

INFLUENCE OF SURFACE-ACTIVE SUBSTANCES ON RHEOLOGICAL AND DIELECTROMETRIC CHARACTERISTICS OF POLYPHENYLSILOXANE SOLUTIONS

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Abstract

The influence of three varieties of surfactants on intermolecular interactions in the bulk phase of a film-forming polyphenylsiloxane was studied by viscosimetric and dielectrometric methods. A linear increase of specific viscosity with increase of polyphenylsiloxane concentration at constant temperature was observed. In solutions of all studied amine derivatives at concentrations above 0.5 g/dm³, a significant deviation from the linear dependence of the specific viscosity with surfactant concentration was found. The results indicated the formation of associated structures. The viscosity incremental growth in the concentration range of 0.5-2 g/dm³ corresponded to the molecule-weight ratio of amino derivatives. Rheological properties of solutions of the studied amino derivatives was slightly effected by the temperature. The specific viscosity of solutions of low molecular weight amines increased at higher temperatures. The most pronounced change was noticed at concentration of surfactant of 0.5 g/dm³. The effect was supposed to be due to solvation processes. In contrast, the specific viscosity of the solutions of high molecular weight amine derivatives decreased with increase of temperature up to T = 313 K. It was supposed that the temperature increase caused an increase in intermolecular interactions within the associates, which was accompanied by a decrease of their dimensions. The formed intermolecular structures folded into a tight ball creating less resistance for a flow and as a result the specific viscosity decreased. At increased surfactant concentrations (CSURF > 0.25 g/dm³), two types of association processes (mono and hetero-) were established depending on the individual characteristics of the organic amino derivatives (composition, structure, shape and hydrocarbon radical length). It has been proved that, the interaction between each other (monoassociation) was energetically more favorable for high-molecular amines with the simultaneous introduction of polyphenylsiloxane solutions macromolecules (mixed micels) into their composition. In the solutions containing low-molecular amines, monoassociation processes were proved.

Keywords: surfactants, polyphenylsiloxane, viscosimetry, dielectrometry, rheology, amino derivatives, intermolecular interactions, surface tension.

Introduction

Organosilicon (silicone) paint and varnishes historically occupy a significant part of the paint and varnishes market [1-3]. These materials are hybrid organo-inorganic composites. Combining the characteristics of both organic and inorganic substances, such structures have great potential in the development of new materials that have a variety of physical, technical and operational characteristics [4].

Organosilicon materials have a number of valuable properties: high heat resistance, frost resistance and light fastness. The protective properties of silicone materials, their low water absorption, stability over a wide temperature range and towards atmospheric factors determined

their wide application as protective, thermo-regulating, electro-insulating coatings with a long heat resistance from 200 to 700 °C. Materials based on polysilanes with high thermal stability and water resistance were studied [5]. The properties of organosilicon varnishes and the possibilities of using paint-and-lacquer materials based on polysilanes as primers have also been discussed.

Like any polymer material of other classes, the properties of silicone coatings, depended on a number of factors: chemical growth and the structure of polymers, the presence of modifying additives, the technological and the drying regime, the quality of preparation of the painted surface.

One of the effective ways to improve the quality of paint and varnishes is to introduce surfactants into their composition [6-8]. It was demonstrated that the introduction of surfactants in paint and varnishes changed not only the dispersability of the pigments and fillers included in them, but also the nature of the adsorption and intermolecular interactions in the system. According to the molecular (adsorptive) theory of polymer adhesion, the adsorption and intermolecular interactions, which were manifested in the establishment of the molecular contact of macrochains with the active centers of the substrate and the following formation of adhesion bonds, depended largely on the polarity and flexibility of the polymer chains [9].

The aim of this work is to study the effect of various surfactants on intermolecular interactions in silicone paint and varnishes.

Experimental

Silicone film-forming (polyphenylsiloxane varnish - PPS), toluene solvent (State Standard 14710-78) and three varieties of amine-based surfactants of different molecule-weight composition (Table 1) were used.

A viscosimetric method was used to assess the nature and regularities of the structure of amino derivatives and polyphenylsiloxane in toluene solutions. The dynamic viscosity of the prepared solutions was measured with a capillary viscosimeter VPZH-1 ($d = 0.56$ mm) in the thermostatic mode [10-11].

Table 1. Surfactants characteristics and notations

Amino derivatives	Chemical formula	Amine number, mg HCl/g	Weight-average molecular weight, a.m.u.	Brief Description
AS	$R'-NH_2$ and $R''-NH-R''$, where R' is n-butyl, R'' is 2-ethyl-2-hexynyl, (at the ratio of 1:3)	30	250	mixture of primary and secondary amines
TELAZ	$(-CH_2-CH(NH_2))_n$	32	2121	condensation product of vegetable oils with diamines
PEPA (brand B)	$(-C_2H_4-NH-C_2H_4-NH-)_n$	31	4950	high-molecular amine mixture

A low-frequency dielectrometry has been successfully applied to detect the physical grid of intermolecular bonds in the process of its formation [12-14]. Orientation polarization, as well as deformation, was recorded for the periods of charge and discharge of the capacitance sensor by a stable current in the frequency range of 1-10 kHz. The experimental values of the dielectric capacitance (ϵ') and the dielectric loss tangent ($\tan \delta$) were used to find the dipole-segment loss

coefficient ϵ'' ($\epsilon'' = \epsilon' \times \text{tg } \delta$) [9], which usually increases with polarity increase and molecular mobility of the polymers.

The volume-surface properties of individual solutions (toluene-additive, toluene-polyphenylsiloxane) and solutions of mixed composition (toluene-polyphenylsiloxane-additive) were studied by varying the content of amines and polyphenylsiloxane (0-2 g/dm³) and at temperatures of 295 and 313. The surface tension was determined by the method of the greatest pressure of air bubbles using Reh binder device [10].

Results and discussions

Study on the characteristics of solutions of PPS and surfactants effect of the concentration

Figure 1 shows the results from rheological studies of individual solutions of PPS, AS, TELAZ and PEPA at 295 and 313 K. As can be seen from the Figure, at both studied temperatures the specific viscosity of polyphenylsiloxane solutions (Fig. 1a) showed linear increase with increase of the concentration. These results indicated weak intermolecular interactions in polyphenylsiloxane solutions. The observed effect corresponded well to the literature data [15]. The latter was connected with the specific structure of polyphenylsiloxane macromolecules where the inorganic chain of silicon and oxygen atoms was surrounded by aryl radicals. The possible explanation could be found in the fact that in amino derivatives containing secondary or ternary amino groups, as well as primary amino groups located at the end of the polymer chains, the dependence of specific viscosity on the concentration had totally different nature and reflected their susceptibility for association processes (Fig. 1b). A significant deviation from the linear dependence of $\eta_{sp}= f(C)$ in solutions of all studied amino derivatives at concentrations above 0.5 g/dm³ was observed. The formation of associated structures in these solutions could be supposed. The further increase of amino derivatives concentration resulted in more pronounced association effects. The increase of viscosity in the concentration range of 0.5-2 g/dm³ corresponded to the molecular weight ratio of amino derivatives. The viscosity increased in the following order: PEPA> TELAZ> AS.

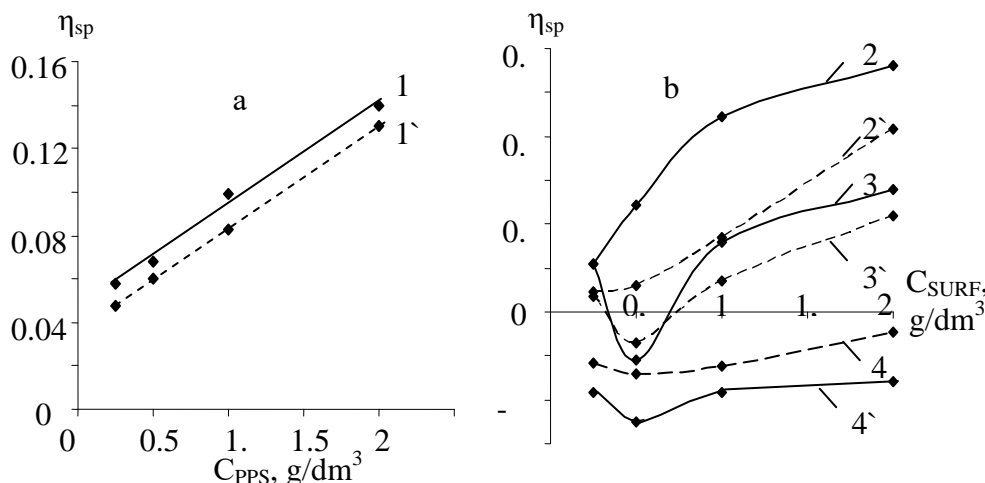


Fig. 1. Dependence of the specific viscosity on the concentration of polyphenylsiloxane (a) and amino derivatives (b): 1 and 1' - PPS; 2 and 2' - PEPA, 3 and 3' - TELAZ; 4 and 4'-AS at 298 K (solid line) and 313 K (dashed line)

The observed changes in the specific viscosity agreed with the results obtained from a study of the surface tension at the interface solution/air. The obtained surface tension isotherms (σ) are presented on Figure 2. As can be seen from the Figure, the concentration dependence of surface activity of amino derivatives showed extreme and the curves differed in intensity and width according to the type of amine derivative. The effects were related with the intermolecular associates formation positions and the localization degree of active functional groups.

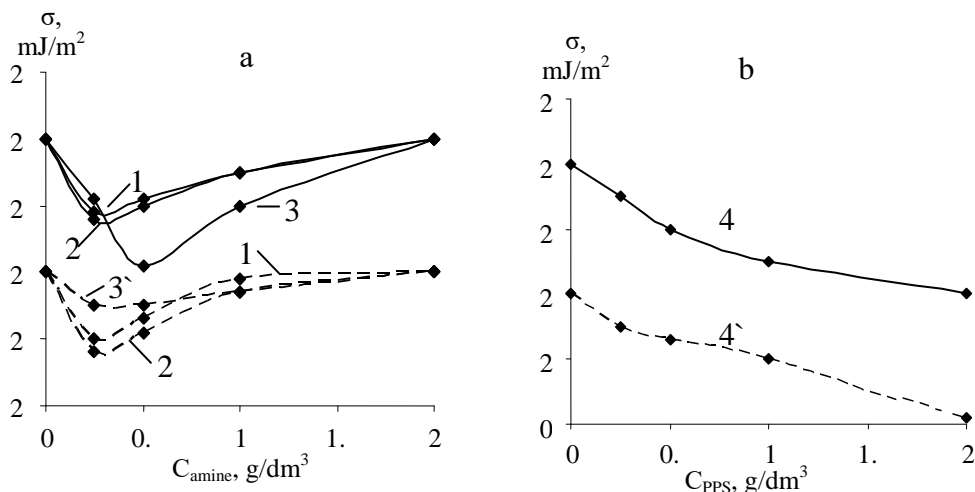


Fig. 2. Isotherms of surface tension at the interface solution/air of individual solutions of: 1, 1' - PEPA; 2, 2' - TELAZ; 3, 3' - AS; 4 - PPS at 298 K (solid line) and 313 K (dashed line)

Based on the obtained surface tension isotherms ($T=298\text{K}$) in the concentration range where association effects were practically not manifested, it could be concluded that in the amino derivatives solutions existed unbound diphilic molecules and their concentration in the surface layer increased. The assumption was confirmed by a decrease in the surface tension values. Two concentration sections on the obtained isotherms can be distinguished, which allow to distinguish between the activity of low-molecular and higher-molecular types of amino-derivatives. In solutions with $C \leq 0.25 \text{ g/dm}^3$, PEPA and TELAZ showed the highest surface activity. However, the surface-active properties of AS (a lower molecular mass amine) were enhanced in more concentrated solutions. The maximum depression of surface tension ($\Delta\sigma = 1.9 \text{ mJ/m}^2$) was recorded in AS solutions at a concentration of 0.5 g/dm^3 . As the concentration further increases ($C > 0.5 \text{ g/dm}^3$) the structure formation processes was accompanied by the spontaneous decrease in the unbound (free) molecules of the amino derivatives and the corresponding continuous deterioration of the surface properties (ascending isotherms). At $C = 2.0 \text{ g/dm}^3$ the surface tension was stabilized in solutions at a level of 28.0 mJ/m^2 , which corresponds to the σ value of the solvent (toluene). Two effects could be supposed: (1) depletion of amino derivatives in the surface layer and (2) complete localization of the functional groups in the internal structure of the intermolecular associates formed in the bulk of the solution.

Effect of the temperature

It should be noted that the effect of the temperature in the range 295-313 K on the indices η_{sp} and σ depended on the molecular weight of the studied amino derivatives. The specific viscosity of the PEPA and TELAZ solutions decreased with increasing the temperature up to

T=313K (Fig. 1 b). In contrast the specific viscosity of AS solutions (low-molecular amine variety) increased at higher temperatures. The most pronounced effect was observed at $C_{AS}=0.5$ g/dm³ (Fig. 1b). The latter might due to the intensification of solvation of AS. The hypothesis was additionally supported by the observed sharp deterioration of the AS surface activity (Fig. 2a). The values of depression of surface tension ($\Delta\sigma$) at 313 K were 2-4 times lower compared to the obtained values at 298 K. At 313 K, the depression of surface tension of AS solution regarding the pure solvent ($\Delta\sigma$) was equal to 0.5 mJ/m². In the same concentration range, the depression of surface tension of PEPA and TELAZ solutions remained at the same level ($\Delta\sigma=1.2\pm 0.2$ mJ/m²).

The surface activity deterioration in the first case and the invariance in the second case excluded the release of amines and, consequently, the destruction of intermolecular structures at T=313K. which could be suspected given the natural increase in the associates thermal motion at increased temperatures. At the same time, it is well known that the specific viscosity values that exclude the influence of solvent thermal expansion were affected not only by the number of associates, but also by the steric restrictions they created for the liquid flow [16].

To summarize, in AS solutions, characterized by smaller hydrocarbon radical dimensions, the improved thermodynamic quality of the solvent led to swelling of the associate particles and, thus, to an increase in the specific viscosity. In higher molecular amine solutions, the temperature increase caused an increase in intermolecular interactions within the associates accompanied by a decrease of the size of associate particles. The intermolecular structures folded into a tight ball gave less resistance to the flow. As a result, the specific viscosity of the studied solutions decreased 2.4-2.6 times at 1 g/dm³ and 1.3-1.4 times - in more concentrated solutions ($C = 2$ g/dm³).

The results from the viscosimetric analysis were confirmed by the change of surface tension of PPS solutions (Fig. 2b). The behavior of PPS solutions followed the traditional form of silicone surfactants isotherms not prone to association processes. From the Figure 2b it could be seen that as the PPS concentration increased up to 2 g/dm³, σ decreases from 28 to 26 mJ/m². The same maximum depression of surface tension (2 mJ/m²) was observed at increased temperature (T=313K).

Study of the characteristics of mixtures of PPS and amine additives

Specific viscosity and surface tension of solutions containing polyphenylsiloxane at fixed concentration of 0.5 g/dm³ and the studied amines varieties at different concentrations ranged from 0.25 to 2.0 g/dm³ were studied at 295 and 313 K. The results are presented in Table 2 and Fig. 3. As a quantitative measure of the processes developed in the bulk and on the interphase boundaries, the calculated values of the indices η_{sp} and σ for an ideal system (in the absence of intermolecular interactions between the mixture components) were used along with their experimental values. In addition, for a comparative evaluation of these processes, the surface tension differential changes ($\sigma_{exp.-} \sigma_{calc.}$) and relative change of specific viscosity: $\gamma = \frac{\eta_{sp.exp.}}{\eta_{sp.calc.}}$ were calculated.

Table 2. Calculated and experimental values of specific viscosity of PPS (0.5 g/dm³) and amine additives at different concentrations in toluene

C, g/dm ³	T = 298K			T = 313K		
	$\eta_{sp.exp.}$	$\eta_{sp.calc.}$	γ	$\eta_{sp.exp.}$	$\eta_{sp.calc.}$	γ
	AS					
0.25	0.033	0.031	1.050	0.039	0.037	1.05
0.5	0.063	0.018	3.500	0.048	0.032	1.50
1	0.077	0.031	2.480	0.056	0.035	1.60
2	0.089	0.036	2.470	0.083	0.051	1.63
	TELAZ					

C, g/dm ³	T = 298K			T = 313K		
	$\eta_{sp.exp.}$	$\eta_{sp.calc.}$	γ	$\eta_{sp.exp.}$	$\eta_{sp.calc.}$	γ
0.25	0.092	0.090	1.020	0.089	0.067	1.33
0.5	0.078	0.066	1.180	0.073	0.046	1.59
1	0.089	0.100	0.890	0.112	0.074	1.51
2	0.107	0.124	0.860	0.131	0.104	1.86
PEPA						
0.25	0.078	0.090	0.870	0.092	0.090	1.02
0.5	0.102	0.118	0.860	0.078	0.066	1.18
1	0.121	0.157	0.770	0.089	0.100	0.89
2	0.140	0.187	0.770	0.107	0.124	0.86

The data obtained (Table 2) showed that in the studied concentration range, there were deviations from the ideal system due to an association of molecules of amino derivatives with PPS macromolecules. The most pronounced change in the specific viscosity (by a factor of 3.5) was observed in solutions of AS at $C = 0.5 \text{ g/dm}^3$ and $T=298 \text{ K}$. Hence, the development of heteroassociation processes in solutions of a low molecular mass amines was much more intensive compared to other studied amines. The formation of intermolecular structures was confirmed by an increase in the cohesive interaction strengths in AS solutions and a shift of the surface activity maximum to the region of lower concentrations (Fig. 3a).

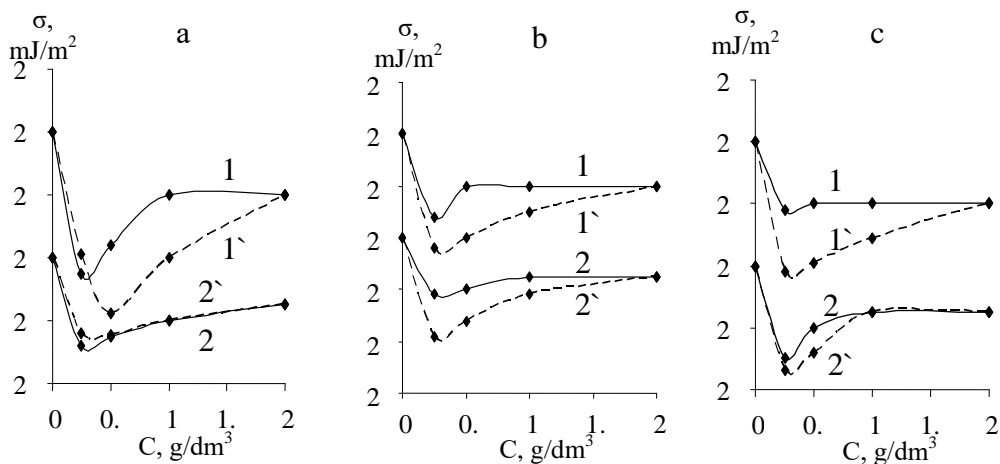


Fig. 3. Experimental (solid lines) and calculated (dashed lines) dependence of the surface tension of polyphenylsiloxane solutions ($C=0.5 \text{ g/dm}^3$) on the concentration of amine-containing surfactants: (a) AS; (b) PPS; (c) TELAZ at different temperatures (1) 298 K and (2) 313 K

As can be seen from the data presented on Fig. 3, in a narrow range of surfactants' concentrations ($C \leq 0.25 \text{ g/dm}^3$), a negative deviation of the surface tension (-0.5 mJ/m^2) from the ideal system behavior was observed. Hence, in the absence of intermolecular interactions in the solution ($\gamma=1.05$) a synergism was observed in the surface properties of the binary mixture. Outside this interval, a positive deviation of the surface tension experimental values from the additive contribution of the two components (PPS and AS) was noted. The maximum intensification of heteroassociation processes at $C=0.5 \text{ g/dm}^3$ ($\gamma = 3.5$) corresponded to the maximum increase in σ ($\Delta\sigma=+1.03 \text{ mJ/m}^2$), due to the decrease in unbound amines. Stabilization of the structure formation processes ($\gamma=2.47-2.48$) at $C=1-2 \text{ g/dm}^3$ was consistent with the invariance of the surface tension in this concentration region. The surface tension of the mixtures (27.0 mJ/m^2) practically coincided with the surface tension of PPS solutions.

The temperature increase (up to $T=313\text{K}$) resulted in change in surface tension and a decrease of the values of γ by a factor of 1.5-2. Hence, a quantitative destruction of

heteroassociates, indicated by the additive contribution of PPS macromolecules, and released amines, as a result of breaking bonds, could be supposed.

Based on the significant increase in σ values, a formation of associated structures was not excluded in solutions of higher molecular amines (Fig. 3b, c). In the mixtures containing high molecular amines the association processes and inversion of surface activity developed at lower concentrations compared with AS containing mixtures. If in toluene individual solutions with $C = 0.25 \text{ g/dm}^3$, as it was mentioned above, the TELAZ and PEPA had the greatest surface activity, the opposite effect was observed in the mixtures with PPS.

The stability of the formed heteroassociates and the different trends in the changes of the η_{sp} ($\gamma < 1$ and $\gamma > 1$) in solutions with higher molecule amines indicated some differences in the mechanisms of amine association with PPS macromolecules.

Based on the results from dielectrometric measurements presented on Figure 4a, it could be suggested that the amino derivatives, depending on individual characteristics (composition, structure, spatial orientation), underwent two types of over- and intramolecular transformations. The first corresponded to the association of AS molecules with PPS macromolecules, i.e. the formation of kind of surfactant-polymer complexes. AS easily penetrated into the polymer structure and after reaching a critical concentration for association ($C_{CCA} > 0.25 \text{ g/dm}^3$), it was fixed (due to hydrogen and weaker Van-der-Waals forces) along the length of the PPS macromolecule. In this way AS promoted the expansion of PPS molecules and the formation of additional bonds between them. As a result, the chain mobility decreased (Fig. 4a), and the structure strength increased, which reflected the increase in dynamic viscosity (Fig. 4b). Process stabilization at a concentration range of 1-2 g/dm^3 was confirmed by the invariance of the indices ϵ'' and η .

A significantly longer length of the hydrocarbon radical of TELAZ and PEPA would limit their migration in the bulk of the solution, thus creating steric restrictions for this type of heteroassociation. For TELAZ and PEPA, the interaction between each other (monoassociation) was energetically more advantageous with the simultaneous introduction into their composition of PPS macromolecules (mixed micelles). As the PPS macromolecules were included in the association composition, a continuous decrease in the chain mobility and a synchronous increase in the dynamic viscosity (curves 1 and 2 in Fig. 4a, b) were observed.

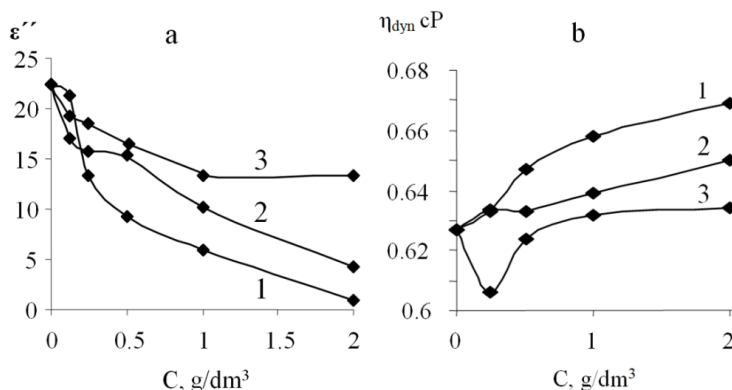


Fig. 4. The concentration effect of amine-containing surfactants on the dipole-segmental coefficient (a) and the dynamic viscosity (b) of polyphenylsiloxane solutions ($C=0.5 \text{ g/dm}^3$) at $T=298 \text{ K}$

Conclusions

The effect of surfactants on the dielectric and rheological characteristics of polyphenylsiloxane solutions was studied. It has been established that an increase in the content

of surfactants in PPS solutions led to an increase in the dynamic viscosity and a decrease in the dipole-segmental loss coefficient. The observed result was supposed to be due to the effect of surfactants on the opening of cycles in PPS molecules and the formation of additional bonds between them.

Dynamic viscosity of PPS solutions in the presence of amine-containing surfactants was studied. It was established that the dynamic viscosity of studied mixtures increased with increasing surfactant content in PPS solutions. Depending on the ability to increase the dynamic viscosity of PPS solutions, surfactants could be arranged as follow: AS < TELAZ < PEPA.

The dielectric characteristics (dielectric loss tangent and permittivity) of PPS solutions in the presence of amine-containing surfactants were studied. Based on the results from dielectrometric measurement, it could be supposed that the surfactants promoted structuring PPS solutions due to the effect of amine surfactant on cycles disclosure in PPS molecules and the formation of additional bonds between them.

Thus, the formation of macromolecular structures was observed in all three varieties of amines and was substantially enhanced in concentrated solutions. The processes of heteroassociation reduced the amines surface activity and shifted it into the region of lower concentrations ($C_{\text{SURF}} \leq 0.5 \text{ g/dm}^3$)

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