



THE INFLUENCE OF NONIONIC SURFACTANTS ON THE CARBOPOL-PEG INTERPOLYMER COMPLEXES

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Mixtures of Carbopol 980 [a cross-linked poly(acrylic acid) (PAA)] and poly(ethylene glycol) (PEG) of 400, 2000 and 8000 molecular weights were investigated by ATR FTIR spectroscopy. The spectra were different of those of the individual components and prove interpolymer complex (IC) formation through hydrogen bondings. The effect of nonionic surfactants [*i.e.*, polydisperse ethoxylated nonylphenol (NPEO₁₀) and ethylene oxide-propylene oxide-ethylene oxide (EO₇₆-PO₃₀-EO₇₆) triblock copolymer (Pluronic F68)] on Carbopol 980/PEG mixtures was studied by surface tension, viscosity and pH methods. The CMC and several critical concentrations for surfactant interaction with IC were determined. The data were discussed taking into account the interaction of both the ethoxylated and the hydrophobic moieties of the surfactant with IC and their competition with PEG for the binding sites of Carbopol.

INTRODUCTION

Interpolymer complexes (IC) stabilized by hydrogen bonds usually form between polymers containing proton donor groups, like the poly(carboxylic acids) and polymers with proton acceptor groups such as poly(ethylene glycol) (PEG), poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), poly(vinyl pyrrolidone) (PVP), poly(vinyl alcohol) (PVA), etc. Examples of polymer pairs that form such complexes are poly(acrylic acid) (PAA) and poly(acryl amide),¹ PAA and PVA,² poly(methacrylic acid) (PMA) and PEG,³ PMA and PVP,⁴ PMA and PEG,^{3,5} and many others. The topic has a history of more than 50 years and begins with a paper describing a tough, rubber-like elastomer obtained after water evaporation from a mixture of high molecular weight PEO and PAA.⁶ Since that time, many papers have been published and the information on IC preparation, properties

and applications has been systematized in several reviews,⁷⁻¹³ and books.¹⁴⁻¹⁶

On the other hand, complexes are also formed by ethoxylated nonionic surfactants (ENS) and linear PAA,¹⁷⁻²⁴ PMA²⁵ or cross-linked PAA.²⁶⁻²⁸ The data on PAA unveil that this polymer interacts with nonionic surfactants having a much lower PEO chain length than PEO alone. The interaction starts at a certain surfactant concentration called the critical aggregation concentration (CAC or T₁), which is smaller than the critical micelle concentration (CMC). Other critical points of the interaction are the appearance of free surfactant molecules (T₂') and of free micelles (T₂) into solution.

Since both PEG and ethoxylated nonionic surfactants form complexes with PAA, it is important to establish their ability to interact with this polymer. In this respect, we prepared PAA-PEG interpolymer complexes from a cross-linked PAA (Carbopol 980) and PEG of different

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molecular weights. The interpolymer complex formation was proved by FTIR. The effect of nonionic surfactants [*i.e.*, ethoxylated nonylphenol with an average of 10 ethylene oxide (EO) units, NPEO₁₀, and block copolymer PEO-PPO-PEO, Pluronic F68] on IC was tested by surface tension, viscosity and potentiometry.

EXPERIMENTAL

Materials and Methods

Carbopol 980 and the nonionic surfactants were the same as previously used.^{27,28} The producer of Carbopol does not mention neither the molecular weight of PAA nor the cross-linking agent. The information available about this product is scarce and reveals that the commercial name of Carbopol belongs to a class of homopolymers of acrylic acid cross-linked with allyl ethers of pentaerythritol, sucrose or propene,²⁹ and "Carbopol 980 has a very high molecular weight (believed to be about 4 millions)".³⁰ Poly(ethylene glycol)s with molecular weights of 400 (PEG 400), 2000 (PEG 2000) and 8000 (PEG 8000) were purchased from Fluka, Switzerland and used as received. Solutions were prepared with water obtained from a Simplicity UV Millipore apparatus.

FTIR measurements were done in the attenuated total reflection (ATR) mode by putting the samples on the diamond crystal of a Bruker Tensor 37 spectrometer. Thirty-two scans were recorded at a resolution of 4 cm⁻¹, from 4000 to 450 cm⁻¹.

Surface tensions were measured by the ring method using an Easy Dyne, Krüss tensiometer, with an error of ± 0.08%. Viscosity determinations were carried out with the aid of an Ostwald viscometer having the flow time of water > 100 s. The error of measurement was ± 0.1 s. The relative viscosity was taken as the ratio between the flow time of polymer-surfactant complex and that of surfactant solution. pH was measured with an Orion model 420 ATI digital pH-meter with an accuracy of ± 0.005 pH units. All the measurements were done at 25 ± 0.1 °C.

Preparation of Complexes and Measurements

Aqueous stock solutions of Carbopol and PEG of different MW were prepared first. Their concentrations were expressed in mol·L⁻¹, in monomer units. For FTIR measurements, the Carbopol and PEG solutions were mixed together to obtain the desired concentration ratio. After mixing, the samples were magnetically stirred and left one day to attain equilibrium. Then, the samples were freeze-dried and the obtained solid subjected to FTIR.

The effect of surfactant on IC was studied by measurements of surface tension, viscosity and pH on interpolymer complexes having the molar ratio equal to 1. This ratio was chosen in accord with literature data³¹⁻³³ and with our results.³⁴ They show that the stoichiometry of the interpolymer complex between PEG and PAA is 1:1. The samples were homogenized by stirring and allowed to equilibrate for one day at room temperature. Surfactant stock solutions were separately prepared and added to the interpolymer complexes. The ternary systems had a constant amount of interpolymer complex (0.1 %, wt.) and surfactant concentrations in the range from 10⁻⁵ to 20 % (wt.).

RESULTS AND DISCUSSION

1. Fourier-transform infrared (FTIR) spectroscopy

Infrared spectroscopy is a useful tool in detecting the formation of interpolymer complexes by hydrogen bonds.^{32,35-37} Because the results obtained for the Carbopol-PEG mixtures are quite similar, the following discussion will refer only to the system containing PEG 8000.

Figure 1 illustrates the hydroxyl region of spectra for Carbopol, PEG 8000 and their mixtures. In the Carbopol spectrum the broad bands at about 3550 and 3150 cm⁻¹ correspond to the free hydroxyl groups and to hydroxyls forming the hydrogen bonds.³⁸ In the Carbopol-PEG mixtures, the increase of PEG content decreases the intensity of the band at 3150 cm⁻¹, and shifts to lower wavenumbers the band at 3550 cm⁻¹. The former effect signals the replacement of intrapolymer hydrogen bonds among the carboxyls of Carbopol with interpolymer hydrogen bonds between the Carbopol and PEG. The shift to lower wavenumbers of the band at 3550 cm⁻¹ points out that new types of interactions are present in the Carbopol-PEG mixtures. The shift of free and bonded hydroxyl bands indicates that the OH groups in the blend are different than in Carbopol alone. This is supported by the fact that the ether oxygen of PEG is less available for hydrogen bonding than the carbonyl oxygen of Carbopol. However, the shape of hydroxyl band indicates that both free and associated hydrogen bonds exist in the Carbopol-PEG blends.

Figure 2 shows the carboxyl region of spectra. The broadening of the carbonyl stretching vibration band in the blends is due to the formation of intra- and intermolecular hydrogen bondings, but free carbonyl groups still exist and, in the PEG-rich blends, the intensity of this band decreases. The carbonyl peak in Carbopol 980 appears at 1703 cm⁻¹. In Carbopol-PEG complexes it shifts to higher wavenumbers as the amount of PEG increases. For example, it is at 1705, 1724 and at 1730 cm⁻¹ for the Carbopol-PEG mixtures having the mole ratios of 3:1, 1:1 and respectively, 1:3. The shift is attributed to concomitant disruption of intramolecular hydrogen bonding in the Carbopol as the two polymers merge and interact each other. These data confirm that some self-associated hydrogen bonds Carbopol-Carbopol are replaced by new inter-associated bindings Carbopol-PEO, as suggested above by the observed changes in the hydroxyl region.

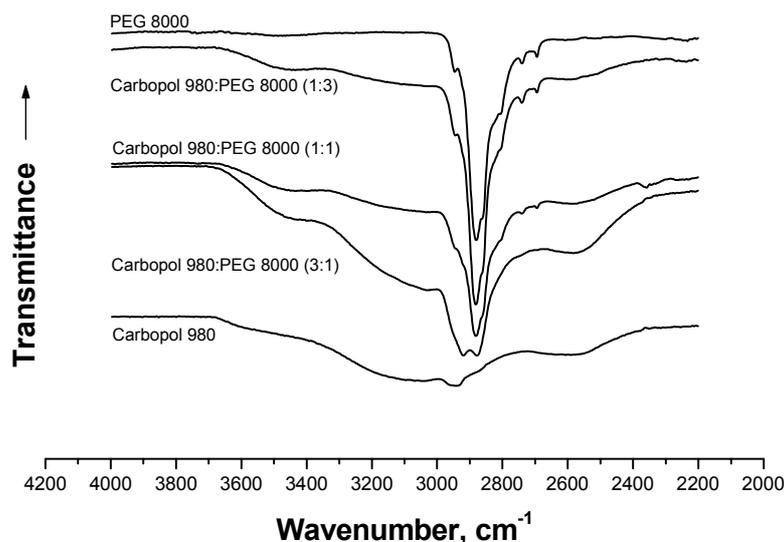


Fig. 1 – FTIR spectra for Carbopol 980, PEG 8000, and their mixtures in the region of 4000-2200 cm⁻¹.

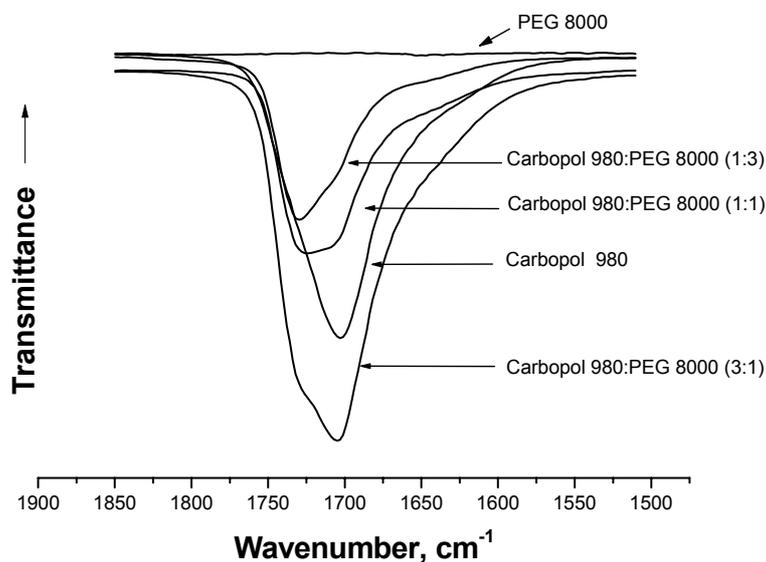


Fig. 2 – FTIR spectra for Carbopol 980, PEG 8000, and their mixtures in the region of 1850-1500 cm⁻¹.

The 1500-800 cm⁻¹ range is called the fingerprint of the compound. In our case, it gives information about the macromolecular chain order or crystallinity of PEG. Thermodynamically, it is well established that the most stable structure of PEG is the gauche form of the 7/2 helix.³⁹ However, a *trans* planar zig-zag structure was observed in samples under tension or when water is added to the polymer.⁴⁰ The energy difference between the helical and the *trans* planar structure is very small (about 0.1 kcal mol⁻¹), and reveals the high molecular flexibility of PEG.⁴¹

Spectra of PEG, Carbopol and their blends in the 1500-800 cm⁻¹ region are shown in Figure 3. In the spectrum of PEG, one may observe bands

characteristic to both *trans* planar and helical structure. The former are located at 1342 cm⁻¹ (CH₂ wagging), 1240 cm⁻¹ (CH₂ twisting) and 960 cm⁻¹ (CH₂ rocking). The bands of the helical structure appear at 1359 cm⁻¹ (CH₂ wagging), 1279 and 1240 cm⁻¹ (CH₂ twisting), 960 and 841 cm⁻¹ (CH₂ rocking) and 1059 cm⁻¹ (coupled C-O and C-C stretching).⁴² Other bands are less important but those at 1146, 1097 and 1059 cm⁻¹ can be assigned to ether groups. These bands are also present in Carbopol-PEG 1:3 and 1:1 blends, but merge and shift to lower wavenumbers in the 3:1 mixture. For example, the 1359 and 1342 cm⁻¹ doublet is replaced by the single band at 1348 cm⁻¹ in Carbopol-PEG 3:1 blend. Similarly, the 960 and

945 cm^{-1} bands are replaced by one band at 945 cm^{-1} in the 3:1 complex. The data suggest that PEG crystallization is hampered by the cross-linked PAA. The band at 842 cm^{-1} is also very weak in the blend containing 75 % cross-linked PAA. It is associated with the mixed motion of CH_2 rocking, C-O-C deformation and with the gauche form of the 7/2 helix of PEG.

The FTIR data point out that the cross-linked PAA and PEG form in solid-state interpolymer complexes by hydrogen bondings. Furthermore, they show that the cross-linked PAA has a considerable effect on the helical structure of PEG.

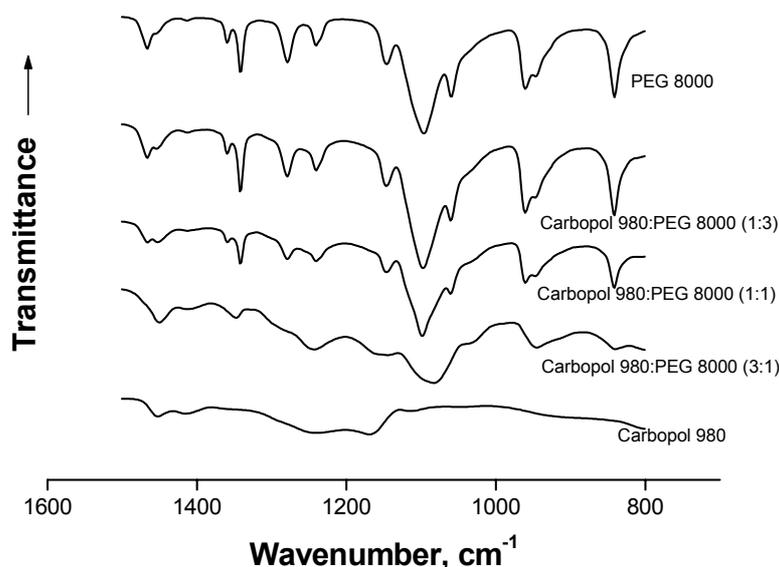


Fig. 3 – FTIR spectra for Carbopol 980, PEG 8000, and their mixtures in the region of 1500-800 cm^{-1} .

2. Surface Tension

The surface tension isotherm of NPEO₁₀ is shown in Figure 4. Its allure is typical for surfactants and the intersection of the descending with the horizontal line indicates a concentration of 6×10^{-3} % (wt.), which marks the CMC. The value agrees with that reported in the literature for this surfactant.²⁷ In the ternary systems, the data in Figure 4 show that the interpolymer complex alters the surfactant isotherm. The most notable change is the appearance of a new plateau situated at higher surface tensions than those corresponding to the micellar zone. One may also observe several break points denominated by T_1 , T_2' and T_2 according to Jones.⁴³ T_1 occurs below CMC and is located at the intersection of the descending portion of the curve with the first plateau of surface tension. It represents the concentration at which micelle-like aggregates of surfactants begin to form in the interpolymer complex. Because in the first plateau region the surface activity at the air-solution interface is constant it is safely to assume that all the surfactant introduced into system binds to the interpolymer complex. The plateau extends up to

another point designated as T_2' , which marks the saturation of IC with surfactant. Thereafter, the surface tension decreases again, and joins the surfactant isotherm at T_2 , which indicates the appearance of free surfactant micelles into solution.

The surface tension measurements reveal the existence of several critical points of interaction between the IC and the surfactant. The shape of the curves allow us to assume that the interaction proceeds by a similar mechanism to that acting in systems of ethoxylated surfactants and cross-linked,²⁷ or linear PAA.²² The interaction is initiated by hydrogen bonds and is reinforced by hydrophobic forces. The values of critical points of surfactant-IC ternary systems are given in Table 1. The data in Figure 4 also point out that the isotherm of PEG 2000 has an intermediary position in-between those of the other PEGs. According to our best knowledge such a behavior has not been reported yet for ternary systems like those of the present study being observed only in binary mixtures of PEG with PAA or PMMA.⁴⁵ Moreover, Figure 4 shows that T_1 moves towards smaller surfactant concentrations by decreasing the molecular weight of PEG. The difference between

the value of the surface tension plateau at T_1 and that corresponding to the surfactant micellization becomes smaller with increasing the molecular weight of PEG. In contrast, the plateau between T_1 and T_2' increases with the molecular weight of PEG due to a stronger interaction between the

surfactant and IC. It is important to note that the plateau of the surface tension has a value of 31 mN/m for NPEO₁₀/(Carbopol-PEG 8000) being lower than for the NPEO₁₀/(Carbopol-PEG 400), which is of 33 mN/m.

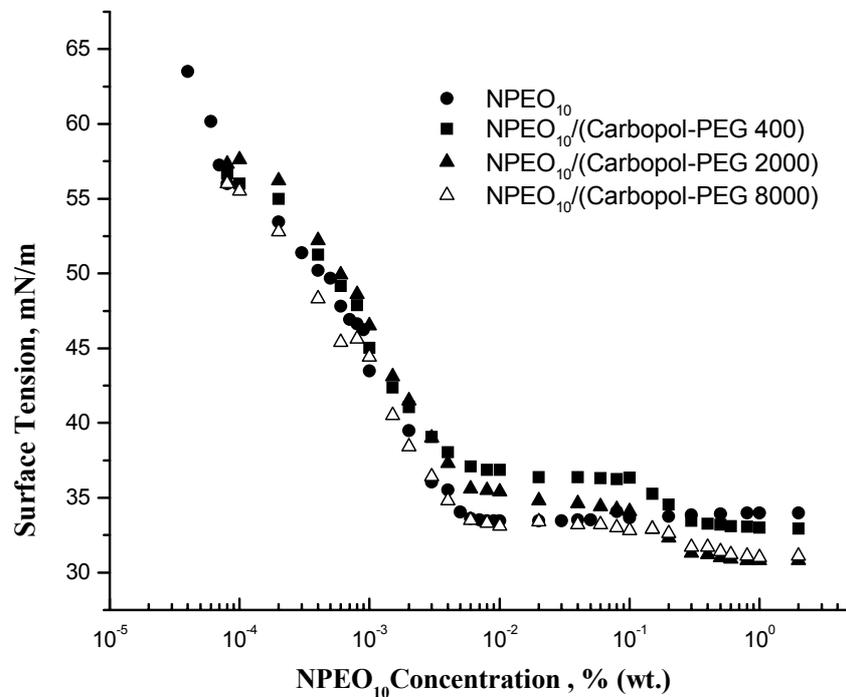


Fig. 4 – Surface tension isotherms of NPEO₁₀ without and with Carbopol-PEG interpolymer complexes.

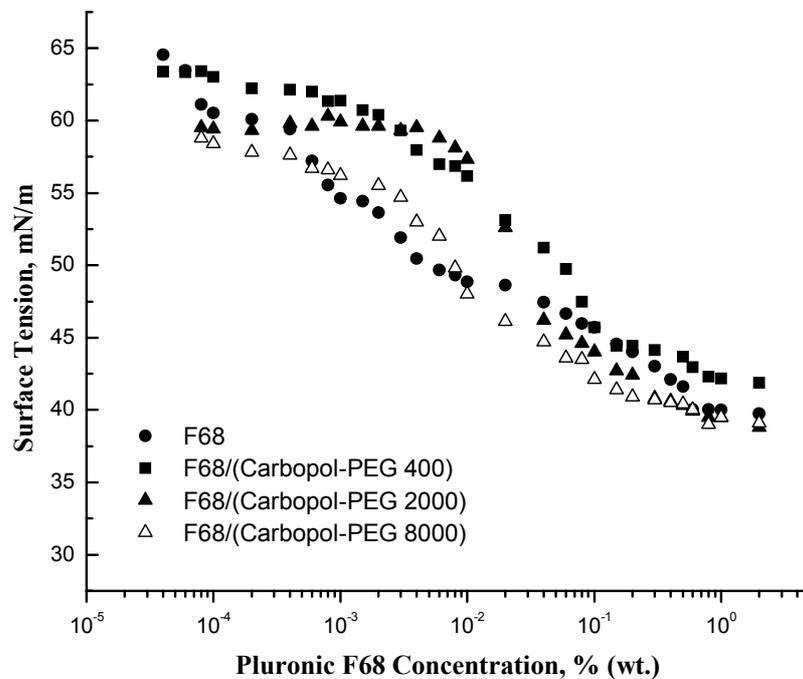


Fig. 5 – Surface tension isotherms of Pluronic F68 without and with Carbopol-PEG interpolymer complexes.

Surface tensions of Pluronic F68 in the absence and presence of interpolymer complex are illustrated in Figure 5. In the Pluronic F68/(Carbopol-PEGs) systems some differences appear in comparison with the formerly studied Pluronic F68/Carbopol 980 system.²⁷ In the region of low surfactant concentrations the presence of IC does not influence the surface tension. By

increasing the surfactant concentration, the surface tension decreases monotonously. This tendency disappears at T_1 , which is also smaller than CMC. After that the surface tension remains constant. The surface tensions of surfactant-IC are higher than those of NPEO₁₀ complexes because of the polymeric nature of Pluronic F68 and its lower surface activity.

Table 1

Critical points of the NPEO₁₀/(Carbopol-PEGs) and of the Pluronic F68/(Carbopol-PEGs) complexation by Surface Tension, pH and by Viscosity measurements at 25 °C.

System	Method					
	Surface Tension and Viscosity				pH	
	T_1 (wt.) %	T_2' (wt.) %	T_2 (wt.) %	T_v (wt.) %	T_1 (wt.) %	T_2 (wt.) %
NPEO ₁₀ /(C980-PEG400)	5×10^{-3}	1×10^{-1}	3×10^{-1}	2×10^{-1}	8×10^{-2}	1.5×10^{-1}
NPEO ₁₀ /(C980-PEG2000)	4×10^{-3}	1×10^{-1}	4×10^{-1}	2×10^{-1}	8×10^{-3}	1×10^{-1}
NPEO ₁₀ /(C980-PEG8000)	1×10^{-2}	2×10^{-1}	5×10^{-1}	1.5×10^{-1}		6×10^{-2}
PF68/(C980-PEG400)	8×10^{-4}	2×10^{-2}	1×10^{-1}	1×10^{-1}	6×10^{-3}	1.5×10^{-1}
PF68/(C980-PEG2000)	4×10^{-3}	3×10^{-2}	2×10^{-1}	1×10^{-1}	4×10^{-3}	1×10^{-1}
PF68/(C980-PEG8000)	6×10^{-3}	3×10^{-2}	1.5×10^{-1}	1×10^{-1}		1.5×10^{-1}

3. Viscosity

Viscosity is one of the major tools for experimental assessing the properties of interpolymer complexes^{45,46} and polymer-surfactant (PS)²⁵ systems. The technique is simple, expedient, easy of handling and cheap. In case of interpolymer complexes, the viscosity gives information about the stoichiometry of reaction, whereas in polymer-surfactant systems it allows to determine the critical points of interaction.

Figure 6 illustrates the effect of nonionic surfactants on the viscosity of cross-linked PAA/PEG interpolymer complexes. One may observe that the results are different and depend on the molecular weight of PEG. For the interpolymer complexes of PEG 400 and PEG 2000, addition of surfactant produces similar viscosity effects as those in systems of linear⁴⁵ or cross-linked PAA.⁴⁷ At minute amounts of surfactant the relative viscosity is constant having practically the same value as that of the parent IC (1.7). Further addition of surfactant decreases the viscosity, which passes through a minimum and increases at high surfactant levels. The surfactant concentration

where viscosity starts decreasing is coincident with T_1 , and the minimum of viscosity (T_v) matches the T_2 determined by surface tension.

The IC of PEG 8000 behaves differently. The data in Figure 6 show that viscosity is considerably lower than of IC. Moreover, it does not change until the surfactant concentration reaches a value around T_v . Thereafter, the viscosity increases by further surfactant addition. These peculiarities should be explained taking into account the cross-linking of Carbopol 980 and the molecular weight of PEG. Although the producer does not unveil the cross-linking agent and the degree of cross-linking, it is safely to assume that Carbopol has a 3D network with holes that can accommodate polymers like our PEGs. Having lower molecular weights, PEG 400 and PEG 2000 are easily displaced from IC by the surfactant, and the IC behaves alike the linear¹⁷ or the cross-linked PAA alone.²⁷ In contrast, PEG 8000 fits well the Carbopol network, and can not be removed by addition of low or moderate amounts of surfactant. This explains the allure of viscosity curves recorded in Figure 6. At high surfactant levels, *i.e.* above T_v , the system is similar to those of the

interpolymer complexes with low molecular weight PEGs. It means that PEG 8000 is displaced from the IC and replaced by surfactant micelles, which produces a more bulky Carbopol-surfactant complex than that of Carbopol-PEG 8000. Alternatively, it is possible that surfactant micelles do not replace PEG 8000 in IC. Instead, they may bring together several Carbopol-PEG 8000 in new

supramolecular structures. However, these structures need further investigation to ascertain which one of the above-mentioned hypotheses is correct. In this respect, we are undertaking dynamic light scattering and fluorescence measurements and the results will be presented in a separate paper.

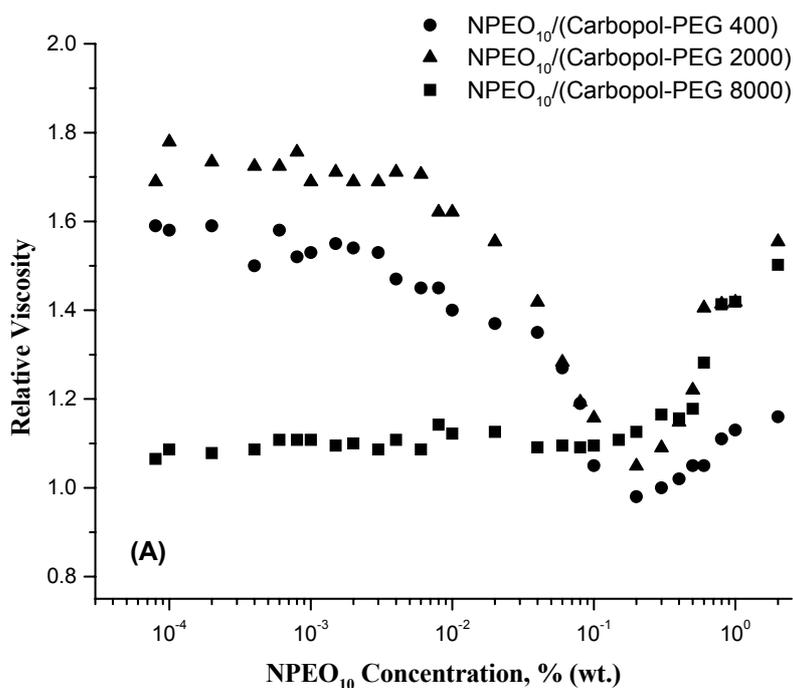


Fig. 6 A

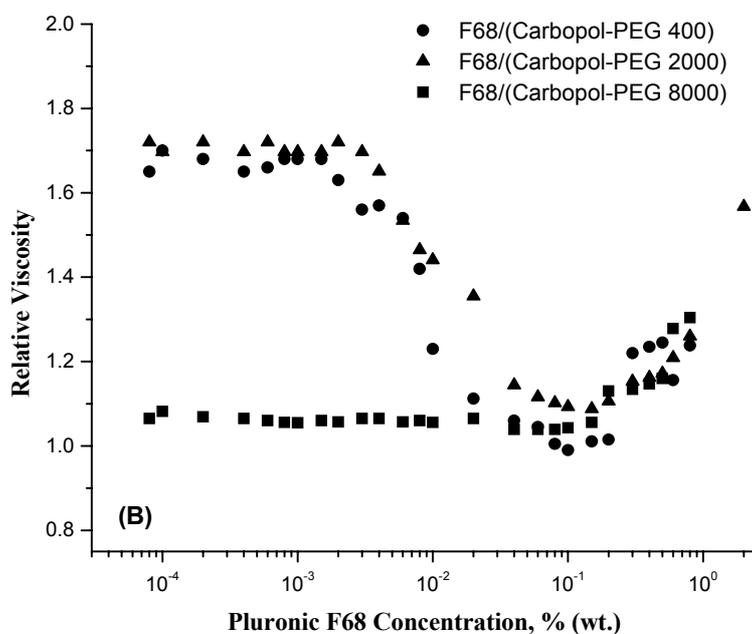


Fig. 6 B

Fig. 6 – Plots of the relative viscosity of IC versus the surfactant concentration. Surfactants: (A) NPEO₁₀, (B) Pluronic F68.

4. pH

The pH results presented in Figure 7 show the influence of surfactant on the PEG-Carbopol binary complexes. In the domain of low surfactant concentrations, the pH is practically constant having a value of about 3.5. At a certain surfactant concentration, the curve starts rising followed by a plateau at higher surfactant concentrations and by a descending region. The pH starts to increase at a surfactant concentration, which corresponds to T_1 from the surface tension isotherms (see Figures 2 and 3). The increase of pH can be explained by the involvement of Carbopol protons in the formation of

H bonds with the EO chains of the surfactants. Such a behavior was registered for systems with linear PAA in interaction with ethoxylated nonionic surfactants¹⁷ and for aqueous mixtures of Carbopol with NPEO₁₀ and Pluronic F68,²⁷ or Carbopol and Tween 80 or Pluronic F127.²⁶ The curves in Figure 7 also indicate a saturation of the H bonds between IC and surfactants corresponding to T_2 , after which the pH decreases. The values of T_1 and T_2 are given in Table 2. By comparing the viscosity with the pH data, one may observe that the surfactant concentration at the relative viscosity minimum appears as a narrow plateau in the pH curve.

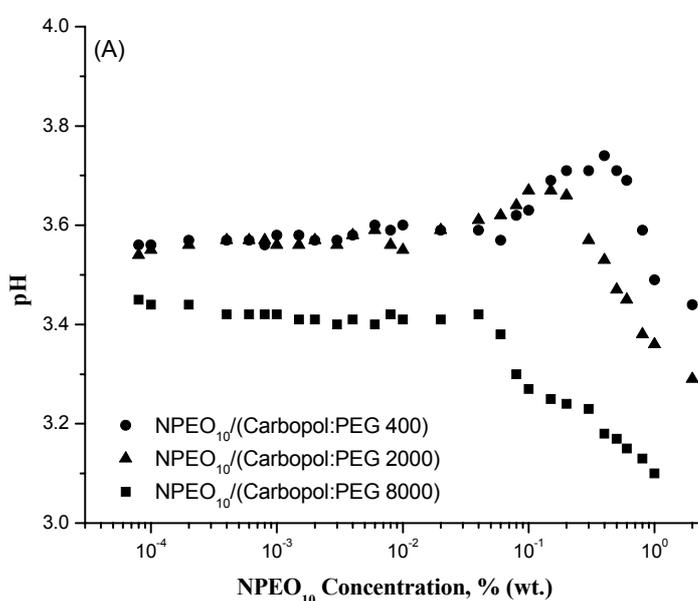


Fig. 7 A

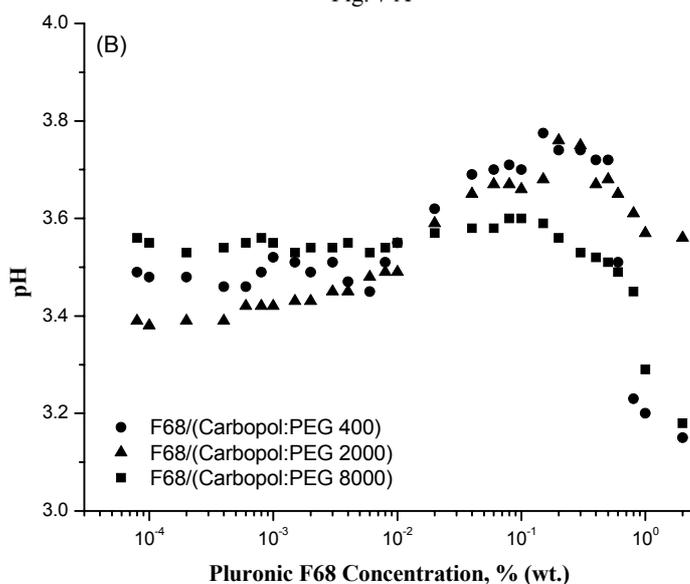


Fig. 7 B

Fig. 7 – The effect of surfactant concentration upon the pH of Carbopol-PEG interpolymers complexes. Surfactants: (A) NPEO₁₀, (B) Pluronic F68.

CONCLUSIONS

The FTIR results obtained in this study demonstrate that the cross-linked PAA interacts with PEG and forms interpolymer complexes. The carboxyl-carboxyl hydrogen bonds are broken and replaced by hydrogen bonds between carboxyl and PEG. Information about the effect of nonionic surfactants on the interpolymer complexes obtained by surface tension, viscosity and pH measurements revealed different behavior that depends on the molecular weight of PEG. They show that IC with PEG 400 and 2000 behave in a similar manner with linear PAA or cross-linked PAA. The IC with PEG 8000 behaves differently, and PEG is either displaced from the IC by the surfactant micelles or the micelles form with IC supramolecular structures. In this respect, work is in progress to assess which mechanism does apply.

REFERENCES

- M. A. Moharram, L. S. Balloomal and H. M. El-Gendy, *J. Appl. Polym. Sci.*, **1996**, *59*, 987-990.
- J. Byun, Y. M. Lee and C. S. Cho, *J. Appl. Polym. Sci.*, **1996**, *61*, 697-702.
- M. J. Krupers, F. J. Van der Gaag and J. Feijen, *Eur. Polym. J.*, **1996**, *32*, 785-790.
- A. Vsaitis, S. L. Maunu and H. Tenhu, *Eur. Polym. J.*, **1997**, *33*, 219-223.
- V. Y. Baranovsky and S. Shenkov, *J. Polym. Sci., Polym. Chem. Ed.*, **1996**, *34*, 163-167.
- K. L. Smith, A. E. Winslow and D. E. Petersen, *Ind. Eng. Chem.*, **1959**, *51*, 1361-1364.
- E. A. Bekturov and L. A. Bimendina, *Adv. Polym. Sci.*, **1981**, *41*, 99-147.
- E. Tsuchida and K. Abe, *Adv. Polym. Sci.*, **1982**, *45*, 1-147.
- M. Jiang, M. Li, M. L. Xiang and H. Zhou, *Adv. Polym. Sci.*, **1999**, *146*, 121-196.
- Z. S. Nurkeeva, G. A. Mun and V. V. Khutoryanskiy, *Macromol. Biosci.*, **2003**, *3*, 283-295.
- V. V. Khutoryanskiy, *Int. J. Pharm.*, **2007**, *334*, 15-26.
- A. K. Bajpai, S. K. Shukla, S. Bhanu and S. Kankane, *Progr. Polym. Sci.*, **2008**, *33*, 1088-1118.
- E. Kharlampieva, V. Kozlovskaya and S. A. Sukhishvili, *Adv. Mater.*, **2009**, *21*, 3053-3065.
- P. Dubin, J. Bock, R. M. Davies, D. N. Schultz and C. Thies, "Macromolecular Complexes in Chemistry and Biology", Springer-Verlag, Berlin, Germany, 1994.
- C. Vasile and A. K. Kulshreshtha, "Handbook of Polymers and Polymer Composites", Rapra Technology Ltd., Shawbury, United Kingdom, vol. 3A, 2003.
- V. V. Khutoryanskiy and G. Staikos, "Hydrogen-Bonded Interpolymer Complexes: Formation, Structure and Applications", World Scientific Publishing Co. Pte. Ltd., Singapore, 2009.
- D. F. Anghel, S. Saito, A. Iovescu and A. Baran, *Colloids Surf. A*, **1994**, *90*, 89-94.
- M. Vasilescu, D. F. Anghel, M. Almgren, P. Hansson and S. Saito, *Langmuir*, **1997**, *13*, 6951-6955.
- D. F. Anghel, S. Saito, A. Baran and A. Iovescu, *Langmuir* **1998**, *14*, 5342-5346.
- V. Raicu, A. Băran, D. F. Anghel, S. Saito, A. Iovescu and C. Rădoi, *Progr. Colloid Polym. Sci.*, **1998**, *109*, 136-141.
- S. Saito and D. F. Anghel, in "Polymer-Surfactant Interactions", J. C. T. Kwak (Ed.), Marcel Dekker, New York, 1998, p. 357-408.
- D. F. Anghel, F. M. Winnik and A. N. Galatanu, *Colloids Surf. A*, **1999**, *149*, 339-345.
- D. F. Anghel, S. Saito, A. Baran and A. Iovescu, *Rev. Roum. Chim.*, **2005**, *50*, 571-578.
- G. D'Errico, D. Ciccarelli, O. Ortona, L. Paduano and R. Sartorio, *J. Colloid Interface Sci.*, **2007**, *314*, 242-250.
- Anghel D. F., Saito S., Băran A., Iovescu A. and Cornițescu M. *Colloid Polym. Sci.*, **2007**, *285*, 771-779.
- R. Brreiro-Iglesias, C. Alvarez-Lorenzo and A. Concheiro, *Int. J. Pharm.*, **2003**, *258*, 165-177.
- C. Ilie, M. Balcan, A. Băran, A. Iovescu, G. Stîngă, M. Cornițescu and D. F. Anghel, *Rev. Roum. Chim.*, **2009**, *54*, 533-538.
- C. Ilie, D. F. Anghel, M. Balcan, A. Iovescu, G. Stîngă and A. Băran, *Rev. Roum. Chim.*, **2010**, *55*, 341-347.
- <http://encyclopedia.thefreedictionary.com/Carbopol>.
- D. B. Braun, *Seifen, Ole, Fette, Wachse*, **1991**, *117*, 509-512.
- F. E. Bailey, R. D. Lundberg and R. W. Callard, *J. Polym. Sci. Part A*, **1964**, *2*, 845-851.
- S. H. Jeon and T. Ree, *J. Polym. Sci. Part A, Polym. Chem.*, **1988**, *26*, 1419-1428.
- I. Iliopoulos and R. Audebert, *Macromolecules*, **1991**, *24*, 2566-2575.
- C. Ilie, Ph D. Thesis, "Ilie Murgulescu" Institute of Physical Chemistry, Bucharest, Roumania, 2010.
- L. A. Kanisi, F. C. Viel, J. S. Crespo, J. R. Bertolino, A. T. N. Pires and V. Soldi, *Polymer*, **2000**, *41*, 3303-3309.
- P. E. Kireeva, G. A. Shandryuk, J. V. Kostina, G. N. Bondarenko, P. Singh, G. W. Cleary and M. M. Feldstein, *J. Appl. Polym. Sci.*, **2007**, *105*, 3017-3036.
- A. S. Hadj-Hamou, A. Habi and S. Djadoun, *Thermochim. Acta*, **2010**, *497*, 117-123.
- Y. He, B. Zhu and Y. Inoue, *Prog. Polym. Sci.*, **2004**, *29*, 1021-1051.
- Y. Takahashi and H. Tadokoro, *Macromolecules*, **1993**, *6*, 672-675.
- Y. Takahashi, I. Sumita and H. Tadokoro, *J. Polym. Sci., Polym. Phys. Edn.*, **1993**, *11*, 2113-2122.
- K. Tai and H. Tadokoro, *Macromolecules*, **1974**, *7*, 507-515.
- J. I. Marcos, E. Orlandi and G. Zembi, *Polymer*, **1990**, *31*, 1899-1903.
- M. N. Jones, *J. Colloid Interface Sci.*, **1967**, *23*, 36-42.
- D. F. Anghel, F. M. Winnik and A. N. Galatanu, *Colloids Surf. A*, **1999**, *149*, 339-345.
- A. D. Antipina, V. Y. Baranovsky, I. M. Papisov and V. A. Kabanov, *Vysokomol. Soyed.*, **1972**, *A14*, 941-949.
- G. G. Bumbu, C. Vasile, J. Eckelt and B. A. Wolf, *Macromol. Chem. Phys.*, **2004**, *205*, 1869-1876.
- E. A. Bekturov, V. A. Frolova and G. K. Mamytkbekov, *Macromol. Chem. Phys.*, **1999**, *20*, 1031-1036.

