

RHEOLOGIC PROPERTIES OF POLYELECTROLYTES AT LIQUID/LIQUID
INTERFACES

I. THE EFFECTS OF SURFACE-ACTIVE SUBSTANCES ON POLYELECTROLYTIC
ADSORPTIVE LAYERS

by

I.B. Musabekov and K.K. Ibraev

Kirov Kazakh State University, Alma-Ata, U.S.S.R.

(Received 12 December 1986)

Viscosity and strength of adsorption of layers of polyelectrolytes - poly(acrylic acid) (PAA), poly(methacrylic acid) (PMAA), polyethyleneimine (PEI) - on the boundary of their aqueous solutions with cationic (octadecylamine (ODA)) and anionic (stearic acid (HSt)) surface-active substances (SAS) dissolved in benzene. Associations of oppositely charged polyelectrolytes and SAS (PAA-ODA, PMAA-ODA, PEI-HSt) have the most structure-forming properties at interfaces.

Synthetic polyelectrolytes (SPE) are widely used in foam and emulsion stabilization. This is connected with their ability to accumulate in interfacial layers and form concentrated protective films. A very perspective trend in this field is SPE interfacial adsorptive layer (IFAL) modification by means of surface active substances (SAS).

The aim of the present work is to study the effects of the oil-soluble SAS stearic acid (HSt) and octadecylamine (ODA) on the interfacial shear viscosity of the IFAL SPE poly-methacrylic acid (PMAA), polyethyleneimine (PEI) and polyethyleneglycol (PEG). The methods of production and preparation of PMAA for work and the purification of the SAS are described in /1-3/. The branched PEI was kindly supplied by P.A. Gembitsky PEG produced by Schuchardt was used without preliminary purification. C.d.a. benzene was distilled twice (n_D^{20} 1.5006). The interfacial shear viscosity (η^s) was measured at 293 K by the method of Trapesnikov /4/ and was calculated via the formula:

$$\eta^{\sigma} = 2 K M (\lambda/T - \lambda_{\omega}/T_{\omega}) \quad (1)$$

where M is the effective value of the inertial moment of the suspension system in water, kg m^2 ; λ and λ_{ω} are the decrements of the disk vibration damping in the tested solution and in distilled water; and T and T_{ω} are the disk vibration periods in the tested solution and in distilled water, s.

$$K = (4\pi)^{-1} (1/R_1^2 - 1/R_2^2) \quad (2)$$

where R_2 is the internal radius of the cell immersed in the tested liquid, m; and R_1 is the glass disk radius, m. A 15 mm radius disk, a 50 mm diameter cell and tungsten filaments 0.53 m long and 0.05-0.14 mm wide were used in the study.

Figure 1 illustrates the kinetics of η^{σ} change at the aqueous PMAA and PEG solution/pure benzene and ODA benzene solution interfaces.

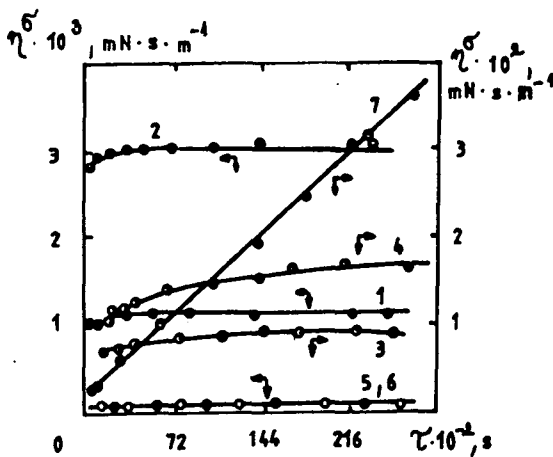
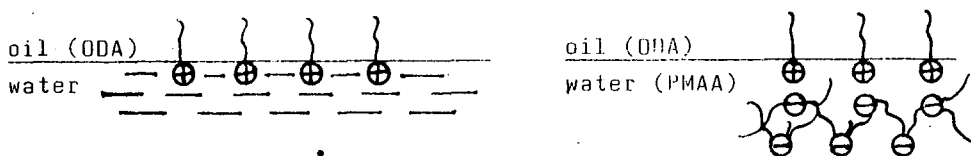


Fig. 1. Kinetics of η^{σ} change on the boundary of aqueous PEI (1,2) or PMAA (3,4,7) solutions with benzene (1,4), or with a $7.4 \cdot 10^{-4} \text{ mol dm}^{-3}$ ODA

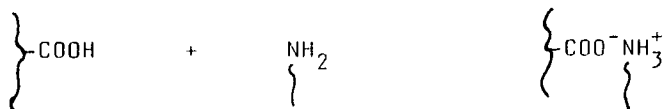
solution in benzene (7), and of water with $1 \cdot 10^{-3} \text{ mol dm}^{-3}$ ODA solution in benzene (5) or $7.04 \cdot 10^{-4} \text{ mol dm}^{-3}$ HSt solution in benzene (6). Concentrations of SPE (in mol dm^{-3}): PEI $2.28 \cdot 10^{-3}$ (1), $2.28 \cdot 10^{-2}$ (2); PMAA $4.7 \cdot 10^{-4}$ (3,5), $17.9 \cdot 10^{-4}$ (4).

That for the ODA benzene solution IFAL ζ^{σ} versus distilled water is also shown. It can be seen from the Figure that in the tested concentration interval ODA does not form adsorptive layers with noticeable viscosity and the absolute values of ζ^{σ} are within the limits of experimental error. Similar data are obtained with HSt. The PEI adsorptive layer viscosity is also small, though an insignificant increase in ζ^{σ} is observed with rise of the polyelectrolyte concentration. On the other hand, the equilibrium value of ζ^{σ} in PEI solutions is obtained rather rapidly, which may be connected with the weak adsorption of PEI due to its small chain difility. In contrast the equilibrium value ζ^{σ} in a PMAA solution is obtained after a long response time (2-8 hours), most likely because of delayed macromolecule diffusion to the interfacial surface in the dilute solutions and their slow denaturation in IFAL /5/ formed from concentrated solutions.

When an aqueous PMAA solution comes into contact with an ODA benzene solution, an abrupt rise in ζ^{σ} is observed, change in ζ^{σ} taking place over a long time period (Fig. 1, curve 7). The absolute value of ζ^{σ} is much larger than the summed value of ζ^{σ} for PMAA at the pure benzene - ODA benzene solution/water interface. In other words, a synergetic effect is observed in the ζ^{σ} increase, which may be connected with PMAA+ODA complexation at the interface. This process can be represented schematically in the following way:



The ODA positive charge probably arises as a result of amino group protonation by the polyacid carboxylic group proton:



The slow change in ζ^{σ} may be a result of the delayed macromolecule conformation equilibrium in IFAL.

Figure 2 gives η^{σ}/C_{SPE} isotherms for PEG, PMAA and PEI/HSt mixtures. The nonionic polymer PEG having an average molecular mass of $4 \cdot 10^4$ is weakly adsorbed at the water/benzene interface and forms adsorptive layers with low η^{σ} values. The IFAL viscosity gradually rises with PMAA

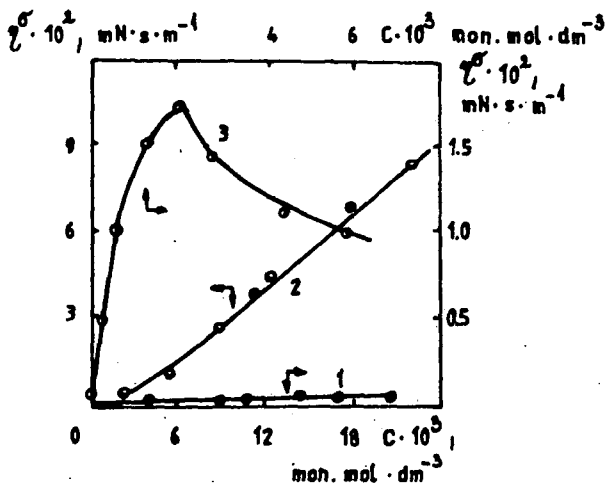


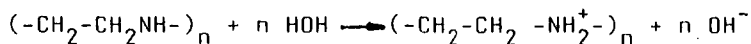
Fig. 2. η^{σ} isotherms of aqueous solutions of PEG (1), PEI (2) and PMAA (3) on the boundary of contact with benzene (1,3) and $7.04 \cdot 10^{-4} \text{ mol dm}^{-3}$ HSt solution in benzene (2).

concentration increase, passing through a maximum; this may be connected with the difficulty of macromolecule adsorption from concentrated solutions due to structure-forming /6/.

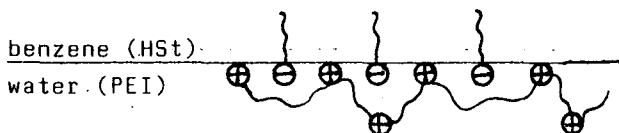
When an aqueous PEI solution comes into contact with an HSt solution, a linear rise in η^{σ} is observed, accompanied by a high-molecular component concentration increase.

The introduction of oil-soluble SAS into the nonpolar phase does not essentially affect the η^{σ} of an aqueous PEG solution. The absolute value of η^{σ} greatly exceeds the IFAL viscosity of the separate components for the aqueous PEI solution/HSt benzene solution system. As in the above-mentioned PMAA/DDA system, the considerable rise in η^{σ} is connected

with the formation of a PEI/HSt association in the interfacial adsorptive layer. The HSt concentration at the interface leads to the appearance of the negative charge at the benzene surface. On the other hand, PEI receives positive charge as a result of interaction with water:



Thus, a PEI/HSt electrostatic interaction in the adsorptive layer becomes possible and is expressed by the following scheme:



The interaction of the SPE and SAS functional groups stimulates stronger hydrophobic segment interaction, and also leads to PEI chain fixation at the interface. All this causes a sharp viscosity increase for the PEI/HSt associations in IFAL. The increase in η^6 at the aqueous polyelectrolyte solution/SAS benzene solution interface, the two compounds being oppositely charged, is enhanced by the concentration increase of both components, irrespective of their nature. Thus, an increase of the initial PEI concentration in its aqueous solution is accompanied by an increase in the rate of rise of η^6 at the interface of HSt benzene solutions of increasing concentration /Fig. 3/. A similar effect is observed at the aqueous PMAA solution/ODA benzene solution interface (Fig. 4).

In both cases, however, the introduction into the nonpolar phase of SAS charged similarly to SPE leads to a substantial decrease in η^6 (Fig. 3, curve 4; Fig. 4, curve 4). This is not surprising, for the accumulation of SAS charged similarly to SPE at the interface leads to a decreased polymeric ion adsorption, in accordance with the SPE adsorption theory relating to charged surfaces /7/.

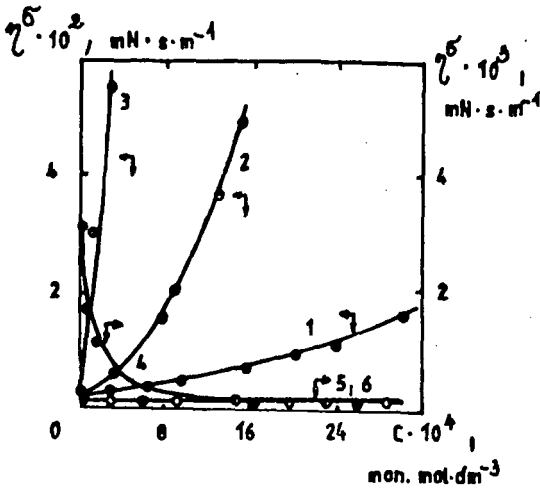


Fig. 3. ζ^{σ} isotherms of benzene solutions of HSt (1-3,6) and ODA (4,5) on the boundary of contact with water (5,6) and aqueous solutions of PEI (1-4).

Concentration of PEI (mol dm⁻³): $2.28 \cdot 10^{-3}$ (1), $6.84 \cdot 10^{-3}$ (2) $2.28 \cdot 10^{-2}$ (3,4).

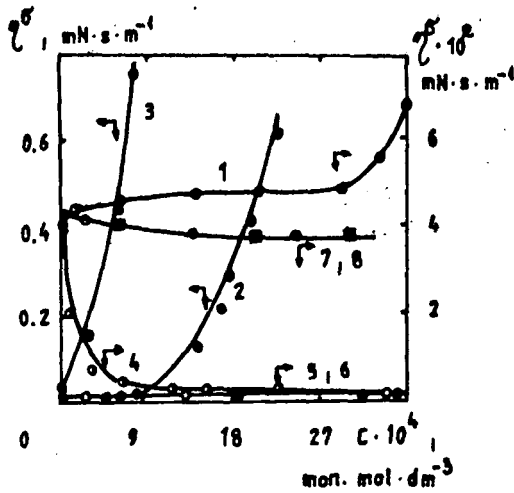


Fig. 4. ζ^{σ} isotherms of benzene solutions of ODA (1-3,5,7) and HSt (4,6,8) on the boundary of contact with water (5,6) and aqueous solutions of PMAA (1-4) and PEG (7,8). Concentration of SPE (mol dm⁻³): PMAA $3.5 \cdot 10^{-4}$ (1), $4.7 \cdot 10^{-4}$ (2), $17.9 \cdot 10^{-4}$ (3,4); PEG $1.6 \cdot 10^{-2}$.

The SAS have practically no influence on the IFAL ²⁶ of an aqueous PEG solution. (Fig. 4, curve 7).

Conclusion: the rheologic properties of IFAL polyelectrolytes at a water/hydrocarbon interface can be regulated by means of SAS introduced into the nonpolar phase.

References

- /1/ Aidarova, S.B., K.B. Musabekov: Kolloidn. Zh. 41, 117 (1979)
- /2/ Wiederhorn, N.M., A.R. Brown: J. Polym. Sci., 8, 651 (1952)
- /3/ Musabekov, K.B., K.K. Ibraev: V knige: Fiziko—chimicheskie issledovaniya v rastvorach, Alma-Ata, 123 (1982)
- /4/ Vins, V.G., A.A. Trapeznikov: Dokl. Akad. Nauk (USSR), 248 1352 (1979)
- /5/ Tanchuk, Yu.V., G.S. Pop: Kolloidn. Zh. 40, 1209 (1978)
- /6/ Lipatov, Yu.S., L.M. Sergeeva: Adsorptsiya polimerov, Kiev, Naukova dumka, 1972
- /7/ Kuzkin, S.V., V.P. Nebera: Sinteticheskie flokulyanty v protsesakh obezvozhivania, Moskva, Gostekhizdat, 1963

РЕОЛОГИЧЕСКИЕ СВОЙСТВА ПОЛИЭЛЕКТРОЛИТОВ НА ГРАНИЦЕ ЖИДКОСТЬ—ЖИДКОСТЬ. I. ВЛИЯНИЕ ПОВЕРХНОСТНО—АКТИВНЫХ ВЕЩЕСТВ НА АДсорбЦИОННЫЕ СЛОИ ПОЛИЭЛЕКТРОЛИТОВ.

К.Б. Мусабеков, К.К. Ибраев

Изучены вязкость и прочность адсорбционных слоев полиэлектролитов /полиметакриловой (РММА) кислоты, полиэтиленimina (PEI)/ на границе их водных растворов с растворенным в бензоле катионным /октадециламин (ОДА)/ или анионным /стеариновая кислота (HSt)/ поверхностно—активным веществом (SAS). Наибольшими структурообразующими свойствами в межфазных слоях обладают ассоциаты противоположно заряженных полиэлектролитов и SAS: РММА—ОДА, PEI—HSt.