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Ammonia and carbon dioxide permeability through perfluorosulfonic membranes

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Transmembrane transport of ammonia and carbon dioxide through perfluorosulfonic membranes in ionic forms of transition metals was studied in a wide temperature interval. The different patterns of the temperature plots of the permeability coefficient of ammonia were found for different ionic forms of the membrane. An increase in the ammonia permeability with an increase in the moisture contents of the membrane also depends on its ionic form. The effects observed are explained by the different structures of water—ammonia complexes formed with metal ions. The mechanism of transmembrane transport of ammonia through perfluorosulfonic membranes in various ionic forms is discussed.

Key words: gas permeability, ammonia, carbon dioxide, perfluorosulfonic membranes, mass transfer mechanism.

Application of the membrane technology for the separation of gas mixtures requires highly selective and efficient membranes, in particular, ion-exchange membranes containing ionogenic groups and counterion fixed on the polymeric matrix. Such groups are capable of reversible interacting with one of the components of the gas mixture to be separated. The interaction itself induces the formation of additional channels of accelerated mass transfer in the membrane. Ion-exchange membranes based on the perfluorinated copolymer, which possess high chemical and thermal stability, are of great interest.[1,2] They manifest high efficiency for the separation of NH_3 [3] and CO_2 [4] from gas mixtures. Highly selective transport of NH_3 and CO_2 in ion-exchange membranes is due to the specific interaction of these gases in the polymeric matrix with a movable "mediator" (for NH_3, with the H^+ ion; for CO_2, with the ethylenediamine cation). The transfer of NH_3 through hydrolyzed membranes manufactured from the perfluorinated copolymer depends, to a great extent, on the moisture content in the membranes.[3] A decrease in the moisture contents with temperature decreases the flow of transferred NH_3.

For the development of efficient methods to recover NH_3 at a reduced moisture content of membranes, studying its transmembrane transport through perfluorosulfonic membranes in the ionic forms of transition metals is needed. The sorption of NH_3 by these membranes results in the formation of ammonia complexes of transition metals. The NH_3 transfer in these membranes is due to the exchange of the ligands with ammonia molecules, which are outside the coordination spheres of the ammonia complexes. The type of the metal ion determines the stability of such complexes, the mechanism of their exchange reactions, and their rate constants. The exchange rate is strongly affected by the presence of other molecules in the coordination sphere of the ammonia complexes, in particular, water, which makes it possible to regulate selectivity of the diffusion through the membrane.

We proposed that the choice of the ionic form of the membrane influences both the solubility of the NH_3 molecules and their mobility in the membrane and, hence changes the permeability coefficient of ammonia. In this work, we studied the effect of the ionic form of the polymer (Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, and Cr^{3+} ionic forms) on the mechanism and intensity of the transmembrane transfer of NH_3 and CO_2 through the perfluorosulfonic membranes in the temperature interval from 295 to 473 K.

Experimental

The studies were carried out for films of the copolymer of tetrafluoroethylene and perfluoro-5-methyl-3,6-dioxaoct-1-en-8-sulfonyl fluoride (thickness 240 μm) designated as a mixture of the 118 and 125 batches (produced at the J. S. Company

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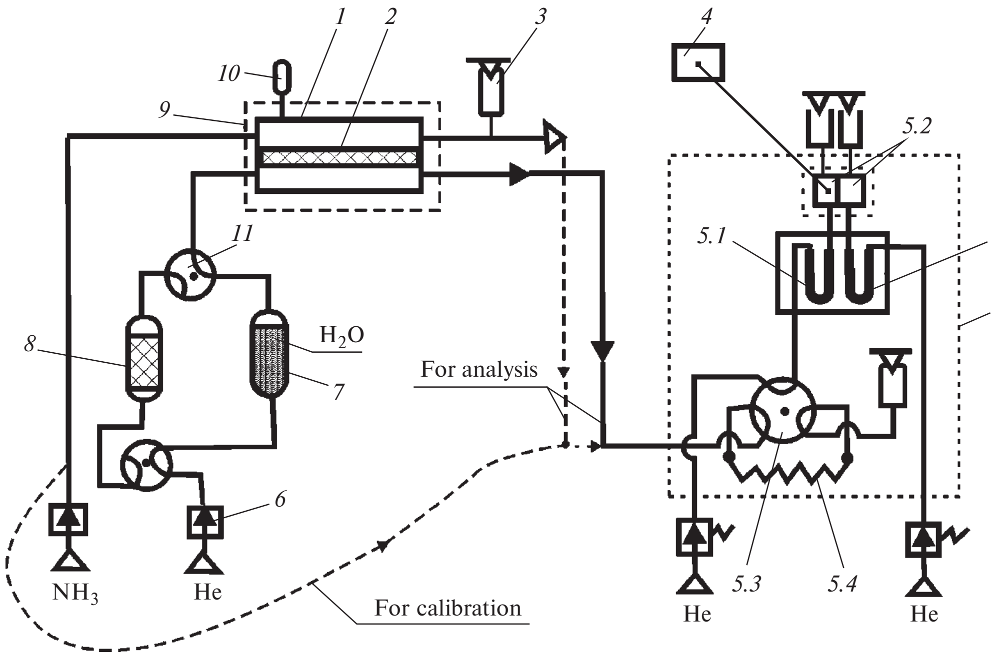

Fig. 1. Scheme of the experimental setup for measuring coefficients of gas permeability through polymeric membranes: *1*, diffusion cell; *2*, studied membrane; *3*, flowmeter; *4*, integrator of the chromatograph; *5*, Tsvet-132 gas chromatograph: adsorption column packed with Porapak N (*5.1*), adsorption column packed with Tseolit 5 (*5.1′*), thermal conductivity sensor (*5.2*), change-over valve (*5.3*), change loop with fixed adjusting volume (*5.4*); *6*, valves for regulating gas flows; *7*, gas humidifier (vessel with water); *8*, dessicant; *9*, air thermostat; *10*, thermometer; and *11*, valves.

"Plastopolimer," St. Petersburg) with an exchange capacity of 0.87 mg-equiv g^{-1} for a dry sample. Membranes were obtained by saponification of the initial films in a 6 *N* NaOH solution for 6 h at $T = 371$ K followed by their transformation into various ionic forms (Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, and Cr^{3+} forms), which were prepared by contacting the membranes with 0.5—1.0 *N* solutions of $CuCl_2$, $ZnSO_4$, $NiSO_4$, $CoSO_4$, $FeCl_3$, and $CrCl_3$ for 1—3 days with repeated renewal of the external solution. Membranes were washed with distilled water to remove the electrolyte, which was not sorbed upon exchange.

Coefficients of gas permeability of ion-exchange membranes (P) were measured on the setup with the chromatographic analysis of the effluent (Fig. 1). Prior to experiments the setup was calibrated with respect to all gases used. The equipment makes it possible to measure the gas permeability of membranes at different temperatures (20—200 °C) and partial gas pressures at the inlet to the membrane and different humidities of the carrier gas (helium).

The studied gas (NH_3 or CO_2) and carrier gas were fed into diffusion cell *1* (see Fig. 1) under the pressure $p = 100$ kPa. The gas mixture pressure was maintained constant at the inlet of the cell during the experiment. At the outlet of the reservoir, ammonia was collected by a special absorber. The target gas diffused through the polymer into a flow-type receiver and was removed from the external surface of the membrane by the carrier gas. After the stationary regime of permeability was achieved, a gas sample was taken at the outlet of the receiver and fed to a column packed with a sorbent.

The gas humidity (degree of moistening of the membrane) has a substantial effect on the gas permeability of membranes.[3,4] Therefore, experiments were performed in two modes corresponding to different partial pressures of water vapor (p_{H_2O}) in the receiver. In the first case, the carrier gas from a cylinder was fed into working cell *1* after passing through dessicator *8* ($p_{H_2O} = 0$); in the second case, after passing through humidifier *7* (p_{H_2O} in the receiver, which was close to the pressure of saturated water vapor at $T = 295$ K and $p_{H_2O} = 2.46$ kPa, was maintained constant). In both cases, the membranes were preliminarily dried at $T = 373$ K in a helium atmosphere for 1.5—2 h. The IR spectra of the film sample from the hydrolyzed copolymer in the Cr^{3+} ionic form (thickness 25 μm) were recorded on a Perkin—Elmer 580 spectrophotometer.

Results and Discussion

The permeability coefficients of NH_3 (P_{NH_3}) and CO_2 (P_{CO_2}) through the perfluorosulfonic membranes in the Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} ionic forms were determined for the temperatures 295—474 K. Measurements were conducted after the samples were stored for 1.5 h at $T = 373$ K under the conditions of NH_3 transfer through the membranes. The plots of P_{NH_3} *vs.* T are presented in Fig. 2. It is seen that for the Cr^{3+}, Fe^{3+}, Co^{2+}, and Ni^{2+} ionic forms they have a pronounced minimum (see Fig. 2, *a*) at 373 K. On going from the Cr^{3+} to Ni^{2+} form, the permeability decreases, especially at temperatures below 373 K. For the Cu^{2+} and Zn^{2+} ionic forms, the plots in the P—T coordinates are monotonically ascending functions in the whole studied temperature interval. The permeability of the Zn^{2+} form is much

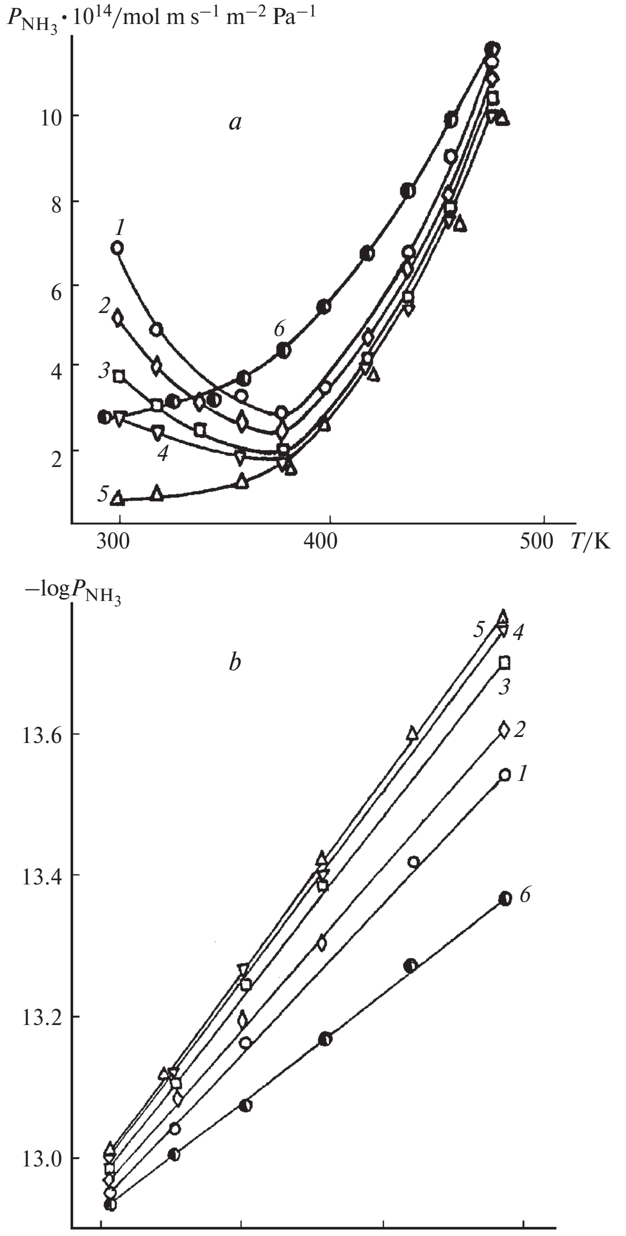

Fig. 2. Temperature influence (T) on the permeability coefficients of NH_3 (P_{NH_3}) through perfluorosulfonic membranes in the Cr^{3+} (*1*), Fe^{3+} (*2*), Co^{2+} (*3*), Ni^{2+} (*4*), Cu^{2+} (*5*), and Zn^{2+} (*6*) ionic forms in the coordinates P_{NH_3}—T (*a*) and ($-\log P_{NH_3}$)—(T^{-1}) (*b*).

higher than that of the Cu^{2+} form. This is especially noticeable at low temperatures.

The distinctions observed for P_{NH_3} (see Fig. 2, *a*) are due to the specific features of the transfer mechanism, which includes the interaction of the NH_3 molecules with the complex ions of the corresponding transition metals. The character of this interaction is determined by the structure of the complex formed in the membrane, its stability and polarizing ability, and the presence of water molecules near the ligands.

In the high-temperature region (373—473 K), the $P_{NH_3}(T)$ plots are well described by the Arrhenius equation (see Fig. 2, *b*) and can be approximated by the expression

$$P_{NH_3}(T) = P_0\exp(-E_{P,NH_3}/RT),$$

where P_0 is the pre-exponential factor, and E_{P,NH_3} is the activation energy of NH_3 permeability.

The calculated E_{P,NH_3} values for the ion-exchange membranes in different ionic forms of transition metals ($p_{H_2O} = 0$, $T = 373$—473 K) are presented below

Ionic form	Cr^{3+}	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
E_P/kJ mol^{-1}	19.9	21.6	24.2	25.1	26.9	14.2

The plots of the permeability coefficient of CO_2 (P_{CO_2}) *vs.* T through the same materials are presented in Fig. 3. It is seen that the permeability of CO_2 in the whole studied temperature interval is independent of the ionic form of the membrane. The activation energy of CO_2 permeability (E_{P,CO_2}) is 31 kJ mol^{-1}, which is higher than E_{P,NH_3} for all ionic forms of the membranes.

In the high-temperature region, the P_{NH3} values are close to the corresponding P_{CO_2} values (*cf.* Figs. 2, *a* and 3, *a*) except for the membrane in the Zn^{2+} form. It can be assumed that in this temperature interval, its transfer, as well as that of CO_2 molecules, occurs over the perfluorinated support of the polymeric matrix due to a high stability of ammonates and a low rate of ligand exchange with diffusing NH_3 molecules.

In the octahedral complexes characteristic of ammonates of the Cr^{3+}, Fe^{3+}, Co^{2+}, and Ni^{2+} ions, the reaction of ligand substitution proceeds[5] *via* the S_N1 mechanism: at first the existing complex dissociates to form a transition complex (coordination number five), which then again adds a new molecule.

In the studied temperature range (295—473 K), the membrane in the Cu^{2+} form has the lowest P_{NH_3} values (see Fig. 2, *a*) close to P_{CO_2} (see Fig. 3, *a*), and the E_{P,NH_3} value virtually coincides with the corresponding value for CO_2. The transfer of NH_3 through the membrane in the Cu^{2+} form occurs over the perfluorinated support of the polymeric matrix involving no ammonia copper complexes.

The ESR method allowed us to establish[6] that when NH_3 is sorbed into the perfluorosulfonic membrane containing the hydrated Cu^{2+} ions, the $Cu(H_2O)_6{}^{2+}$ hexaaqua complexes give the $[Cu(NH_3)_4]^{2+}$ ammonia complexes in the form of octahedra with strong tetragonal distortions. In these complexes, four ligands in the same plane are shifted toward the metal ion, and two ligands on the axis perpendicular to the plane with four ligands are simulta-

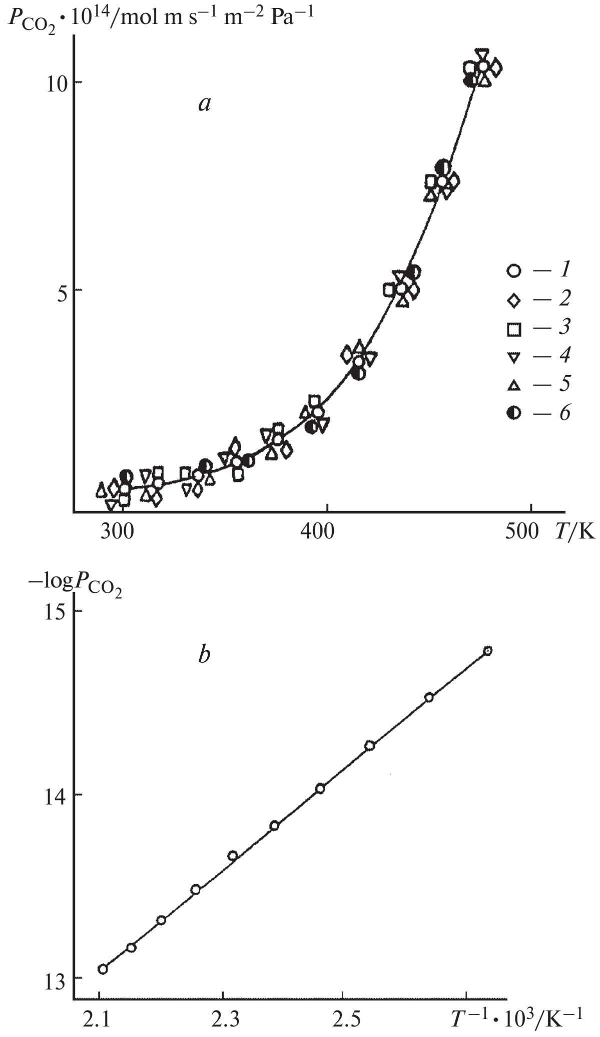

Fig. 3. Temperature influence (*T*) on the permeability coefficients of CO_2 (P_{CO_2}) through perfluorosulfonic membranes in the Cr^{3+} (*1*), Fe^{3+} (*2*), Co^{2+} (*3*), Ni^{2+} (*4*), Cu^{2+} (*5*), and Zn^{2+} (*6*) ionic forms in the coordinates P_{CO_2}—*T* (*a*) and ($-\log P_{CO_2}$)—(T^{-1}) (*b*).

neously shifted in the opposite direction, and they are so much far from the ion that their field can be neglected.

Water in the perfluorosulfonic membrane exists as hydrate shells of counterions (in particular, Cu^{2+}).[7] The NH_3 molecules sorbed into the membrane from the gas phase are additionally polarized in the electric field of the Cu^{2+} ions during their interaction with the Cu^{2+} complex, which results in a higher dipole moment of the NH_3 molecules compared to that of H_2O. In this process, the interaction of the NH_3 molecules with the Cu^{2+} ions is enhanced and the H_2O molecules are displaced from the coordination sphere of the complex. The $[Cu(NH_3)_4]^{2+}$ complexes thus formed can add two H_2O molecules to each axial position. These H_2O molecules are weakly bonded to the Cu^{2+} ion and on contacting the flow of dry gas or on heating can easily be evolved from the complexes and removed from the membrane.[6] In this case, the complexes approach the sulfonic groups, and the bonds are formed through the oxygen atom of the sulfo group, which is in the axial position of the ammonia complex. This way of coordination decreases the mobility of this complex, enhances its stability, and almost completely suppresses the exchange between the ligands and NH_3 molecules not involved in these complexes. The observed ESR spectrum of the $[Cu(NH_3)_4]^{2+}$ complexes at $T = 373$ K confirms[6] their stability in the membrane.

In the high-temperature region (373—473 K), P_{NH_3} for the membranes with different metal ions increases in the series $Ni^{2+} < Co^{2+} < Fe^{3+} < Cr^{3+} < Zn^{2+}$ (see Fig. 2, *a*). The similar sequence of decreasing E_{P,NH_3} values (see above) is exhibited by the corresponding ionic forms of the membrane. The observed effects correlate with the series of stability of the complexes of bivalent metals of the Transition Period.[5] In this series, regardless of the nature of the donor group, the stability of these complexes changes in the sequence $Fe^{2+} < Co^{2+} < Ni^{2+} < Zn^{2+} < Cu^{2+}$. The Fe^{3+} complexes (in particular, ammonates) are still less stable than the Fe^{2+} complexes. The P_{NH_3} values are higher when the value of the NH_3 flow is substantially affected by processes of exchange interactions of its molecules with complexes of ions of the corresponding metals.

For the membrane in the Cr^{3+} form, this influence is especially pronounced, and the E_{P,NH_3} value is relatively low, although the stability constant (K_N) for the $[Cr(NH_3)_6]^{3+}$ complexes is highest among the ions studied and is close to the corresponding value for the $[Cu(NH_3)_4]^{2+}$ complex.[5] In the indicated temperature interval, mixed aquaamino complexes participate in the NH_3 transfer through the membrane containing introduced Cr^{3+} ions.

The data of IR spectroscopy confirm this assumption. Figure 4 presents the IR spectra of the film prepared from the hydrolyzed perfluorinated copolymer in the Cr^{3+} form. It is seen that heating of the film does not virtually change the spectrum and only decreases the intensity of the band at 3500 cm^{-1} attributable to stretching vibrations of the O—H bond in the water molecule. This implies some decrease in the water content of the complex involving Cr^{3+} ion. The process of hydration of the Cr^{3+} and Fe^{3+} ions are characterized[5] by the highest reaction heats and, correspondingly, the highest bonding energies of the H_2O molecules with the Cr^{3+} and Fe^{3+} ions. It can be assumed that in the membrane doped with the Fe^{3+} ions the H_2O molecules are in the composition of the solvate shells around introduced ions, and the mixed aquaamino complexes also participate in the NH_3 transfer. Water molecules coordinated in the Cr^{3+} and Fe^{3+} complexes exist in the reversible interaction with the sorbed NH_3 molecules, and that increases the flow of ammonia through the membrane in the considered temperature interval.

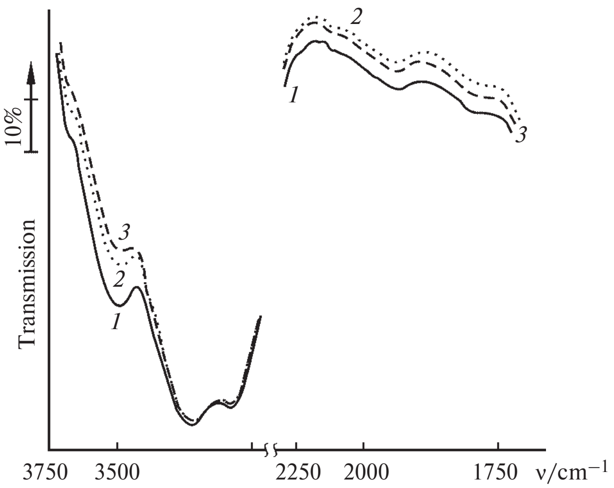

Fig. 4. IR spectra of the film of the hydrolyzed perfluorinated copolymer in the Cr^{3+} ionic form stored for 2 h at $T = 295$ K in NH_3 (*1*), then dried by blowing with an inert gas (He) for 2 h at $T = 373$ K (*2*), and stored for 2 h at $T = 423$ K in NH_3 (*3*).

Still stronger distinctions in the P_{NH_3} values for the perfluorosulfonic membranes in the ionic forms of transition metals are observed at low temperatures (from 295 to 373 K) (see Fig. 2, *a*). These differences can be accounted for by different mechanisms of NH_3 transfer in which the determining role belongs to water, either being already in the membrane or coming into it together with NH_3 during its transmembrane transfer. The water in the membrane is localized near the complexes, and its considerable portion form ligands in the mixed aquaamino complexes.

The following equilibria are established in aqueous solutions of aquaamino complexes of transition metals:

$$M^{z+}\cdot aq + L \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (ML)^{z+}\cdot aq,$$

$$(ML_{n-1})^{z+}\cdot aq + L \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (ML_n)^{z+}\cdot aq,$$

where M is the transition metal, z^+ is the ion charge, L = NH_3, and n is the number of ligands. The stability constant of the complex $K_N = [(ML_n)^{z+}]/\{[(ML_{n-1})^{z+}][L]\}$ decreases with the successive substitution of the H_2O molecules for NH_3.[8] An increase in the number of the H_2O molecules in the complex enhances its stability and decreases the dissociation rate of the complex to NH_3. The dissociation rate constants of the $[Ni(H_2O)_5NH_3]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ complexes at 25 °C are[5] 6.6 and $6.6 \cdot 10^4$ s^{-1}, respectively, and the rate of exchange of the NH_3 molecules is independent of the concentration of free molecules of the latter. The results obtained confirm the dissociative mechanism of ligand exchange in such complexes.

One can assume that in the 295—373 K interval the "specific" transfer including the exchange of the NH_3 molecules in the mixed aquaamino complexes additionally contributes to the general NH_3 flow through the membrane. In this case, one can expect that the P_{NH_3} values for the membranes in the Cr^{3+}, Fe^{3+}, Co^{2+}, and Ni^{2+} forms would increase with temperature. However, the experimental data indicate the opposite trend: the permeability of ammonia in the low-temperature region decreases with increasing temperature (see Fig. 2, *a*).

Since transition metal ions possess a high polarizing power, hydroxo complexes are formed from their aqua complexes. This occurs due to hydrolysis (acidic ionization) with removal of a proton from the internal sphere of the complex ion and its addition to the H_2O molecule[5]:

$$[M(H_2O)_n]^{z+} + H_2O \rightleftharpoons [M(H_2O)_{n-1}(OH)]^{(z-1)+} + H_3O^+.$$

The hydrolysis constants (pK_a) of some aqua ions are presented[8] below.

Metal ion	Cr^{3+}	Fe^{3+}	Co^{2+}	Ni^{2+}	Zn^{2+}	Cu^{2+}
pK_a	3.8	2.2	8.9	10.6	8.8	6.8

When ammonia is transferred through the membrane containing the aqua and mixed aquaamino complexes, an H^+ ion detached from the H_2O from the internal sphere of the complex can interact with a sorbed NH_3 molecule to form the NH_4^+ ion

$$[M(H_2O)_n]^{z+} + NH_3 \rightleftharpoons [M(H_2O)_{n-1}(OH)]^{(z-1)+} + NH_4^+.$$

The NH_4^+ ion is hydrated by the water molecules, which lie outside the coordination spheres of the complexes, and, being localized near them, plays the role of the sorption center for the transmembrane transfer of the NH_3 molecules. These ions, along with the water molecules in the membrane matrix and transferred NH_3 molecules, form a single system of interrelated particles with hydrogen bonds. The transmembrane transfer of ammonia occurs just along this system.

The permeability coefficients of NH_3 in the 295—373 K interval for the membranes in the Cr^{3+} and Fe^{3+} forms are higher than those for the membranes in the Co^{2+} and Ni^{2+} forms (see Fig. 2, *a*). The Cr^{3+} and Fe^{3+} ions (unlike the Co^{2+} and Ni^{2+} ions) exist only as aqua complexes and, therefore, the hydrolysis of the coordination sphere of the complexes increases the content of the NH_4^+ ions in the membrane, enhances the solubility of the NH_3 molecules, and increases the P_{NH_3} value.

The lowest P_{NH_3} value was observed for the membrane in the Cu^{2+} form (see Fig. 2, *a*, curve *5*). This is due to the high stability of the $[Cu(NH_3)_4]^{2+}$ complexes and the low polarizing power of the Cu^{2+} ions in them.

The membranes in the Zn^{2+} form are characterized by the different character of the plot of P_{NH_3} *vs.* *T*. For the

NH_3 transfer, the membrane with the introduced Zn^{2+} ions contain tetrahedral $[Zn(NH_3)_4]^{2+}$ complexes, which are typical of d^{10} metal ions. Exchange processes in these complexes are interpreted in the framework of the mechanism of nucleophilic substitution S_N2,[5,9] whose rate is determined by nucleophilicity of the reactant. The correlation of the type[5]

$$\log(K/K_0) = \alpha P_m + \beta H,$$

is used for such reactions, where K_0 is the equilibrium constant for water, K is the equilibrium constant for various nucleophiles, α and β are constants, P_m is polarizability, and H is the basicity with respect to proton determined as $H = 1.74 + pK_a$. The pK_a values for OH^-, NH_3, and H_2O are 15.7, 9.5, and −1.7, respectively.

During ammonia transfer, its easily polarized molecules completely substitute water molecules in the coordination spheres of the Zn^{2+} complexes. The exchange rate of the NH_3 molecules combined in the zinc complexes with ammonia molecules outside the complexes is higher than that in other complexes studied. Consequently, a relatively high contribution of ammonia transfer over the "specific" sorption sites to the overall flow of transferred NH_3 can be expected. Note that E_{P,NH_3} for the transfer through the membrane in the Zn^{2+} form is lowest among the membranes containing transition metal ions (see above).

The influence of water on the permeability of NH_3 can be seen by the comparison of the results of NH_3 transfer through the membrane in the Zn^{2+} form and in the mixed Cu^{2+}—Zn^{2+} form.* With this purpose, we constructed the plot of P_{NH_3} *vs.* molar fraction of Cu^{2+} in the membrane (X) (Fig. 5). It is seen that at $X < 0.3$ the value of P_{NH_3} increases linearly with the molar fraction of Cu^{2+} and decreases at $X > 0.3$. The increase in X to 0.3 increases the number of the H_2O molecules coordinated to the Cu^{2+} ions in the axial positions of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complexes near the $[Zn(NH_3)_4]^{2+}$ complexes. Due to the polarizing effect of the Zn^{2+} ions, the water molecules can dissociate to form the H^+ and OH^- ions, which are capable of substituting the NH_3 molecules in the coordination spheres of the $[Zn(NH_3)_4]^{2+}$ complexes. The NH_4^+ ions formed by the interaction with protons act as additional sorption centers for the transferred NH_3 molecules increasing P_{NH_3}. At $X > 0.3$ the contribution from the NH_3 transfer involving the $[Zn(NH_3)_4]^{2+}$ complexes goes down because their concentration in the membrane decreases. However, an increase in the Cu^{2+} concentration in the membrane increases the moisture content. As a result, the P_{NH_3} value approaches the corresponding value for the membrane in the Zn^{2+} form. The further increase in the moisture content of the membrane in the ionic forms of transition metals can considerably enhance their permeability with respect to NH_3.

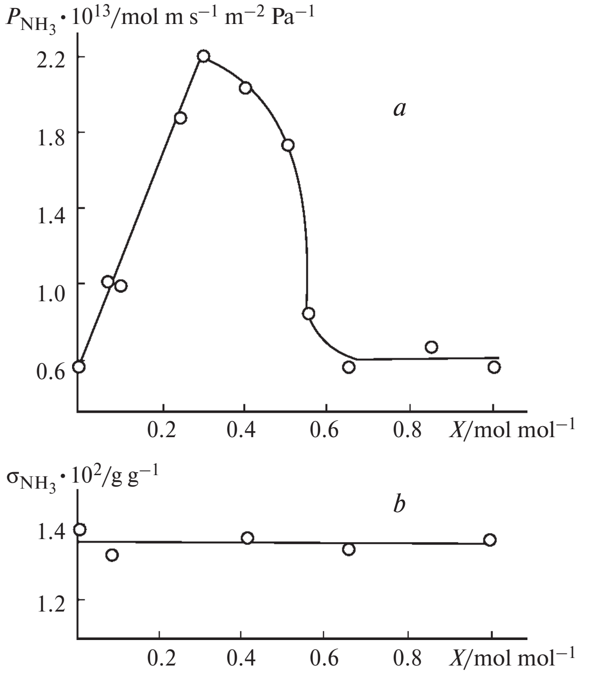

Fig. 5. Permeability coefficient of NH_3 (P_{NH_3}) (*a*) and coefficient of its solubility σ (*b*) for the perfluorosulfonic membranes in the mixed Cu^{2+}—Zn^{2+} form as functions of the molar fraction of Cu^{2+} (X) in the membrane at $T = 295$ K ($p_{H_2O} = 0$).

Table 1 contains the data on the influence of the ionic form of the membrane on P_{NH_3} at ~20 °C. It is seen that in the dry carrier gas, on going from the Cu^{2+} to Cr^{3+} ionic form, the permeability of NH_3 increases more than six-

Table 1. Influence of the nature of the ionic form of the membrane on the permeability coefficients of NH_3 (P_{NH_3}) at different pressures of water vapor (p_{H_2O}) in the carrier gas fed on the membrane ($T = 295$ K)

Ionic form	$P_{NH_3} \cdot 10^{14}$/mol m s^{-1} m^{-2} Pa^{-1}	
	$p_{H_2O} = 0$	$p_{H_2O} = 2.46$ kPa
Cr^{3+}	6.9	129.0
Fe^{3+}	5.2	63.4
Co^{2+}	3.8	24.3
Ni^{2+}	2.8	14.6
Cu^{2+}	1.1	5.3
Zn^{2+}	2.8	46.2

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* To obtain mixed Cu^{2+}—Zn^{2+} forms, the membrane was stored in 0.1 *M* aqueous solutions of copper and zinc sulfates with different ratios of the Cu^{2+} and Zn^{2+} ions. The overall concentration of ions remained unchanged at any ratios of these components. The concentration of the Cu^{2+} ions in samples of the membranes was monitored[10] using ESR spectra.

fold (from $1.1 \cdot 10^{-14}$ to $6.9 \cdot 10^{-14}$ mol m s^{-1} m^{-2} Pa^{-1}). Note for comparison that in the membranes based on polysulfone $P_{NH_3} = 1.1 \cdot 10^{-14}$ mol m s^{-1} m^{-2} Pa^{-1}. Moistening of the carrier gas substantially affects the permeability of NH_3 through the membranes in different ionic forms.

It follows from the data in Table 1 that the increase in P_{NH_3} depends on the ionic form of the membrane and is associated with the specific features of the state of water in the polymeric matrix. For the membrane in the Cu^{2+} form, the observed increase in P_{NH_3} is due to the additional dissolution of the NH_3 molecules in "swelling" water, which comes to the membrane and is weakly bound to the $[Cu(NH_3)_4]^{2+}$ complexes. Due to hydrolysis additional sorption sites as NH_4^+ ions can be formed in the membranes in the Ni^{2+} and Co^{2+} forms. The H_2O molecules coming with the moistened carrier gas are coordinated with these ions to form hydrated shells and participate in NH_3 transfer. In the membranes with the introduced Fe^{3+} and Cr^{3+} ions, along with the formation of the hydrated shells around the hydrolyzed NH_4^+ ions, these hydrated shells can additionally be bound to produce a branched network of hydrogen bonds between the NH_4^+ ions and H_2O molecules. This increases the solubility of NH_3 in the membrane, the exchange rate of the NH_3 molecules in the NH_4^+ ions and, finally, P_{NH_3}. When the moisture content in the Zn^{2+}-membrane increases, the OH^- ions formed due to the hydrolysis of water molecules partially substitute the NH_3 molecules in the coordination spheres. This decreases the stability of the Zn^{2+} complexes, weakens the bonds of the Zn^{2+} ion with the coordinated NH_3 molecules, and increases the exchange rate with the NH_3 molecules, which are not constituents of the considered complexes. The NH_4^+ ions yielded by the interaction of NH_3 with water molecules and the OH^- ions form together with the water molecules developed networks of hydrogen bonds. The net result is an increase in P_{NH_3}.

Thus, the structure of the NH_3 complexes with transition metal ions introduced into the membrane governs the transmembrane transfer of ammonia. The role of the complexes increases substantially when the membrane contains water molecules, which affect the rate of reversible interactions of the NH_3 molecules with the metal ions and also participate in the formation of channels serving to facilitate ammonia transfer.

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