

Raman spectroscopic study of anion-exchange membranes in modified photographic fixer solution

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FT-Raman spectroscopy was applied for adsorption studies of anions at various anion-exchange membranes (ACS, AMX, AMI-7001, and MA-40) from an aqueous modified fixer solution containing Br^- , $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} , and SO_3^{2-} ions. Difference spectra constructed from membranes incubated in the modified fixer and 1M KBr reference solutions revealed presence of bands corresponding to internal vibrations of $\text{S}_2\text{O}_3^{2-}$ and SO_4^{2-} anions. A shift of S-O symmetric stretching vibration to higher frequencies compared with the ion in solution, and an opposite shift of stretching S-S mode evidenced coordination of $\text{S}_2\text{O}_3^{2-}$ ion with ACS, AMX, and AMI-7001 membranes through the S atom. Formation of sulfur clusters, predominantly in the form of S_8 rings, inside the MA-40 membrane was observed. The present results demonstrate a potential of FT-Raman spectroscopy for probing the competition adsorption and coordination of anions at anion-exchange membranes.

Key words: anion-exchange membrane, thiosulfate, photographic fixer, Raman spectroscopy

INTRODUCTION

The regeneration of the spent photographic fixer solution is based mainly on the removal of the surplus of silver and halide ions [1–3]. In praxis this process can be performed by electrolysis, using a cell with separated electrode compartments by anion-exchange membranes [3]. It enables to avoid the anodic oxidation of fixer components. On the other hand, the surplus of halide ions can be removed from a solution placed in cathodic compartment via migration through the membrane to the anodic compartment. Evidently, the membrane should be selective to the anions to be separated. Recently, we have studied the selectivity of four anion-exchange membranes, AMX, ACS (Neosepta, Japan), AMI-7001 (UltraxTM, USA), and MA-40 (PO Stchekin, Russia) to the migration of Br^- , $\text{S}_2\text{O}_3^{2-}$, CH_3COO^- , SO_4^{2-} , and SO_3^{2-} anions [3]. These anions are present in real fixer solutions. It has been established that ACS membrane is the most selective to Br^- ions [3]. The current efficiency to Br^- movement through the ACS membrane reached ~ 70% and considerably exceeded this parameter for other membranes. The ACS membrane was characterized by Br^- selectivity which was ~2–5 times higher than the other membranes studied.

It was interesting to elucidate the reasons of this difference in membrane selectivity. Presumably, the primary cause of this phenomenon lies in the peculiarities of competitive adsorption of anions on the membrane surface. The second penetration step through the membrane is the interaction between the anion-exchange groups and anions. The anion migration kinetics depends on various factors, such as conformation of the adsorbed species, interaction strength with membrane components, and properties of the double layer at the charged interface. All these factors may depend on the material from which the membrane is made.

To understand the adsorption process at a molecular level, we have employed the Raman spectroscopic technique which is highly sensitive to the conformation and bonding of molecular species under investigation [4–6].

In this work, the sorption of anions Br^- , $\text{S}_2\text{O}_3^{2-}$, CH_3COO^- , SO_4^{2-} , and SO_3^{2-} into anion-exchange membranes AMX, ACS, AMI-7001, and MA-40 is examined by means of Fourier transform Raman (FT-Raman) spectroscopy.

EXPERIMENTAL

Materials

Modified fixer solution was prepared in proportions corresponding to industrial Kodak fixer solution [3]:

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0.84 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$ + 0.16 M $\text{Na}_2\text{S}_2\text{O}_3$ + 0.50 M CH_3COOH + 0.10 M $\text{Al}_2(\text{SO}_4)_3$ + 0.10 M Na_2SO_3 + 0.19 M KBr. Reagents: $\text{Na}_2\text{S}_2\text{O}_3$, CH_3COOH , $\text{Al}_2(\text{SO}_4)_3$, Na_2SO_3 and KBr (purum, p. a) were obtained from Fluka and $(\text{NH}_4)_2\text{S}_2\text{O}_3$ (purum, p.a.) from Aldrich.

Four types of anion-exchange membranes were used in this work: ACS, AMX (Neosepta, Japan), AMI-7001 (Ultrax™, USA), and MA-40 (PO Shchekino, Russia). The size of the membranes was $\sim 1.0 \times 1.0 \text{ cm}^2$. In Raman experiments, two membrane samples were investigated: one incubated for 20 h in 1 M KBr reference solution and the other incubated for the same time in a modified fixer solution. After incubation the membranes were washed with the Millipore-Q purified (18.2 M Ω cm) water and maintained in water for 16 h. Finally, the membranes were dried with filter paper and pressed between two alumina holders, one of which contained a rectangular window for Raman measurements.

Raman spectroscopy

Raman measurements were carried out with a FT-Raman spectrometer (Perkin-Elmer, Model Spectrum GX) equipped with an InGaAS detector operating at room temperature. The excitation was provided by an air-cooled diode-pumped Nd-YAG laser with an emission wavelength of 1064 nm. The laser beam was focused to a spot of area $\sim 1 \text{ mm}^2$, and the laser power at the sample was set to 600 mW (400 mW for modified solution studies). In order to reduce photo / thermo effects, the holder with the sample was moved linearly with respect to the laser beam ($\sim 20 \text{ mm s}^{-1}$) [7]. No differences, except a lower signal-to-noise (S/N) ratio, were observed in the spectra recorded with 50 mW laser power, indicating absence of photo / thermo degradation effects on the sample. The experiments were carried out in 180° geometry. The spectral resolution was set at 4 cm^{-1} and the wavenumber increment per data point was 1 cm^{-1} . The spectra were acquired by 30–100 scans. None of the spectra presented has been smoothed.

Molecular modeling

All calculations have been performed using the GAUSSIAN 98W software [8]. The structure of the cluster composed of $\text{S}_2\text{O}_3^{2-}$ anion and three water molecules was optimized and the vibrational spectrum was calculated by using density functional theory (DFT) with Becke's three-parameter hybrid functional in conjunction with the Lee, Yang, and Parr correlation functional (B3LYP) [9, 10]. A high level basis set 6-311+G(d,p) was employed. In brief, we did the molecular modeling at a B3LYP/6-311+G(2d,p) level. The calculated frequencies in the range from 200 to 700 cm^{-1} were scaled by a linearly varying scaling factor from 1.2 to 1.06, respectively.

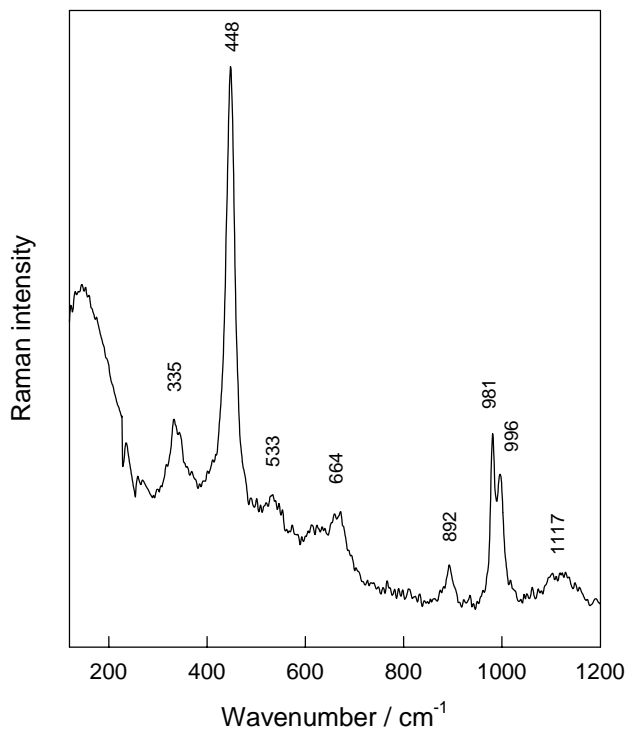


Fig. 1. FT-Raman spectrum of modified fixer solution: 0.84 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$ + 0.16 M $\text{Na}_2\text{S}_2\text{O}_3$ + 0.50 M CH_3COOH + 0.10 M $\text{Al}_2(\text{SO}_4)_3$ + 0.10 M Na_2SO_3 + 0.19 M KBr. FT-Raman excitation was 1064 nm, with 400 mW power. 30 scans were averaged

RESULTS AND DISCUSSION

Figure 1 shows the FT-Raman spectrum of modified fixer solution prepared from 0.84 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 0.16 M $\text{Na}_2\text{S}_2\text{O}_3$, 0.50 M CH_3COOH , 0.10 M $\text{Al}_2(\text{SO}_4)_3$, 0.10 M Na_2SO_3 , and 0.19 M KBr components. Vibrational bands of thiosulfate anion dominated the spectrum. Assignments of the Raman bands were performed based on previous vibrational spectroscopic studies of $\text{S}_2\text{O}_3^{2-}$ anion [11–14] and our own spectral calculations. According to C_{3v} symmetry, the free $\text{S}_2\text{O}_3^{2-}$ anion has six normal modes of vibration, which are distributed by symmetry as follows: $3A_1$ (IR, R) + $3E$ (IR, R) [11, 12]. All vibrations are both infrared and Raman active. Indeed, we are able to assign six features in the spectrum of the modified fixer solution (Fig. 1) associated with thiosulfate anion. It should be noted that we observed a frequency shift and variation in the relative intensity of some bands in the solution $\text{S}_2\text{O}_3^{2-}$ spectrum upon isotopic substitution of H_2O by D_2O . This observation points to a strong interaction of water with $\text{S}_2\text{O}_3^{2-}$ and coupling between the anion and water vibrational modes. Therefore, in the calculations we have used a cluster consisting of a $\text{S}_2\text{O}_3^{2-}$ anion and three water molecules. The most intense 448-cm^{-1} feature in the experimental spectrum (Fig. 1) corresponds to the predominant symmetric S-S stretching vibration, ν (S-S) (A_1). In the calculated spectrum of the $\text{S}_2\text{O}_3^{2-}$ anion,

the $\nu(\text{S-S})$ mode was found as a highly polarized band (depolarization ratio = 0.13) at 446 cm^{-1} . Considerable polarizability of the non-polar S-S bond is responsible for the high intensity of corresponding vibrational band. The broad peak at 337 cm^{-1} belongs to deformation vibration of SO_3 group. Based on calculations, we assigned this mode to rocking vibration, $\rho(\text{SO}_3)$ (E). Symmetric, $\nu_s(\text{SO}_3)$ (A_1), and asymmetric, $\nu_{as}(\text{SO}_3)$ (E), stretching vibrations of SO_3 group are detected in the experimental spectrum at 996 and 1117 cm^{-1} , respectively. In the calculated spectrum these modes were observed at 934 and a doublet at $1055/1095\text{ cm}^{-1}$, respectively. It should be noted that the experimentally observed $\nu_{as}(\text{SO}_3)$ mode (Fig. 1) is considerably broadened. In the calculated spectrum the intense band at 663 cm^{-1} (depolarization ratio = 0.007) was found to be associated with a highly coupled symmetric deformation mode of SO_3 group and S-S stretching (labeled in this work as $\delta_s(\text{SO}_3)$ (A_1)). The corresponding band in the experimental spectrum was detected at 644 cm^{-1} (Fig. 1). Finally, we assigned the low intensity 533-cm^{-1} feature to the asymmetric deformation vibration of SO_3 group, $\delta_{as}(\text{SO}_3)$ (E), which was observed in the calculated spectrum at 496 cm^{-1} . The remaining two peaks at 892 and 981 cm^{-1} were assigned to the C-C stretching motion, $\nu(\text{C-C})$, of acetic acid [15] and symmetric stretching vibration, $\nu_s(\text{SO}_4)$, of the sulfa-

te anion [16, 17], respectively. For a “free” SO_3^{2-} ion (C_{3v} symmetry) vibrational bands in the Raman spectrum are expected at 933 [$\nu_s(\text{SO}_3)$], 967 [$\nu_s(\text{SO}_3)$], 620 [$\delta_s(\text{SO}_3)$], and 469 [$\nu_{as}(\text{SO}_3)$] [18]. However, because of a low concentration of sulfite ions these bands were not observed in the solution spectrum (Fig. 1).

Figure 2 compares the FT-Raman spectra of the ASC membrane incubated in the working modified fixer and reference 1M KBr solutions. Vibrational bands of both incorporated anions from fixer solution and membrane itself are expected to be observed in the spectrum (a) of Fig. 2, while only membrane modes can be visible in the spectrum (b), because the Br^- anion does not possess a vibrational spectrum. The difference spectrum (c) of Fig. 2 immediately indicates that Br^- ions are replaced by other anions when the membrane has been incubated in a model fixer solution. Analysis of the difference spectrum in principle provides the possibility to elucidate the nature and relative amount of adsorbed anions in the membrane as well as structural transformations of the anions induced by the membrane. The substantial difference between the solution and membrane spectrum suggests an interaction between the solution components and the membrane. First, vibrational features in the high frequency region will be assigned. Because of a high relative intensity, the doublet at 1033 and 1046 cm^{-1} must belong to the symmetric stretching S-O vibration. However, neither of $\nu_s(\text{SO}_4)$ and $\nu_s(\text{SO}_3)$ modes of sulfate and sulfite ions, respectively, ever shift to the $1030\text{--}1050\text{ cm}^{-1}$ frequency region upon complexation with cations [18]. Thus, the observed doublet belongs to the thiosulfate anion. It has been demonstrated that stretching vibrations of SO_3 group of the thiosulfate ion may serve as a useful indicator of coordination mode of the anion [11, 13, 14]. The frequency increases if the $\text{S}_2\text{O}_3^{2-}$ ion interacts through the sulfur atom, while an opposite shift is expected for coordination mode via the oxygen atoms. A considerable upshift of $\nu_s(\text{SO}_3)$ mode as compared with an unbonded ion in solution (from 996 to $1033/1046\text{ cm}^{-1}$; Figs. 1 and 2) evidences binding of the thiosulfate anion with the membrane through the sulfur atom. The splitting of the band (1033 and 1046 cm^{-1} components) is most likely associated with the presence of two slightly different binding modes. The asymmetric $\nu_{as}(\text{SO}_3)$ band in the membrane spectrum is observed in the vicinity of 1227 cm^{-1} (Fig. 2c), at a higher frequency as compared with the solution spectrum (1117 cm^{-1} , Fig. 1). Such a shift is consistent with the proposed binding mode [11, 13, 14].

Let us consider the $380\text{--}440\text{ cm}^{-1}$ spectral region where the S-S stretching vibrational mode is expected. Three positive-going features located at 381 , 410 , and 438 cm^{-1} are visible in the difference FT-Raman spectrum of the ASC membrane (Fig. 2c). The fre-

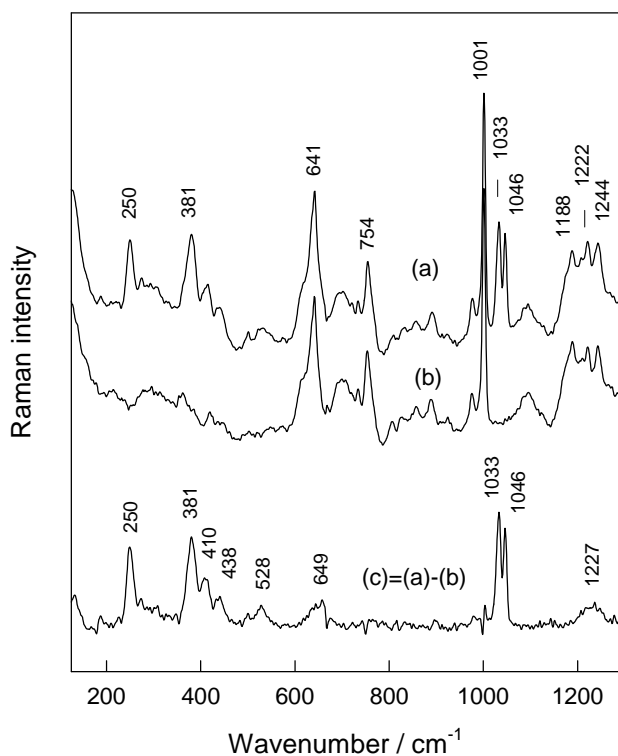


Fig. 2. FT-Raman spectra of ACS membranes incubated in modified fixer solution (a) and reference solution 1 M KBr (b). The difference spectrum (c) is also shown. FT-Raman excitation was 1064 nm , with 600 mW power. 100 scans were averaged

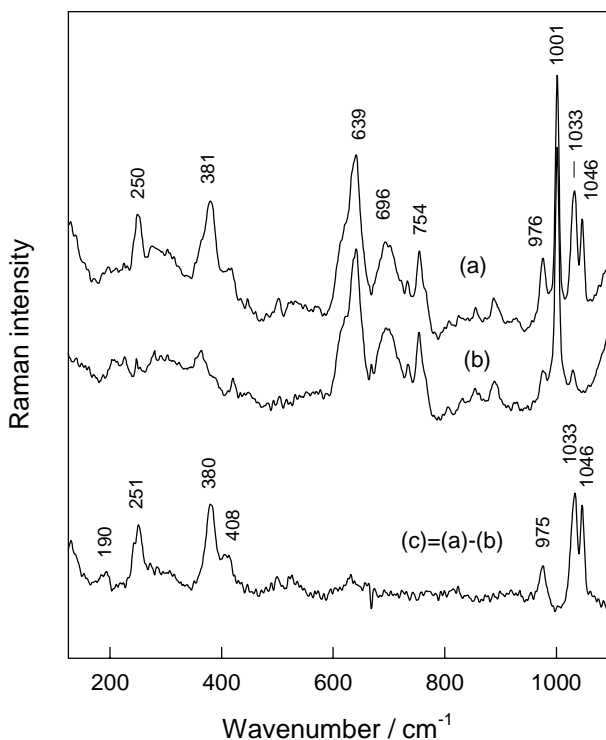


Fig. 3. FT-Raman spectra of AMX membranes incubated in modified fixer solution (a) and reference solution 1 M KBr (b). The difference spectrum (c) is also shown. FT-Raman excitation was 1064 nm, with 600 mW power. 100 scans were averaged

quencies of these bands are lower as compared with the $\nu(\text{S-S})$ mode of the solution $\text{S}_2\text{O}_3^{2-}$ ion detected at 448 cm^{-1} (Fig. 1) in agreement with the proposed coordination mode through the sulfur atom. The splitting of the $\nu(\text{S-S})$ band into several components is most likely associated with the presence of several different $\text{S}_2\text{O}_3^{2-}$ ion binding modes with the membrane. Two peaks at 528 and 649 cm^{-1} (Fig. 2c) were attributed to the $\delta_{\text{as}}(\text{SO}_3)$ and $\delta_{\text{s}}(\text{SO}_3)$ modes of the thiosulfate anion in the ACS membrane. The assignment of the positive-going low-frequency band at 250 cm^{-1} (Fig. 2c) is not obvious. This peak might be associated with (i) the rocking mode of the bonded thiosulfate anion, (ii) thiosulfate–ligand stretching mode, or (iii) vibrational mode of sulfur clusters formed within the membrane from SO_3^{2-} or $\text{S}_2\text{O}_3^{2-}$ anions.

Figure 3 compares the FT-Raman spectra obtained from the AMX membrane immersed in modified fixer (Fig. 3a) and reference KBr (Fig. 3b) solutions. The difference spectrum (Fig. 3c) reveals an intense doublet at $1033/1046\text{ cm}^{-1}$, similarly as observed for the ASC membrane, indicating a bonding of thiosulfate anions with the membrane through the sulfur atom. The low frequency doublet at $380/408\text{ cm}^{-1}$ most likely belongs to $\nu(\text{S-S})$ vibration of the thiosulfate anion. The lower frequency as compared with the unbonded anion in the solution is consistent with the interaction of the anion with the mem-

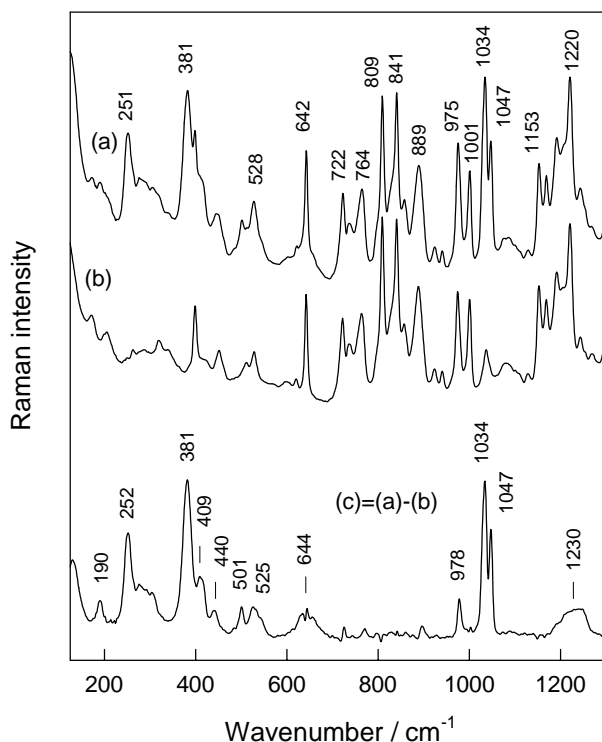


Fig. 4. FT-Raman spectra of AMI-7001 membranes incubated in modified fixer solution (a) and reference solution 1 M KBr (b). The difference spectrum (c) is also shown. FT-Raman excitation was 1064 nm, with 600 mW power. 100 scans were averaged

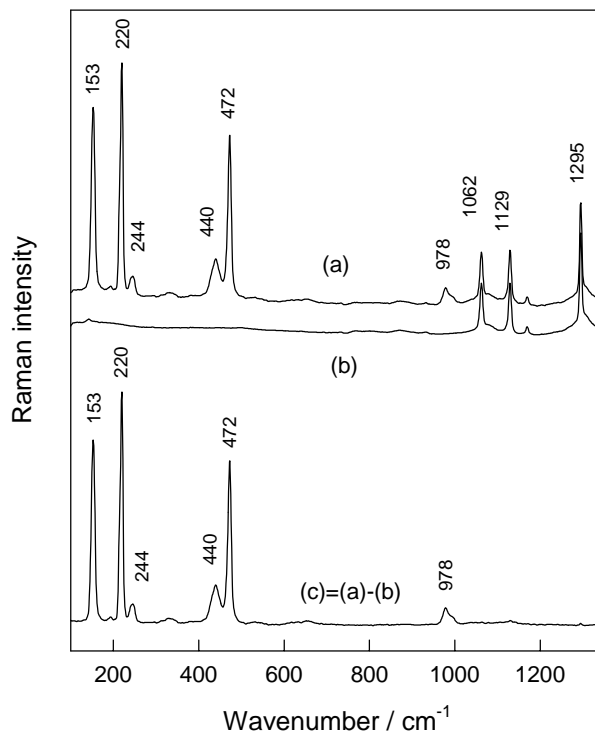


Fig. 5. FT-Raman spectra of MA-40 membranes incubated in modified fixer solution (a) and reference solution 1 M KBr (b). The difference spectrum (c) is also shown. FT-Raman excitation was 1064 nm, with 600 mW power. 100 scans were averaged

rane through the sulfur atom [11, 13, 14]. However, in the difference spectrum of AMX membrane a new band, absent in the spectrum of the ACS membrane, clearly emerged at 975 cm^{-1} (Fig. 3c). We assign this peak to a S-O symmetric stretch, $\nu_s(\text{SO}_4)$, of the sulfate anion [16, 17]. The frequency of the $\nu_s(\text{SO}_4)$ peak from the SO_4^{2-} anion in the membrane is downshifted by 7 cm^{-1} as compared with the unbonded ion in solution (Fig. 1), indicating an interaction of the ion with the membrane. Thus, contrary to ACS membrane, the AMX membrane coordinates not only thiosulfate, but sulfate anions as well. A similar difference spectrum was obtained for the AMI-7001 membrane (Fig. 4); among the prominent thiosulfate $\nu_s(\text{SO}_3)$ bands at 1034 and 1047 cm^{-1} , the $\nu_s(\text{SO}_4)$ mode from sulfate anions at 978 cm^{-1} was clearly visible.

A completely different spectral pattern was shown by the MA-40 membrane (Fig. 5). First, no thiosulfate $\nu_s(\text{SO}_3)$ peaks in the frequency region from 1030 to 1050 cm^{-1} were observed, indicating that $\text{S}_2\text{O}_3^{2-}$ ion did not coordinate with the MA-40 membrane. Second, a set of intense positive-going bands emerged in the difference spectrum at 153 , 220 , 440 , and 472 cm^{-1} . Based on extensive Raman spectroscopic studies of polymeric sulfur compounds [19–22], we assigned the observed low frequency modes primarily to S_8 rings. The intensive 472 cm^{-1} peak was demonstrated to be characteristic of S_8 rings and belong to S-S symmetric stretching vibration [21], while the lower intensity 222 and 154 cm^{-1} bands were assigned to S-S-S symmetric and asymmetric bending modes, respectively [20]. It should be noted that some contribution to the observed FT-Raman spectrum from polymeric linear sulfur species and polysulfides was also possible. Finally, the weak peak at 978 cm^{-1} (Fig. 5c) was due to $\nu_s(\text{SO}_4)$ vibration [16, 17] and demonstrated presence of sulfate anions within the MA-40 membrane. Thus, spectroscopic data presented in Fig. 5 provide evidence for the presence of sulfur clusters primarily in the form of S_8 rings and SO_4^{2-} anions in the MA-40 membrane after incubation in a modified fixer solution.

CONCLUSIONS

Using the Fourier transform Raman (FT-Raman) spectroscopy with excitation at 1064 nm , we have studied the adsorption and structure of anions and sulfur clusters formed upon incubation of ACS, AMX, AMI-7001, and MA-40 anion-exchange membranes in a modified fixer solution containing Br^- , $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} , and SO_3^{2-} anions. Difference spectra constructed by subtraction of the reference spectrum of a membrane incubated in 1 M KBr solution from the sample spectrum obtained by immersion of the membrane in a modified fixer solution revealed adsorption of thiosulfate anions on ACS, AMX, and

AMI-7001 membranes. A considerable blue shift ($37\text{--}51\text{ cm}^{-1}$) of the S-O symmetric stretching mode as compared with the unbonded ion in solution (996 cm^{-1}) evidenced a strong interaction of the thiosulfate anion with the membrane through the sulfur atom. Adsorption of SO_4^{2-} ions was also identified from a characteristic S-O symmetric stretching band at $975\text{--}978\text{ cm}^{-1}$ in the difference spectra of AMX, AMI-7001, and MA-40 membranes. Contrary to other membranes, FT-Raman spectrum of MA-40 showed intense peaks at 153 , 220 , 440 , and 472 cm^{-1} , indicating formation of sulfur clusters, predominantly in the form of S_8 rings, upon incubation of the MA-40 membrane in the modified fixer solution.

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**ANIJONINIŲ MEMBRANŲ, IŠLAIKYTŲ
MODIFIKUOTAME FIKSAŽO TIRPALE, TYRIMAS
RAMANO SPEKTROSKOPIJOS METODU**

Santrauka

FT-Ramano spektroskopijos metodu buvo tiriama anijonų adsorbcija ant anijoninių membranų (ACS, AMX, AMI-7001 ir MA-40), išlaikytų modifikuotame fiksažo tirpale su Br^- , $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} ir SO_3^{2-} jonais. Skirtuminiuose spektruose, gautuose nuo membranų išlaikytų modifikuotame fiksažo ir 1 M KBr palyginimo tirpaluose, buvo matomos $\text{S}_2\text{O}_3^{2-}$ ir SO_4^{2-} anijonų virpesių smailės. S-O jungties simetrinio, valentinio virpesio dažnio sumažėjimas ir priešingas S-S valentinio virpesio dažnio poslinkis parodė, kad $\text{S}_2\text{O}_3^{2-}$ anijonas sąveikauja su ACS, AMX ir AMI-7001 membranomis per S atomą. Nustatyta, kad MA-40 membranoje susidaro daugiausia S_8 žiedų struktūros sieros klasteriai. Pateikti rezultatai rodo FT-Ramano spektroskopijos galimybes, tiriant anijonų konkurencinę adsorbciją ir sąveiką su anijoninėmis membranomis.