

Conductivity and Intermolecular Interactions in Proton-Conducting Gel Electrolytes

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ABSTRACT: Proton-conducting gel electrolytes based on poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVdF), and mixtures of PMMA with PVdF or poly(vinyl chloride) doped by acid solutions in aprotic solvents were synthesized and are discussed in this article. The gel conductivity as a function of the concentrations of acid and polymer and the polymeric matrix composition has been analyzed. Extreme dependence of the conductivity on acid and polymer concentrations was found. It was revealed that within the acid concentration range studied, the gel conductivity was higher than the conductivity of the corresponding liquid electrolytes used for the synthesis. The increase in the electrical conductivity with the growth of the systems viscosity is discussed as an indication of a certain involvement of the polymer matrix in the increase of the charge carrier mobility within the frame of a Grotthuss mechanism. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40674.

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INTRODUCTION

Polymeric gels are important objects for materials science. Proton-conducting gel electrolytes (PGEs) are appropriate alternatives to solid electrolytes because of their rather high conductivity values at temperatures close to ambient ones. A scientific basis, giving the groundwork for practical application of PGEs, is being only developed currently, but the peculiarities of these electrolyte structures and their availability and ease of production testify to the reasonableness of further investigations.¹ It should be noted that so far there has been no clear understanding of the law of the gel composition's influence on the proton-transfer process because of the specificity of the mechanism of this phenomenon.

The results of investigations of PGEs based on poly(methyl methacrylate) (PMMA) or other available polymers doped with solutions of mineral and organic acids in aprotic solvents have been represented in a number of works.^{2–12} To increase the conductivity of gel electrolytes, strong acids, such as sulfuric or hydrochloric acid, can be used as a proton donor.^{4,13,14} These acids have rather high values of dissociation constants in many solvents; this results in a high proton concentration. However, the strong chemical activity of the acids in their concentrated solutions can bring about polymer destruction, which is a serious limitation to practical application.⁴

A literature review showed that the PGE conductivity can increase or decrease steadily or pass the maximum;^{8,9,15–21} this

depends on the nature of both the acid and polymer and on their concentrations.

In this connection, despite a large amount of experimental data on gel electrolyte conductivity, their systematization and comparison are rather complicated, as these results refer to different experimental conditions.

The purpose of this study was to examine the effect of both the acid and polymeric matrix natures and their concentrations on the conductivity and parameters of intermolecular interactions in PGEs.

EXPERIMENTAL

PMMA [weight-average molecular weight (M_w) = 350,000, Aldrich], poly(vinylidene fluoride) (PVdF; M_w = 275,000, Aldrich), poly(vinyl chloride) (PVC; M_w = 233 000, Aldrich), methyl trimethylacetate (MTMA; assay > 99%, Aldrich), *o*-phosphoric acid (85 wt % aqueous solution, reagent grade, Khimmed), sulfuric acid (reagent grade, Khimmed), fluorophosphoric acid (70 wt % aqueous solution, Aldrich), *N,N*-dimethylformamide (DMF; 99.9 wt %, Panreac), and propylene carbonate (PC; 99 wt %, Aldrich) were used without additional purification.

The gel conductivity (κ) was determined by an electrochemical impedance method with an impedance/gain-phase analyzer (Solartron 1260A) over the frequency range 0.1 Hz–1 MHz with a signal amplitude of 10 mV and accuracy higher than 0.2%. The resistance magnitude was found from the high-frequency

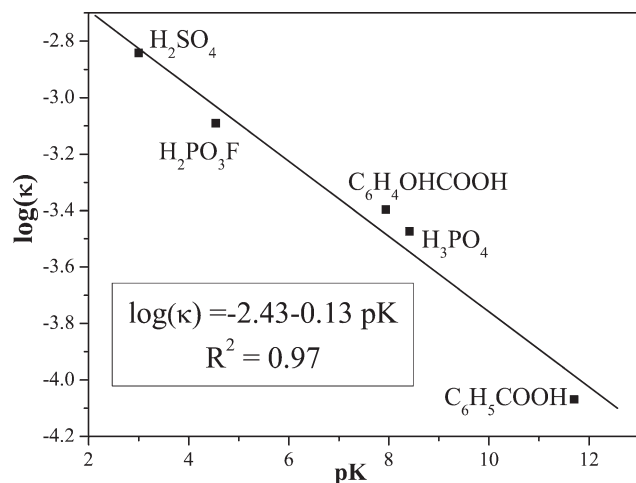


Figure 1. Dependence of the specific conductivity of gel electrolytes with compositions of 9 wt % PMMA-[0.1M acid-DMF] on the acid pK values at 298 K. Data on the acid pK values were taken from the literature for H_2SO_4 ,²⁷ $\text{H}_2\text{PO}_3\text{F}$,^{28,29} $\text{C}_6\text{H}_4\text{OHCOOH}$,³⁰ H_3PO_4 ,²⁸ and $\text{C}_6\text{H}_5\text{COOH}$.³⁰

cutoff corresponding to the bulk gel resistance. All of the measurements were carried out within the temperature range from 298 to 338 K in a cell with platinum electrodes; platinum wire was used to supply the current. The temperature was measured with Haake DC50-K35 thermostat within ± 0.01 K. The cell was calibrated with standards recommended by IUPAC.²² The calibration was done at 298 K; the cell constants at higher temperatures were calculated with an equation from ref. 23.

The viscosities (η) of the gel electrolytes were measured with rotational programmable viscometer (Brookfield DV-II+); the measurement accuracy was equal to $\pm 1\%$.

Attenuated total reflection (ATR) spectra were registered with Bruker Vertex V80 spectrometer over the frequency range 4000–400 cm^{-1} by 128 scans averaging with 2- cm^{-1} resolution at room temperature. All of the ATR spectra, both of the binary liquid and the gel electrolytes, were registered with MVP 2 series attachment (Harrick) with a diamond crystal.

PGEs were prepared according to a procedure described in refs. 24 and 25.

The composition of the gels under investigation was performed as follows:

$$x\text{Pol} - [y(\text{acid}) - \text{solvent}]$$

where x is the polymer content in the gel (wt %) and y is the acid molar concentration in the solvent (mol/l). Here, we would like to note that for the gel synthesis aqueous solutions of some acids were used. Earlier, we showed²⁴ that the contribution of a small amount of water to the PGE conductivity growth was rather low. Moreover, the water contents in both the PGEs and liquid electrolytes were almost the same, so the difference in the conductivity of the liquid and gel systems could not be referred to the water presence.

RESULTS AND DISCUSSION

Earlier,²⁶ it was revealed that the specific conductivity of gel electrolytes with different acids but at their equal concentrations

in doping solutions in DMF increased according to the following acid sequence: Benzoic ($\text{C}_6\text{H}_5\text{COOH}$) < Orthophosphoric (H_3PO_4) < Salicylic ($\text{C}_6\text{H}_4\text{OHCOOH}$) < Fluorophosphoric ($\text{H}_2\text{PO}_3\text{F}$) < Sulfuric (H_2SO_4). The values of the gel specific conductivity were correlated with the acid dissociation constants

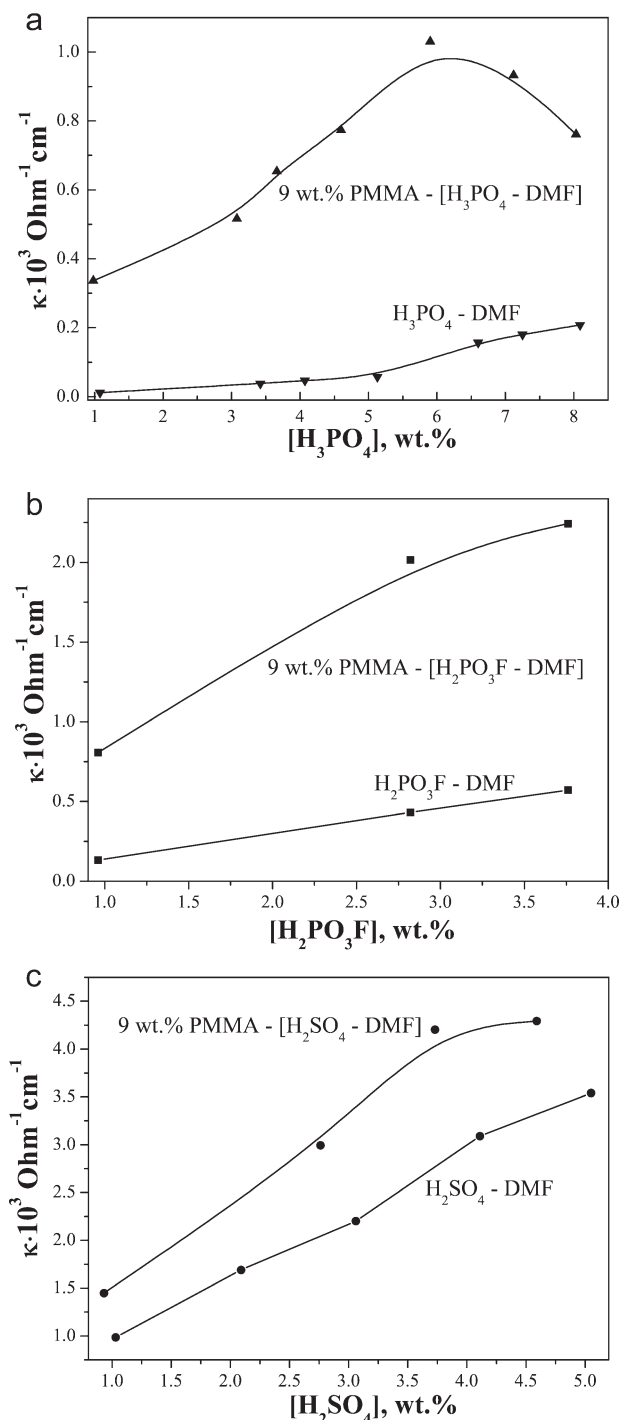


Figure 2. Dependences of the specific conductivity of the binary solutions [y(acid)-DMF] and gel electrolytes with compositions of 9 wt % PMMA-[y(acid)-DMF], prepared on the basis of these binary solutions, on the corresponding acid concentration at 298 K: (a) H_3PO_4 , (b) $\text{H}_2\text{PO}_3\text{F}$, and (c) H_2SO_4 . The data on the conductivity of 9 wt % PMMA-[y H_2SO_4 -DMF] gels were taken from our previous work.²⁵

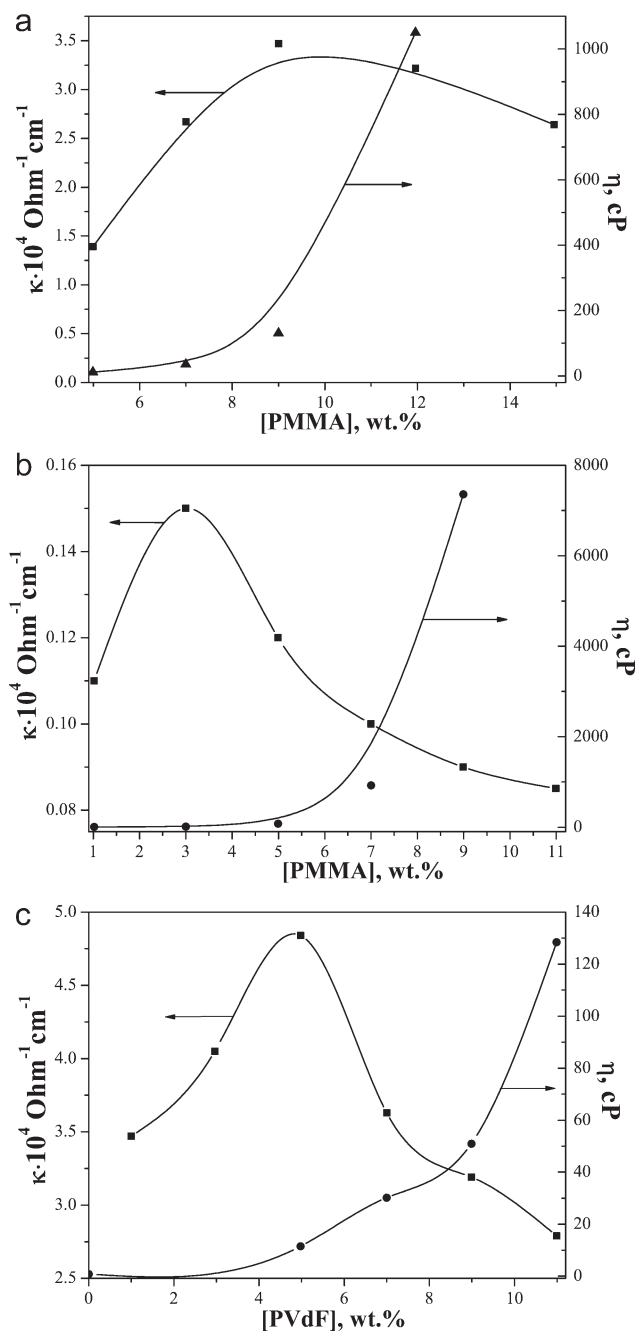


Figure 3. Dependences of the conductivity and viscosity of the PGEs on the polymer concentration: (a) $x\text{PMMA}$ -[0.1M H_3PO_4 -DMF] (these data were taken from our previous work²⁶), (b) $x\text{PMMA}$ -[0.1M H_3PO_4 -PC], and (c) $x\text{PVdF}$ -[0.1M H_3PO_4 -DMF].

in DMF, which could be expressed in the form of the linear equation (Figure 1). Thus, the dependence obtained makes it possible to evaluate the gel conductivity from known pK values of the acids in DMF.

The values of specific conductivity depend not only on the acid nature but on its concentration also. In Figure 2, the dependence of the specific conductivity both of the acid solutions in DMF and the corresponding gel electrolytes on the acid concentration are shown. As shown, the gel conductivity was higher

compared with that of the same acid solution in DMF used for the gel preparation. A similar dependence was observed in the studies in refs.^{9,11,31} Various reasons accounted for this phenomenon, but these explanations were rather ambiguous.^{9,13,20,32} In our opinion, the higher gel conductivity, as compared with that of the binary acid solution, was connected both to the decreasing entropy because of its rotational and translational component changes under passage from the solutions to the gels and to the possible participation of the polymeric matrix in the process of proton transfer.

When the acid concentrations in the solutions increased, their conductivities either steadily increased³³ or passed maxima;^{17,19,21,33,34} this depended on the solvent and acid nature. The appearance of the extreme on specific conductivity concentration dependences is often explained by the simultaneous effect of two opposite phenomena. On the one hand, the content of ionic species increases with increasing total acid concentration; this, consequently, should result in conductivity growth. On the other hand, the strengthening of specific interactions and an increase in the viscosity occur when the acid concentration increases; this depresses the ionic mobility. In the case of the PGEs, the same tendency toward extreme behavior of specific conductivity dependence on the acid concentration

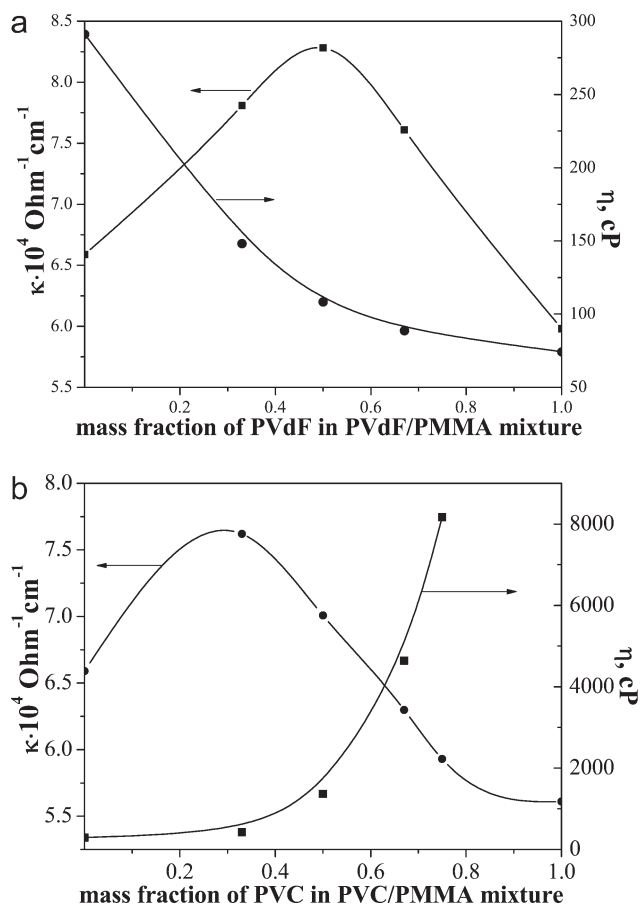


Figure 4. Dependences of the specific conductivity and viscosity of the gel electrolytes 9 wt % mix-[0.3M H_3PO_4 -DMF] on the polymeric matrix composition at 298 K: (a) mix = PVdF/PMMA and (b) mix = PVC/PMMA.

Table I. Activation Energies of the Conductivity and Viscous Flow of the PGEs

| Polymer | PGE composition: xPol-[y(acid)-solvent] | | | | $\Delta G_x^\#$ (kJ/mol) | $\Delta G_\eta^\#$ (kJ/mol) | |
|-----------|---|---------|----------------------------------|-----------|--------------------------|-----------------------------|------|
| | Acid | Solvent | x (wt %) | y (mol/l) | | | |
| PMMA | H ₃ PO ₄ | DMF | 5.0 | 0.1 | 7.9 | 20.3 | |
| | | | 7.0 | 0.1 | 7.9 | 14.3 | |
| | | | 9.0 | 0.1 | 7.0 | 23.1 | |
| | | | 12.0 | 0.1 | 7.5 | 40.2 | |
| | H ₂ SO ₄ | DMF | 9.0 | 0.3 | 8.2 | 33.2 | |
| | | | H ₂ PO ₃ F | 9.0 | 0.1 | 7.7 | 18.3 |
| | | | | 9.0 | 0.1 | 7.8 | 21.7 |
| | | | | 9.0 | 0.3 | 9.1 | 35.6 |
| | H ₃ PO ₄ | PC | 9.0 | 0.4 | 9.5 | 51.2 | |
| | | | 1.0 | 0.1 | 11.4 | 10.3 | |
| | | | 3.0 | 0.1 | 10.1 | 10.8 | |
| | | | 5.0 | 0.1 | 10.7 | 22.9 | |
| PVdF | H ₃ PO ₄ | DMF | 7.0 | 0.1 | 10.8 | 40.8 | |
| | | | 9.0 | 0.1 | 11.7 | 57.1 | |
| | | | 5.0 | 0.1 | 7.5 | 13.6 | |
| | | | 7.0 | 0.1 | 7.3 | 13.2 | |
| PVdF/PMMA | H ₃ PO ₄ | DMF | 9.0 | 0.1 | 11.7 | 18.6 | |
| | | | 11.0 | 0.1 | 12.9 | 18.3 | |
| | | | 4.5/4.5 | 0.3 | 6.9 | 19.2 | |
| | | | 6.0/3.0 | 0.3 | 6.9 | 21.4 | |
| PVC/PMMA | H ₃ PO ₄ | DMF | 3.0/6.0 | 0.3 | 7.3 | 22.9 | |
| | | | 9.0/0 | 0.5 | 7.8 | 22.6 | |
| | | | 6.0/3.0 | 0.3 | 6.8 | 67.0 | |
| | | | 6.7/2.7 | 0.3 | 7.0 | 72.4 | |
| | | | 4.5/4.5 | 0.3 | 6.1 | 42.6 | |
| | | | 3.0/6.0 | 0.3 | 7.8 | 27.5 | |

was also observed (Figure 2). For H₃PO₄-based PEGs, the extreme appearance was rather obvious, whereas for other gels, just some trend toward extreme formation was seen. Probably for PGEs with H₂SO₄ and H₂PO₃F, the extremes would also occur but at higher concentrations of these acids; however, at acid contents higher than 5 wt %, these gels were not stable.

In Figure 3, the dependences of the conductivity and viscosity of the PMMA (PVdF)–[0.1M H₃PO₄–DMF (PC)] systems on the polymer content are shown.

As one can see, with increasing polymer concentration up to the concentrations corresponding to the maxima on the conductivity concentration dependences, the conductivity increased, despite the system viscosity growth; in our opinion, this was due to a decrease in the entropy contribution to the proton-transfer process. The reduction of electrolyte entropy in the confined geometry of the polymeric matrix resulted in an increase in the conductivity at the expense of the more ordered motion of the charge carriers inside polymeric skeleton. The importance of the entropy influence was pointed out in refs. 35 and 36, where the ionic transport processes in membranes were studied. Further increases in the polymer concentration, higher than the one corresponding to the maximal conductivity, led to

substantial viscosity growth and, as a consequence, a decrease in conductivity.

The extreme positions on the concentration dependences of the gel conductivity (Figure 3) were determined by the natures of both the polymeric matrix and the solvent. At the same compositions of doped solution, the PMMA-based gel had a maximal conductivity at about 9 wt % [Figure 3(a)] of the polymer, whereas in the case of the gel with PVdF [Figure 3(c)], this was observed at about 5 wt % of the polymer. When the same polymeric matrix was used for gel synthesis, the conductivity maximum position corresponded to 9 wt % PMMA for the gel with DMF [Figure 3(a)] and to about 3 wt % PMMA in the case of PC [Figure 3(b)]. This phenomenon was probably connected to the substantially higher viscosity of the systems containing PC as compared with those containing DMF.

We also studied PGEs based on mixed polymers (PVdF–PMMA and PVC–PMMA) doped with a 0.3M solution of phosphoric acid in DMF depending on the constituent polymer ratio [Figure 4(a,b)].

The obtained dependences of the PGE conductivity on the mixed polymeric matrix composition (Figure 4) also passed maxima.

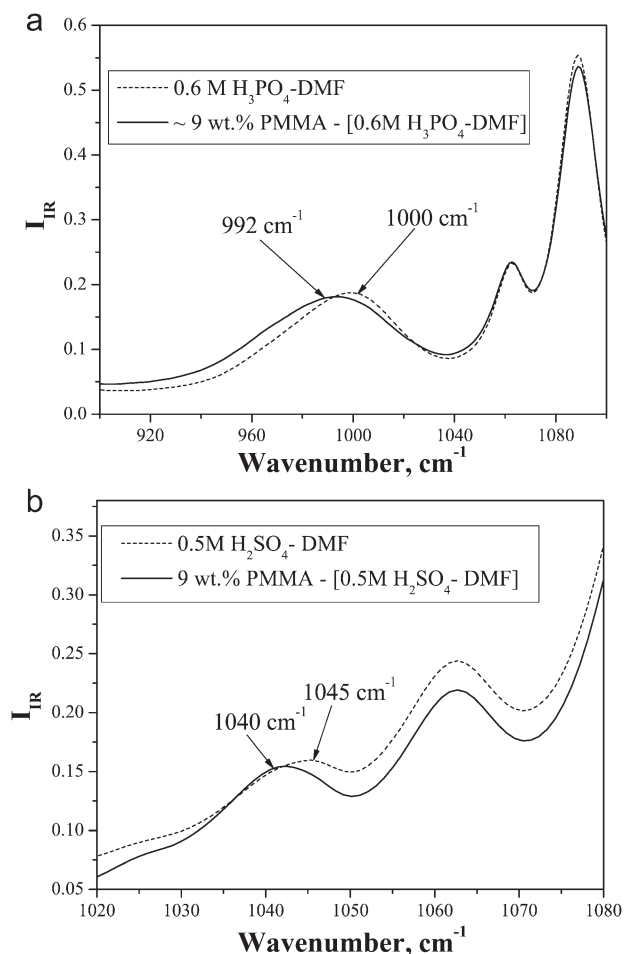


Figure 5. ATR spectra of the gel and liquid electrolytes 9 wt % PMMA-[γ H₃PO₄ (or H₂SO₄)-DMF] within the frequency region of the stretching modes of (a) P-O(H) and (b) S-O(H) groups. Here and further, I_{IR} is the intensity of infrared spectrum (absorbance).

The extreme positions depended on the nature of the polymer mixed with PMMA. In the case of the PVdF-PMMA mixture, the extreme was observed at about a 1:1 mass ratio of polymers, but that of PVC-PMMA was at approximately 1:2. Even though the viscosity of the PVdF-PMMA gels decreased and that of PVC-PMMA increased, the shapes of the conductivity dependences were similar. The structure of the PMMA matrix probably changed in the same way with addition of either PVdF or PVC. This phenomenon requires further investigation.

For all of the PGEs studied, the temperature dependences of the conductivity and viscous flow obeyed the Arrhenius equation over the temperature range from 298 to 338 K:

$$\kappa = A \exp \left[-\frac{\Delta G_{\kappa}^{\#}}{RT} \right]$$

$$\eta = A \exp \left[\frac{\Delta G_{\eta}^{\#}}{RT} \right]$$

where A is an adjustable parameter; R is the gas constant, $J/(\text{mol} \cdot \text{K})$; T is the thermodynamic temperature, K . In Table I, the values of the activation energies of the conductivity and viscous

flow calculated with these equations are shown. As shown in Table I, a weak tendency toward the conductivity activation energy change was observed with increasing concentration of polymers or acid, whereas the viscosity activation energy grew much more substantially because of the increase in the PGE viscosity.

It should be noted that when proton transfer was realized through the diffusion of charge carriers through the solvent (ion migration or vehicle mechanism), the values of the activation energies of the conductivity and viscosity were close to each other. It is shown in the table that the ΔG_{κ} values depended weakly on the natures and concentrations of the acid, solvent, and polymer and varied within 6–13 kJ/mol, whereas the ΔG_{η} values changed from 10 to 70 kJ/mol. The lower values of activation energy of the conductivity against the ones of the viscous flow probably justified the fact that the proton transfer was preferentially realized through a Grotthuss mechanism.

The Grotthuss mechanism of proton transfer was possible because of hydrogen bonds formed in the systems. Such kind of interactions can be revealed with an ATR spectroscopic method. The hydrogen-bond formation between proton acids and DMF is an established fact. However, the conductivity growth in the PGEs against liquid electrolytes evidently pointed out the polymeric matrix participation in the conductivity process as well. Until now, the mechanism of this participation was not established exactly, and there was no definite opinion on hydrogen-bond formation between acidic protons and C=O groups in the polymeric matrix. This process was the object of our spectroscopic investigation. We studied the possibility of hydrogen-bond formation between the components of the PGEs (acid-DMF and acid-PMMA) earlier for PMMA-based electrolytes doped with sulfuric acid solutions in DMF [9 wt % PMMA-(γ H₂SO₄-DMF)],²⁵ where the region of the stretching modes of C=O groups [$\nu(\text{C}=\text{O})$] of DMF (1660 cm^{-1}) and PMMA (1727 cm^{-1}) were considered. The analysis of the same frequency range for PMMA-based electrolytes doped with phosphoric acid solutions in DMF [9 wt % PMMA-(γ H₃PO₄-DMF)] was performed within this study. In addition to this region of stretching vibrations of P-O(H) (1004 cm^{-1})³⁷ and S-O(H) (1040 cm^{-1}),³⁸ groups of phosphoric and sulfuric acids (for H₂SO₄, this region was not discussed in ref. 25) accordingly were considered. All of these modes were examined in both binary liquid electrolytes (acid-DMF) and PGEs doped with corresponding solutions.

The analysis of the IR spectra within frequency range around 1000 cm^{-1} and corresponding to the stretching vibrations of P-O(H) (1004 cm^{-1})³⁷ and S-O(H) (1040 cm^{-1})³⁸ groups showed that in the gel electrolytes, these bands shifted to a low-frequency region as compared with the corresponding liquid binary electrolyte (Figure 5). In our opinion, this fact could be connected with hydrogen-bond formation between the OH groups of the acid molecules and the C=O groups of PMMA.

The frequency region from 1600 to 1800 cm^{-1} , where the stretching modes of C=O groups [$\nu(\text{C}=\text{O})$] both in DMF (1660 cm^{-1}) and PMMA (1727 cm^{-1}) were observed, was of

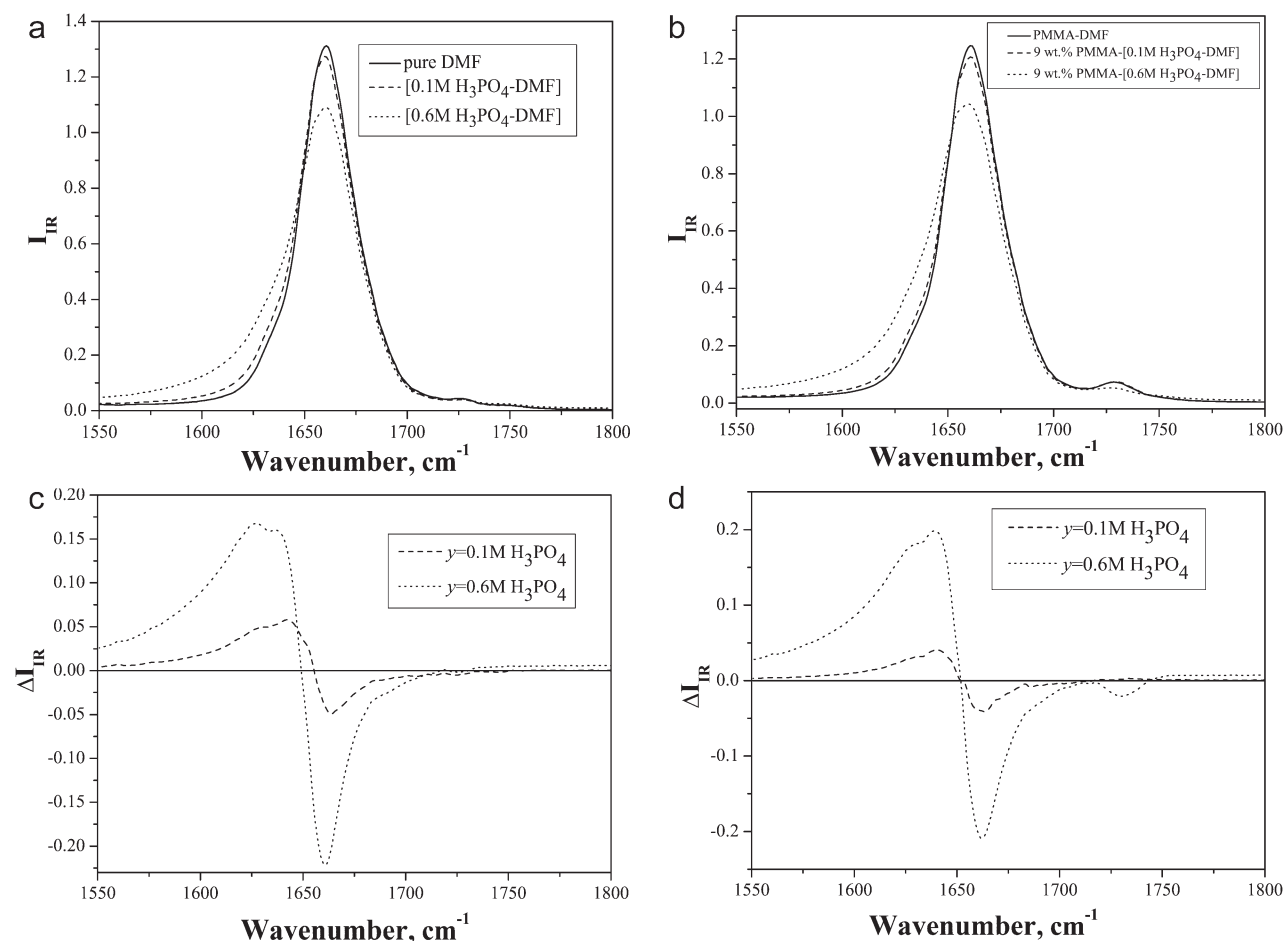


Figure 6. Experimental ATR spectra of the (a) liquid $[y\text{H}_3\text{PO}_4\text{-DMF}]$ and (b) gel 9 wt % $\text{PMMA-[}y\text{H}_3\text{PO}_4\text{-DMF]}$ electrolytes, and (c,d) the difference spectra for these systems over a frequency range corresponding to the $\nu(\text{C}=\text{O})$ mode at various phosphoric acid concentrations.

particular interest under hydrogen-bond consideration. To show the trend of these band changes with the acid concentration variation, the difference spectra method was applied. A detailed description of the method and the interpretation of the results were presented in ref. 39. In this approach, difference (or dynamic) spectra (δI_{IR}) are obtained by the subtraction of the reference spectrum $I_{\text{IR(ref)}}$ from each spectrum of the series $I_{\text{IR(exp)}}$. The reference spectrum can be, for example, the first or last spectrum of the group or the averaged spectrum, depending on the type of information to be inferred. In this study, the reference spectra were the ones of DMF or the PMMA-DMF mixture used for liquid binary and gel electrolytes, respectively.

The difference spectra shown in Figure 6(c,d) at various acid concentrations were obtained by the following equation:

$$\delta I_{\text{IR}} = I_{\text{IR(exp)}} - I_{\text{IR(ref)}}$$

As shown in Figure 6(a,b), the increase in the acid concentration in both systems caused a widening of the low-frequency shoulder of the $\nu(\text{C}=\text{O})$ mode in the experimental spectra. In the difference spectra [Figure 6(c,d)], the appearance of the low-frequency component was more visual. Similar conclusions were drawn for the 9 wt % $\text{PMMA-(}y\text{H}_2\text{SO}_4\text{-DMF)}$ system in ref. 25.

One could expect that the similar changes would be observed for the $\nu(\text{C}=\text{O})$ mode in PMMA (1727 cm^{-1}) when it interacted with the acid molecules by means of hydrogen-bond formation. However, because of the low intensity of this band, its analysis was not proper. Therefore, the possibility in principle of acid and PMMA interaction was examined on the basis of the phosphoric acid-MTMA model system; the latter structurally simulated the single PMMA unit. The schematic structures of PMMA and MTMA are shown in Figure 7.

The reason we chose MTMA as a single structural unit of PMMA was given in ref. 40.

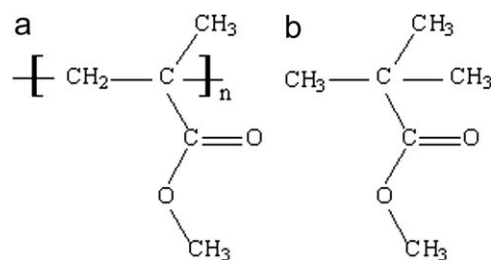


Figure 7. Schematic structures of (a) PMMA and (b) MTMA .

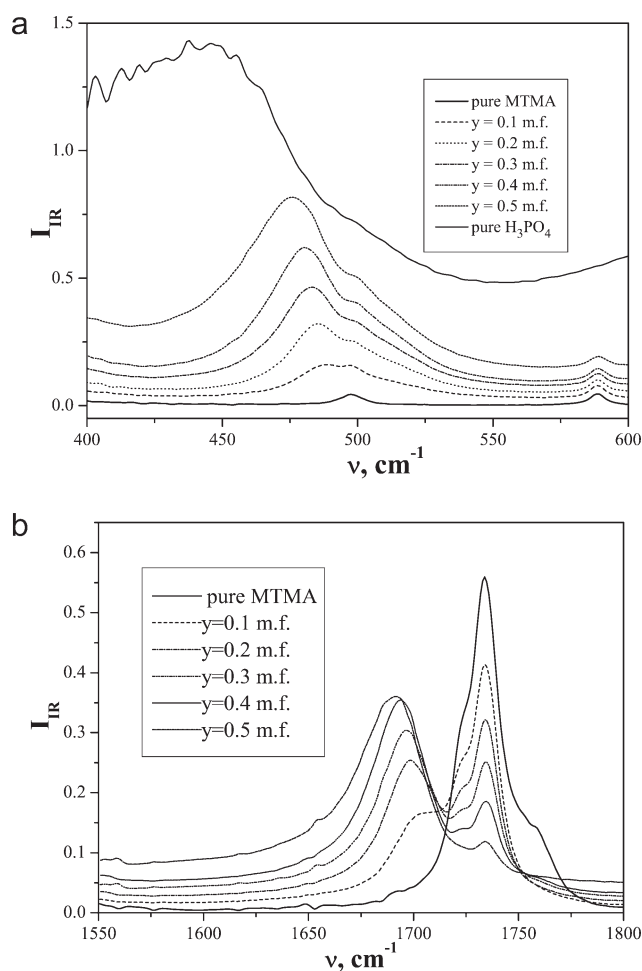


Figure 8. Experimental ATR spectra of the $[\gamma\text{H}_3\text{PO}_4\text{-MTMA}]$ solutions within spectral regions of the (a) $\delta(\text{O-P-O})$ mode of H_3PO_4 and (b) $\nu(\text{C=O})$ mode of MTMA at various γ values.

The ATR spectra of the $\text{H}_3\text{PO}_4\text{-MTMA}$ solutions with various compositions are shown in Figure 8.

When the acid concentration was lowered down to 0.1 mf, a high-frequency shift of the deformation mode of O-P-O groups by about 40 cm^{-1} compared with that of pure H_3PO_4 (446 cm^{-1}) was observed [Figure 8(a)]. This fact testified to the probability of hydrogen-bond formation between H_3PO_4 and MTMA. Also, with increasing acid concentration, a new band appeared in the model system at frequencies lower than $\nu(\text{C=O})$ in pure MTMA (1734 cm^{-1}) [Figure 8(b)]. This new mode appearance might have been the result of hydrogen-bond formation between the acid and oxygen of the MTMA carbonyl group.

Literature data on quantum chemical calculations and molecular dynamics simulations^{40–42} show the possibility of hydrogen-bond formation between phosphoric acid and DMF and between the acid and MTMA. Although the value of charge transfer upon the formation of hydrogen bonds with DMF is larger than with MTMA (the energy of the intermolecular hydrogen bonds between DMF and H_3PO_4 is higher than that between MTMA and H_3PO_4),⁴¹ it was established that when a

ternary complex ($\text{MTMA-H}_3\text{PO}_4\text{-DMF}$) forms, the presence of a stronger proton acceptor (DMF) does not influence the degree of charge transfer during the formation of hydrogen bonds between H_3PO_4 and MTMA. We, therefore, concluded that PMMA was not an inert matrix for the liquid electrolyte, and thus, it affected the proton-transfer process. Thus, the hydrogen-bond formation between the phosphoric acid and C=O groups of the polymers was still probable, especially within the confined geometry of the polymeric matrix.

CONCLUSIONS

The gel conductivity at the same acid concentrations in the doping solutions was correlated with the acid dissociation constants, and this allowed us to evaluate the gel conductivity from known pK values.

The extreme character of the gel conductivity as a function of the acid concentration was found. Like that in liquid electrolytes, such behavior was connected with the influence of two competing factors: the increase in the number of charge carriers and the decrease of their mobility as a consequence of the gel viscosity enhancement.

The gel conductivity dependences on the polymer content were also of extreme character, and this was caused by two phenomena. On the one hand, the electrolyte entropy decreased within the confined geometry of the polymeric matrix and caused the conductivity growth because of ordered proton motion, and trough channels formed. On the other hand, the system viscosity increase led to a depression of the ion mobility. The higher conductivity in the gels as compared with the liquid electrolyte could also be considered a proof of the entropy contribution influence.

The proton transfer in the PGEs was realized mainly through a Grotthuss mechanism.

On the basis of ATR spectroscopy, we established that phosphoric acid molecules formed hydrogen bonds with MTMA, which was the model of a PMMA single fragment, which showed the possibility of similar interaction with the polymeric matrix.

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REFERENCES

- Ivanchev, S. S.; Myakin, S. V. *Russ. Chem. Rev.* **2010**, *79*, 101.
- Reiter, J.; Velicka, J.; Mika, M. *Electrochim. Acta* **2008**, *53*, 7769.

3. Zukowska, G.; Rogowska, M.; Wojda, A.; Zygadlo-Monikowska, E.; Florjanczyk, Z.; Wiczorek, W. *Solid State Ionics* **2000**, 136–137, 1205.
4. Qiao, J.; Yoshimoto, N.; Ishikawa, M.; Morita, M. *Solid State Ionics* **2003**, 156, 415.
5. Jeffrey, K. R.; Zukowska, G. Z.; Stevens, J. R. *J. Chem. Phys.* **2003**, 119, 2422.
6. Tanaka, R.; Yamamoto, H.; Shono, A.; Kubo, K.; Sakurai, M. *Electrochim. Acta* **2000**, 45, 1385.
7. Qiao, J.-L.; Yoshimoto, N.; Ishikawa, M.; Morita, M. *Electrochim. Acta* **2002**, 47, 3441.
8. Harinder, P. S. M.; Sekhon, S. S. *Ionics* **2009**, 15, 635.
9. Kumar, R.; Sekhon, S. S. *J. Appl. Electrochem.* **2009**, 39, 439.
10. Ericson, H.; Svanberg, C.; Brodin, A.; Grillone, A. M.; Panero, S.; Scrosati, B.; Jacobsson, P. *Electrochim. Acta* **2000**, 45, 1409.
11. Sekhon, S. S. *Bull. Mater. Sci.* **2003**, 26, 321.
12. Liu, C.; Zhang, J.; Shi, G.; Qu, L.; Chen, F. E. *J. Appl. Polym. Sci.* **2003**, 90, 1267.
13. Lassegues, J. C.; Desbat, B.; Trinquet, O.; Cruege, F.; Poinsignon, C. *Solid State Ionics* **1989**, 35, 17.
14. Vaivars, G.; Kleperis, J.; Azens, A.; Granqvist, C. G.; Lulis, A. *Solid State Ionics* **1997**, 97, 365.
15. Stevens, J. R.; Wiczorek, W.; Raducha, D.; Jeffrey, K. R. *Solid State Ionics* **1997**, 97, 347.
16. Tang, Q.; Cai, H.; Yuan, S.; Wang, X.; Yuan, W. *Int. J. Hydrogen Energy* **2013**, 38, 1016.
17. Sekhon, S. S.; Arora, N.; Singh, H. P. *Solid State Ionics* **2003**, 160, 301.
18. Singh, H. P.; Sekhon, S. S. *Electrochim. Acta* **2004**, 50, 621.
19. Chandra, S.; Sekhon, S. S.; Srivastava, R.; Arora, N. *Solid State Ionics* **2002**, 154–155, 609.
20. Chandra, S.; Sekhon, S. S.; Arora, N. *Ionics* **2000**, 6, 112.
21. Sekhon, S. S.; Arora, N.; Chandra, S. *Eur. Polym. J.* **2003**, 39, 915.
22. Juhasz, E.; Marsh, K. N. *Pure Appl. Chem.* **1981**, 53, 1841.
23. Barthel, J.; Feuerlein, F.; Neueder, R.; Wachter, R. *J. Solution Chem.* **1980**, 9, 209.
24. Shmukler, L. E.; Safonova, L. P.; Thuc, N. V.; Gruzdev, M. S. *Polym. Sci. Ser. A* **2011**, 53, 44.
25. Shmukler, L. E.; Thuc, N. V.; Fadeeva, Y. A.; Safonova, L. P. *J. Polym. Res.* **2012**, 19, 9770.
26. Shmukler, L. E.; Thuc, N. V.; Safonova, L. P. *Ionics* **2013**, 19, 701.
27. Paul, R. C.; Guraya, P. S.; Sreenathan, B. R. *Indian J. Chem.* **1963**, 1, 335.
28. Safonova, L. P.; Fadeeva, Y. A.; Pryakhin, A. A. *Russ. J. Phys. Chem. A* **2009**, 83, 1747.
29. Perrin, D. D. *Pure Appl. Chem.* **1969**, 20, 133.
30. Juillard, J.; Loubinoux, B. *Compt. Rend.* **1967**, 264, 1680.
31. Grillone, A. M.; Panero, S.; Retamal, B. A.; Scrosati, B. *J. Electrochem. Soc.* **1999**, 146, 27.
32. Raducha, D.; Wiczorek, W.; Florjanczyk, Z.; Stevens, J. R. *J. Phys. Chem. A* **1996**, 100, 20126.
33. Singh, H. P.; Sekhon, S. S. *Eur. Polym. J.* **2003**, 39, 93.
34. Fadeeva, J.; Shmukler, L.; Safonova, L. *J. Mol. Liq.* **2003**, 103–104, 339.
35. Cukierman, S. *Biochim. Biophys. Acta* **2006**, 1757, 876.
36. Elashmawi, I. S.; Hakeem, N. A. *Polym. Eng. Sci.* **2008**, 48, 895.
37. Fadeeva, J. A.; Demina, L. I.; Gorbunova, Y. G.; Shmukler, L. E.; Safonova, L. P.; Tsivadze, A. Y. *Russ. J. Coord. Chem.* **2003**, 29, 515.
38. Givan, A.; Larsen, L. A.; Loewenschuss, A.; Nielsen, C. J. *J. Mol. Struct.* **1999**, 509, 35.
39. Grdadolnik, J. *Vib. Spectrosc.* **2003**, 31, 279.
40. Krest'yaninov, M. A.; Kiselev, M. G.; Safonova, L. P. *Russ. J. Phys. Chem. A* **2013**, 87, 2054.
41. Krest'yaninov, M. A.; Kiselev, M. G.; Safonova, L. P. *Russ. J. Phys. Chem. A* **2012**, 86, 1847.
42. Fedorova, I. V.; Kiselev, M. G.; Safonova, L. P. *J. Chem. Phys.* **2011**, 134, 174506.