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Hydration of heterogeneous cation-exchange membranes in hydrogen and amino acids forms. I. Study by IR-spectroscopy

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Abstract

Hydration characteristics of heterogeneous sulfocation-exchange membranes MK-40 and FTCM-E in hydrogen and amino acid's forms are studied by IR-spectroscopy. Energy of hydrogen bonds in ion-exchange membrane is calculated on the basis of absorption strips displacement in the IR-spectrum. Basic amino acids sorption by the membrane leads to a decrease of total water content in the membrane phase and to an increase of water molecules fraction having high values of hydrogen bonds energy.

Keywords: arginine, histidine, cation-exchange membrane, hydration, IR-spectrum.

Гидратационные характеристики гетерогенных сульфокатионообменных мембран МК-40 и FTCM-E в водородной и аминокислотных формах изучены методом ИК-спектроскопии. Энергия водородных связей в ионообменной мембране рассчитана на основе сдвига полос поглощения в ИК-спектре. Сорбция мембраной основных аминокислот приводит к снижению общего содержания воды в фазе мембраны и к увеличению доли молекул воды с высокой энергией водородных связей.

Ключевые слова: аргинин, гистидин, катионообменная мембрана, гидратация, ИК-спектр

Introduction

Studies of the ion-exchange membranes hydration are an important stage in an analysis of transfer processes in biological and synthetic membranes. They allow refining theoretical concepts of the nature and mechanism of amino acids transport. Thus, such studies are necessary for the development of methods for the isolation and demineralization of substances by membrane methods [1]. The present work deals with amino acid forms of sulfocation-exchange membranes.

Ion-exchange membranes perform only in aqueous media, and irreversibly change their initial separation and structural properties after dehydration. The content and state of water in ion-exchange membranes substantially influence their physicochemical properties and transport characteristics [2-3]. The nature of the polymeric matrix and the type of functional groups and counterions determine the membranes hydration. Close interrelation between the structure and properties of water and membranes determines the importance of studies of the hydration characteristics of ion-exchange membranes. The purpose of this

work is to estimate the hydration of heterogeneous cation-exchange membranes in the arginine, histidine and H^+ -forms.

Experimental

The objects of this study are arginine, histidine and heterogeneous sulfopolysterene cation-exchange membranes: MK-40 (produced by "Shchekinoazot", Russia), FTCM-E (produced by FuMa-Tech, Germany).

The membranes were prepared according to GOST State Standard 17553-72 and converted into the target form according to the technique described in [4].

The solutions of amino acids (produced by Ajinomoto) are analyzed by the method of photometry based on cooper complexes formation [5]. Water sorption is determined by gravimetric method according to GOST 17554-72 [4].IR-spectra of membrane samples are obtained using Vertex-70 Bruker FTIR-spectrometer in the region 4000-500 cm^{-1}.

Results and discussion

The nature of the polymeric backbone and the type of functional groups and counterions in turn determine the hydration of membranes [6]. In this study the hydration of heterogeneous cation-exchange membranes in arginine, histidine and H^+- forms is estimated.

The studied membranes have identical functional groups, however, distinction in the nature and structure of polymer matrix has an influence on the state and quantity of water in membrane phase and, as consequence, on electrodialysis concentration parameters [7]. The hydration of cation-exchange membranes after sorption of basic amino acid is estimated by the gravimetric method. The water content in MK-40 and FTCM-E cation-exchange membranes in arginine and H^+-forms is shown in Table 1. The presence of amino acid's bipolar ions limits the sorption of water and changes the amount and state of water in the membrane phase. It follows from our data that saturation of ion-exchange membranes with arginine or histidine causes decrease of water uptake [8].

Table 1. Water content for MK-40 and FTCM-E cation-exchange membranes in arginine, histidine and H^+ -forms

The membrane	Membrane form	Water content, %	Specific water capacity, mol H_2O/SO_3^-
MK-40	H^+	56.7	12.6
	Arg	36.2	8.0
	His	41.2	9.1
FTCM-E	H^+	39.3	11.5
	Arg	25.6	7.5
	His	28.1	8.2

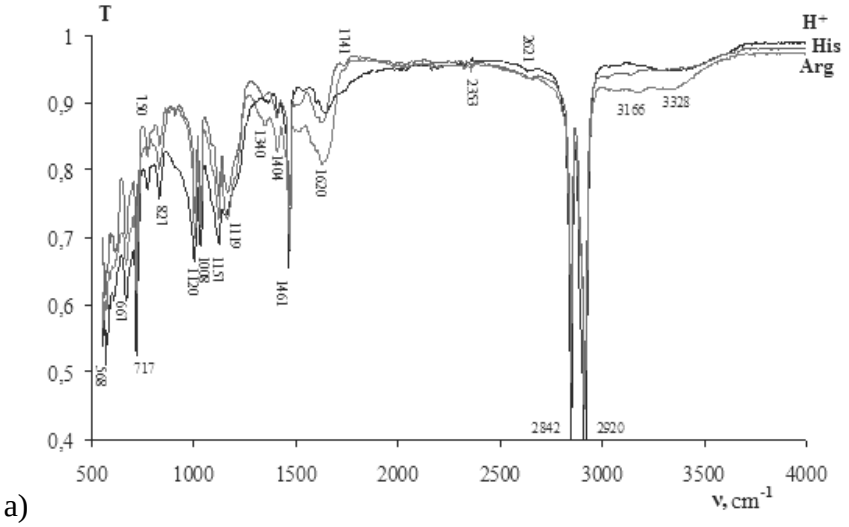
Water content for two membranes (in mass. percentage) differs significantly, but specific water capacity is similar. This is due to the fact that MK-40 membrane has higher value of total exchange capacity (that means - more sulfo-groups) of 2.5 mmol/g of absolutely dry membrane, than FTCM-E membrane, which capacity is equal to 1.9 mol/g.

Hydration of heterogeneous MK-40 sulfocation-exchange membranes in H^+, arginine and histidine forms is studied by IR-spectroscopy method. The energy of

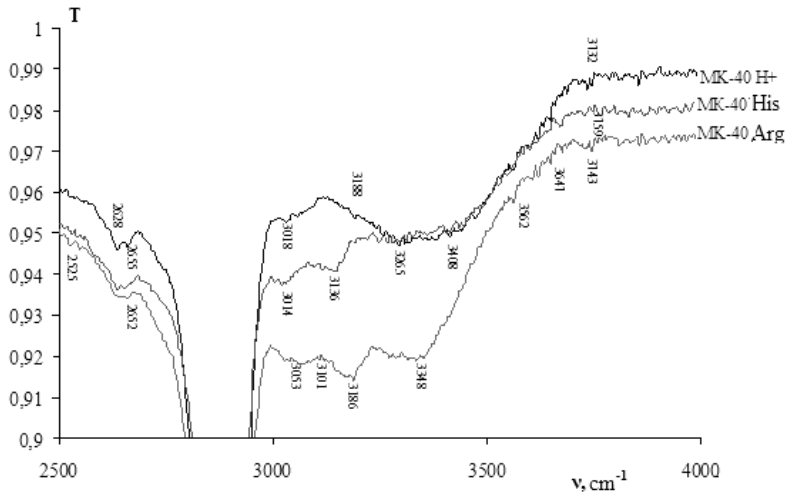
hydrogen bonds between water molecules in ion-exchange membranes is calculated on the basis of bands frequency shift in the IR-spectrum. The existence of structure and energy heterogeneity of water associates in studied membranes is shown.

Vibrational spectra make it possible not only to reveal the bands of absorption corresponding to matrix, functional groups and counter-ions of membrane but also to establish the existence and force of hydrogen bonding. Deformation vibrations of water molecules appear at 1600-1750 cm^{-1} and stretching vibrations of –O–H bonds – at 3000-4000 cm^{-1}. Appearance of distortions in IR-spectrum (shift of frequency and broadening of spectral band, intensity change) accompanying hydrogen bonds formation can be a criterion of their formation and enables to estimate the energy of bonding.

For the assessment of hydration properties of membrane gel phase one can use the bands of stretching vibrations of OH-groups at the region 3700-3000 cm^{-1} which are the most sensitive to hydrogen bonds modification. Fig.1 shows IR-spectra of MK-40 membrane in arginine, histidine and H^+-forms.



a)



b).

Fig. 1. IR-spectra of membrane MK-40 in arginine, histidine and H^+-forms.
a) 500-4000 cm^{-1}, b) 2500-4000 cm^{-1}

The dominant minima of transmission in the spectra of MK-40 membrane are minima at 2920, 2842 cm^{-1}, corresponding to asymmetric and symmetric vibrations of -CH and -CH_2 groups. Minima at 1008, 1120, 1157 cm^{-1} deal with stretching vibrations of –SO_3 groups, minima at 1472, 1462 $см^{-1}$ correspond to deformation vibrations of CH и CH_2

groups. Peaks at 773 and 831 cm^{-1} confirm the appearance of not flat deformation vibrations of -CH in substituted benzene ring [9].

The vibrations of C-S bond of sulfo-group connected with benzene ring are confirmed by the minima at 750 и 721 cm^{-1}. The deformation vibrations of C-H of benzene ring one can observe at 667 cm^{-1}.

IR-spectra of the membrane in histidine and arginine forms contain band at 1620 cm^{-1}– deformation vibrations of NH_3^+ (I amino acid band) [9]. Also it is possible to reveal the appearance of the minimum at 1340 $см^{-1}$ – symmetric vibrations of $–COO^-$ groups.

In IR-spectrum of MK-40 for the region 3000-4000 cm^{-1} shoulder is found at 3 686 cm^{-1} (it shifts to 3560 cm^{-1} for amino acid form indicating the formation of more strong associates) and the wide band including several peaks is situated in the region 3470-3250 cm^{-1}. According to G. Zundel [10-11] a continuous absorption in this region appears in the case of existence of two water molecules per one proton, i.e. in the case of $H_5O_2^+$ formation. It can be confirmed by the appearance of the band at 1740 cm^{-1}. For the membrane in arginine form one can observe also bands corresponding to the stretching vibrations of guanidinium fragment and amino group: 3333, 3285, 3173 cm^{-1}.

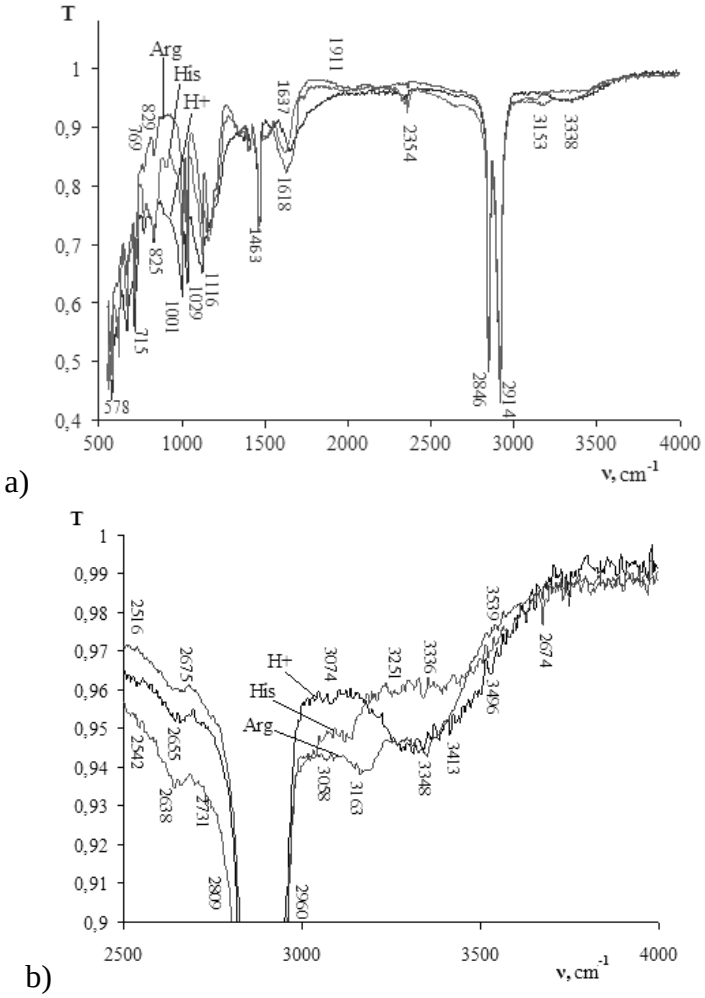


Fig. 2. IR-spectra of FTCM-E membrane in arginine, histidine and H^+-forms. a) 500-4000 cm^{-1}, b) 2500-4000 cm^{-1}

Fig. 2 shows IR-spectra of FTCM-E membrane in arginine, histidine and H^+-forms. The spectrum region 2500-4000 cm^{-1} is presented separately in fig. 2b.

From the IR-spectra analysis we conclude that FTCM-E membrane contains sulfo-groups as functional groups, minima at 1001, 1006, 1033, 1463 cm^{-1} deal with stretching vibrations of $–SO_3$ groups. Several bands characterize the polymer matrix of the membrane. In the spectra of FTCM-E membrane very strong minima at 2914, 2846 cm^{-1}, corresponding to asymmetric and symmetric vibrations of -CH and $-CH_2$ groups are observed. Peaks at 769 and 835 cm^{-1} confirm the appearance of not flat deformation vibrations of -CH in substituted benzene ring. The bands listed above are observed in the spectra of both hydrogen and arginine forms.

IR-spectrum of the membrane in histidine form contains band at 1637 cm^{-1}– deformation vibrations of NH_3^+ (I amino acid band), the arginine form demonstrates I amino acid band at 1618 cm^{-1} [9]. Also it is possible to reveal the appearance of the minimum at 1722 $см^{-1}$ – symmetric vibrations of $–COO^-$ groups.

Note that the intensity in the region 3500-3200 cm^{-1} in histidine form is smaller than in hydrogen form, in the region 3000 -3200cm^{-1} on the contrary the bands intensity in histidine form is larger. So, number of strongly bounded water in the amino acid form of membrane rises and the amount of weak bounded water decreases. For the membrane in histidine form one can observe also band corresponding to the vibrations of imidazol fragment and amino group at 3100 cm^{-1}.

In the membrane saturated with arginine the intensity in the region 3600-3000 cm^{-1} rises and the minima at 3348, 3163, 3058 cm^{-1} are observed, that characterize the guanidinium fragment vibrations.

The energy of hydrogen bonds ($E_н$) for H^+-, arginine and histidine forms of the membranes have been calculated on the basis of the frequency shift value related to the frequency of not-associated OH-group band (3700 cm^{-1}) [12]. These data are presented in the Table 2.

Table 2. Parameters of hydrogen bonds for MK-40 and FTCM-E membranes in H^+, arginine and histidine forms

MK-40			FTCM-E		
Membrane form	$\bar{\nu}_{OH}$, cm^{-1}	Ен, kJ/mol	Membrane form	$\bar{\nu}_{OH}$, cm^{-1}	Ен, kJ/mol
H^+	3560	9.9	H^+	3496	14.4
	3472	16.1		3413	20.3
	3412	20.4		3301	28.2
	3294	28.7		3074	44.3
	3256	31.4			
	3057	45.5			
	3030	47.4			
Arg	3649	3.6	Arg	3539	11.4
	3618	5.8		3348	24.9
	3562	9.8		3163	38.0
	3398	21.4		3058	45.4
	3285	29.4			
	3059	45.3			
	3038	46.8			
His	3678	1.6	His	3678	1.6
	3447	17.9		3472	16.1
	3258	31.3		3331	26.1
	3203	35.2		3260	31.1
	3032	47.2		3148	39.0

The analysis of hydrogen bonds parameters (Ен) leads to the conclusion that water in the phase of cation-exchange membranes saturated in arginine solution forms associates of different structure. In the phase of heterogeneous cation-exchange membrane MK-40 along with the associates $H_2O…SO_3^-$, $H_2O…COO^-$, $H_2O…H_2O$, $H_2O…NH_3^+$ there exist water molecules with distorted, weakened and partially destroyed hydrogen bonds (Ен is lower than the following value for liquid water).

According to Ен values for MK-40 and FTCM-E membrane it is possible to conclude about the presence of water molecules with destroyed hydrogen bonds, of associates water-water in various environment (Ен=20.7-26.0 kJ/mol) and of water molecules participating in hydrogen bonding with sulfo-group (Ен > 30 kJ/mol). For amino acids forms it is evident that energy of hydrogen bonding for water molecules in various states differs substantially. Water molecules with the most strong hydrogen bonding find themselves near the carboxyl-groups of arginine or histidine, intermediate values of Ен correspond to water molecules participating in the formation of water-water bonds. Molecules of water with destroyed hydrogen bonds are located close to hydrocarbon fragments of amino acid and chains of membrane matrix.

Conclusion

Thus, analysis of vibrational spectra of heterogeneous membranes (MK-40 and FTCM-E) confirms earlier drawn conclusions about the different states of water in the phase of membranes with matrix of different chemical nature and structure. In the phase of heterogeneous membrane there exist intergel regions where water structure is the same as in a pure solvent.

To summarize, sorption of arginine and histidine substantially affects the content and state of water in the both membranes. The results obtained can be used to optimize membrane separation, isolation and concentration of basic amino acids.

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