internal pH. The curves $a = f(\text{pH})$ obtained for the radicals in bulk aqueous solutions were used as a calibration system for quantitative calculations. This approach can be considered to be truly thermodynamic because $\Delta \text{p}K_a^* = 0$.

The pH values determined with nitroxide radicals are presented in Figures 6–10.⁴⁸ The curves reflecting pH in the surrounding solution are shown for comparison. All values of pH are lower than the corresponding values of pH inside the phase of cation-exchange resins. The same trend is observed for anion exchanger AN-31 at pH > 6; pH in this system is higher than the acidity of the external solution at pH < 6. Results of the experiments indicate the higher activity of hydrogen ions inside the resin phase in comparison with that in the surrounding solution. This observation includes the sample containing no functional groups (film 0). The only exception, anion-exchange resin AN-31 at pH < 6, will be discussed later. The difference between pH and pH can be explained by the peculiarity of the water structure in the resin phase, where the disorganized structure of water (in comparison with that of aqueous solutions) allows an increase in the hydrogen ions' mobility.^{12,13,15,16,33}

The overall conclusion is that the nitroxide radicals can be used as probes to study equilibria in the resin phase. The following sections show more applications of the method.

4.6. Determination of the Functional Groups' Ionization Constants. Table 4 presents a comparison of the functional groups' ionization characteristics calculated by conventional and proposed methods. The conventional values ($\text{p}K_a$) were calculated by fitting eq 1 to experimental dependencies of the external pH on the volume of the titrant added. The values are in good agreement with data published by other authors who used the same conventional method.^{1,8,9} As reported by some other authors, dependencies of the apparent characteristics on the inter-resin environment (see refs 1, 6–9) can be observed from our experimental results:

- Apparent acidity of the cation-exchange groups decreases with increasing degree of neutralization.

- Increasing ionic strength (μ) causes a significant decrease in $\text{p}K_a$.

- Apparent acidity of the functional groups depends on the degree of resin cross linking. A higher degree of cross linking results in reduced acidity.

Unlike the apparent characteristics, $\text{p}K_a^*$ values were determined from titration experiments with the direct measurement of pH in the resin phase (Figures 6–10). Some titration curves, pH , include intervals of constant acidity of the internal solution (i.e., $\text{pH} = \text{const}$; Figures 6, 7, and 9). These curves

belong to sorbents dissociating in one step. Dependencies, $\alpha = f(\text{pH})$, presented in Figure 3 reflect these phenomena in the corresponding horizontal plateaus. These intervals can be assigned to the regions where the functional groups dissociate. The dissociation reaction provides a certain buffer capacity and maintains a constant pH of the internal solution. These values of $\overline{\text{pH}}$ correspond to $\overline{\text{pK}}_a$ values of functional groups. The obtained values are presented in Table 4. In all cases, $\overline{\text{pK}}_a$ was less than pK_a and did not exhibit any dependence on the degree of neutralization, ionic strength, or cross linking.

Positions of obtained $\text{pH} = f(V)$ titration curves are similar to $\text{pH} = f(V)$ curves, which can be expected for low-molecular-weight substances having the same functional groups. Therefore, no influence of the resin network can be observed. The similarity between low-molecular-weight compounds and the resins are confirmed by a comparison of the pK_a values. For example, $\text{pK}_a = 4.87$ for propionic ($\text{CH}_3\text{--CH}_2\text{--COOH}$) and methylpropanoic ($\text{CH}_3\text{--CH}(\text{CH}_3)\text{--COOH}$) acids, and $\text{pK}_a = 5.03$ for dimethylpropanoic acid ($\text{CH}_3\text{--C}(\text{CH}_3)_2\text{--COOH}$).^{34,35} These values are similar to the values presented in Table 4. This can be considered to be one more disagreement with the conventional theories discussed above explaining the presence of the empirical coefficient $m \neq 1$ in eq 1 by charge redistribution along the matrix.

A horizontal plateau is absent in the titration curve corresponding to resin KRF-2p (see Figure 8). This can be explained by a two-step ionization of the phosphonic groups. The difference between the first and second constants of ionization is not sufficiently large to be reflected in the titration curve. Resin KRF-2p contains a small number of phenyl-phosphine groups that can affect the resolution of the titration curve even more. The absence of horizontal plateaus does not allow for a determination of $\overline{\text{pK}}_a$ for the KRF-2p resin by the same method as for the $\overline{\text{pK}}_a$ of other resins. The fitting of the following equation

$$\overline{\text{pH}} - f\left(\log \frac{\alpha}{1-\alpha}\right) = \overline{\text{pK}}_a + B \cdot \log \frac{\alpha}{1-\alpha} \quad (11)$$

to the experimental data (obtained with nitroxide radicals) was used instead. The results are also presented in Table 4. Obtained values of B can be considered to be empirical correction coefficients.

In contrast to other systems investigated, nitroxide radicals introduced into resin AN-31 are sensitive to the matrix charge. It can be explained by the specific location of functional groups. Functional groups of this resin are not attached to the polymer, being members of the polymeric chains as shown in Figure 1. It is an essential difference between AN-31 and other materials investigated. According to the theoretical ideas expressed by eqs 3 and 6, an increase in the matrix charge must shift the $\alpha = f(\text{pH})$ dependence to the left side and move up the titration curve $\text{pH} = f(V)$. These shifts can be seen in Figures 3 and 9. Hence, the nitroxide radicals cannot provide reliable information about the $\overline{\text{pH}}$ values in the AN-31 resin. However, the plateau in Figure 9 can be reliably used to measure the $\overline{\text{pK}}_a$ value. The measurement results are also presented in Table 4.

The experimental data indicate that the acid–base properties of the functional groups attached to the cross-linked network cannot be described by eq 1. The functional groups of all resins investigated behave similarly to the corresponding monomeric compounds. It explains the observed absence of an influence of the degree of cross linking and of the presence of complexing metal ions in the system.

4.7. Hydrolysis of Mixed Forms of KB-2×4. Attempts to investigate the internal pH in ternary (hydrogen–sodium–copper) systems reveal a significant contribution of hydrolysis to the chemical equilibria. The present section describes the hydrolysis. The results are shown in Figure 10 and Table 3. The three-compound systems are discussed later.

The following can be observed from measurements of pH of the external solution. Initial parts of curves 2, 4, 6, and 8 of Figure 10 are entirely controlled by the hydrolysis. The reason for this statement is the following. Values of pH in the external solutions at equilibrium are much higher than the initial value (pH 3.86) of the solution. (This value of the initial pH was the same in all experiments.) This phenomenon was observed for all four samples. The pH change is much higher than could be predicted from stoichiometric calculations based on the amount of introduced copper. Therefore, the acidity of the external solution is controlled by the following hydrolysis reaction:



This conclusion is confirmed by the measurements of the resin's internal acidity. Similar to data presented in Figure 5, $\overline{\text{pH}}$ in the resin phase is lower than in the surrounding equilibrium solution (Figure 10). In samples 1 and 2, it does not exceed the pH of the initial solution. The value of $\overline{\text{pH}}$ inside the resin is defined by the degree of ionization of the functional groups (α). The dependence is presented by eq 13, which describes the dissociation of a weak electrolyte (carboxylic functional groups):

$$\overline{\text{pH}} = \overline{\text{pK}}_a + \log \frac{\alpha}{1-\alpha} \quad (13)$$

Equation 13 is similar to eq 1. It is obtained using the following assumptions:

- The polyelectrolyte is considered to be a number of independent units carrying one functional group each. Hence, $m = 1$ because charge redistribution cannot occur.
- The composition of the inter-resin solution is homogeneous. The concentration of the independent units is the same in all parts of the inter-resin solution.

Equation 13 was used for theoretical calculation of $\overline{\text{pH}}_0$ in the initial samples (Table 3). The values calculated for samples 1 and 2 are higher than the directly measured values. This indicates that the hydrolysis reaction affects the degree of dissociation of the functional groups. This conclusion is confirmed by α values presented in the last column of Table 3.

The measured and calculated values $\overline{\text{pH}}$ are in good agreement for samples 3 and 4. Hence, contact with the solution does not affect the degree of dissociation. However, as was stated above, the changes in pH of the external solution indicate the hydrolysis process. We believe that the similarity between α_0 and α (Table 3) is due to the buffer behavior of carboxylic groups in the mixed H–Na form of the resin. A detailed discussion of the buffer properties of ion-exchange resins is presented in the next section. In conclusion, we can state that the degree of hydrolysis depends on the initial value of α .

4.8. Buffer Behavior of the KB-2×4 Resin. Each dependence presented in Figure 10 has a region where $\overline{\text{pH}}$ is constant (horizontal plateaus on the corresponding curves). The span of this region decreases with a reduction in the degree of ionization of the sample. This is the result of the buffer behavior of the carboxylic groups contained in the KB-2×4 resin. The

interactions are similar to those in well-known acetic buffers. The system consisting of the cross-linked polyelectrolyte and the internal solution behaves in a way similar to that of solutions of monomeric units. Increases in the $\text{pH} = \text{const}$ regions reflect increases in the buffer capacity that is related to the number of deprotonated functional groups in the initial sample of the resin. The length of the constant pH regions was used to characterize the buffer capacity quantitatively. The buffer capacity was assumed to be equal to the equivalent concentration of copper introduced in the system without altering the pH . The results expressed as fraction of the resin-exchange capacity are presented in Table 3.

4.9. Measuring the Acidity Inside Ion Exchangers Partially Loaded with Transition Metals. We successfully applied nitroxide radicals to indicate the internal acidity in three-compound ion-exchange systems, providing direct information about interactions in the internal solution. The approach is based on the fact that these interactions depend on the state of the resin functional groups that can be affected by the introduction of different amounts of complex-forming ions. We selected Cu^{2+} because this ion is paramagnetic ($3d^9$ electron configuration) and can be studied with the ESR method. Copper sorption on mixed $\text{H}^+ - \text{Na}^+$ forms of the KB-2 \times 4 resin was studied. Four samples with different ratios of sorbed H^+ to Na^+ ions were used. (Sample numbers in the following text correspond to those listed in Table 3.) Because the initial samples did not contain Cu^{2+} (the third ion), the degree of ionization of the functional groups α_0 in the initial samples can be defined as

$$\alpha_0 = \bar{x}_{\text{Na}} \quad (14)$$

assuming that sorbed sodium ions are not associated with resin functional groups and all ionic pairs of hydrogen–functional groups are associated.³⁶

The sorption of copper by samples 3 and 4 preferably proceeds through the following reaction:



This mechanism was verified earlier.³⁷ The ESR characteristics of the formed inter-resin complexes were $g_{\parallel} = 2.332$ and $A_{\parallel} = 14.6$ mT. These complexes are considered to be strong enough to prevent the functional groups from participating in the sodium–hydrogen equilibrium. The involvement of the deprotonated functional groups into copper complexes results in a decrease in their concentration. As a result, the equilibrium



is shifted to the right-hand side. pH of the inter-resin solution (Figure 10) does not depend on the amount of copper introduced (up to some saturation with Cu^{2+} ions). The pH of the external solution decreases with the amount of copper increase. The observed phenomenon is caused by buffer properties of the ion exchanger revealing themselves only inside the grains. These inter-resin interactions do not affect the equilibrium solution. Apparently, the reverse is also valid. The addition of a buffer to the solution in contact with an ion exchanger does not provide constant acidity inside the grains. This result indicates a limitation of the frequently used technique that consists of the investigation of ion-exchange processes in buffer environments.^{38–41} Constant acidity is usually assumed throughout the system. According to our findings, such a technique cannot provide a constant inter-resin pH .

Samples 1 and 2 initially contained less sodium (and have a lower degree of ionization). This resulted in the replacement of a certain amount of hydrogen by Cu^{2+} during the sorption process.



The formation of a $(\text{RCOO})_2\text{Cu}$ complex with ESR characteristics $g_{\parallel} = 2.364$ and $A_{\parallel} = 12.8$ mT was discussed elsewhere.³⁷ A significant amount of hydrogen is released, creating H^+ competition for the copper sorption. Because of the low buffer capacity of samples 1 and 2, reaction 17 shifts down the inter-resin pH (see Figure 10).

Therefore, the incorporation of the protonated carboxylic groups of the sorbent into complexes with Cu^{2+} begins after exhausting the buffer capacity of the samples. This releases a significant number of hydrogen ions with a drastic decrease in the pH of the resin and of the surrounding solution. The pH decrease blocks the sorption process almost completely.

5. Conclusions

This study proposed a new method for the investigation of equilibria in functional polymers. The obtained characteristics (i.e., activity of hydrogen ions in the resins, ionization constants of functional groups, and buffer capacity) identify internal interactions in the resin phase, but apparent values obtained with conventional titration cannot provide such information.

The behavior of nitroxide radicals in most of the investigated functional polymers was found to be different from the behavior known for colloids, micelles, and biomembranes; however, it was similar to that of aqueous solutions.

We suggest that the developed method can be useful for the investigation of ion exchangers, and it also has the potential to increase our understanding of interactions in other porous systems: heterogeneous catalysts, nanostructured materials, biological mixtures, and so forth. Of course, the applicability of the method must be verified for each kind of system in question as described.

Acknowledgment. We thank the International Scientific Foundation (GR NMP300) and the INTAS Committee (GR 96-0911) for financial support of this work, Professor V. V. Kotov and Dr. O. V. D'akonova (Voronezh Agricultural Academy, Russia) for supplying the films, and Professor I. N. Lupunov (Ural State Wood Technology Academy) for valuable remarks. E.G.K. thanks Haldor Topsoe A/S (Denmark) for a personal postgraduate grant. We are grateful to Dr. E. Björkman, Dr. Z. Szabo (Royal Institute of Technology), and Dr. E. Gorokhova (Stockholm University) for valuable comments during the final preparation of the manuscript.

Symbols Used

A_{\parallel}	hyperfine coupling constant of ESR spectra of Cu^{2+} in polycrystalline samples; the index \parallel indicates the parallel orientation of the axis of the magnetic complex relative to the external magnetic field
a	superposition of hyperfine interaction constants (a_N) of ESR spectra characterizing protonated and deprotonated forms of the nitroxide radical
a_N	hyperfine coupling constant of isotropic ESR signals of nitroxide radicals
B, b	empirical coefficients
\bar{C}_{Cu}	concentration of copper in the resin phase
F	Faraday's constant

g	g factor of isotropic ESR signals of nitroxide radicals
$g_{ }$	g factor of anisotropic ESR signals of Cu ²⁺ in polycrystalline samples; the index indicates the parallel orientation of the axis of the magnetic complex relative to the external magnetic field
J	height of the ESR signal
K_a^*	protonation constant of the nitroxide radicals
\bar{K}_a	thermodynamic constant of the resin functional groups' ionization
\tilde{K}_a	apparent constant of the resin functional groups' ionization
m	empirical coefficient reflecting the redistribution of the charge along the polymeric network
pH	pH in solution
$\overline{\text{pH}}$	pH inside the resin phase
pH_0	pH inside the phase of the initial resin (before reaction)
R	general gas constant or matrix of the resin
R^*	nitroxide radical
T	temperature (K)
V	volume
x	equivalent fraction of an ion in the resin
α	degree of ionization of the resin functional groups
α_0	degree of ionization of functional groups of the initial resin (before reaction)
ϵ	dielectric constant of the media
Ψ	electrostatic potential
μ	ionic strength
τ_c	correlation time

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- (42) The degree of ionization is defined as the ratio between the number of functional groups ionized in the inter-resin solution and the total number of functional groups.
- (43) Most classic models of ion-exchange resins consider the delocalization of the functional group's charge along the polymeric matrix. The matrix charge is considered to be constant in strong ion exchangers and can vary with pH in weak cation and anion exchangers because of reactions of protonation and deprotonation.
- (44) The degree of neutralization is defined as the ratio between the amount of alkali added to the cation exchanger or the amount of acid added to the anion exchanger and the total number of functional groups.
- (45) The symbol • denotes a nitroxide radical.
- (46) The bar indicates the solid phase.
- (47) The numbering of these samples corresponds to that given in Table 3. The Table is discussed in detail later in the Discussion.
- (48) We have to mention that the curves presented in Figures 6–10 and Figure 3 are plotted on the basis of the same experimental data. Figures 6–10 differ from Figure 3 by the system of approximations accepted (our approximations and Fromherz's approach, correspondingly).