STABILISATION OF BITUMEN EMULSIONS

M. Georgescu*, **G. Popescu, G. Grâsâc, O. Nita**

Introduction

Bitumen emulsions represent a technologic variant often used at the rehabilitation and construction of the roads, being a cold application process.

The bitumen from oil refinement has a complex chemical composition, its complexity being determined by the "composite" character of this one. Three fundamental types of colloidal structure were defined, depending on the structure of components and their content and type of structure: "gel" type of structure, "sol" type of structure and "sol-gel" type of structure. Most of road bitumen belongs to the last type, and the differences in their behaviour come from sol-gel transition and the aromatic character of the dispersed medium.

It was accepted that the bitumen is a colloidal system made of four groups of components as it follows in Fig. 1 [1].

- asphaltene resins that are present as disperse colloids disposed as micelles (asphaltenes surrounded by the resins);
- saturated and aromatic oils represent the dispersion medium.

The determination of bitumen composition is based on the difference in the four types of components solubility in polar and non-polar solvents and it can be made by combining the extraction with gravimetry or by flame ionisation chromatography detector (IATROSCAN).

Asphaltenes can be found in colloidal bitumen as aggregates, fact proved by X-rays diffraction, the molecules having a great tendency for self-association. Asphaltenes nuclei are quasispheric, forming several layers. Inside the cavities inorganic salts or metals (Fe, Ni, V etc) can be found.

Asphaltenes are not soluble in oils but the presence of the resins having a chemical structure and molecular weight is intermediary between that of the oils and that of the asphaltenes contributing to the maintaining of the asphaltenes in the phase formed from oils

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* Research Center for Macromolecular Materials and Membranes, Splaiul Independentei 202B, sector 6, Bucharest

Analele Universității din Bucureşti – Chimie, Anul XII (serie nouă), vol. I-II, pag. 25–30

and resins, called the “maltenic” phase. A colloidal dispersion can be realised from asphaltenes in maltenic phase by asphaltenes peptisation in oils and resins.

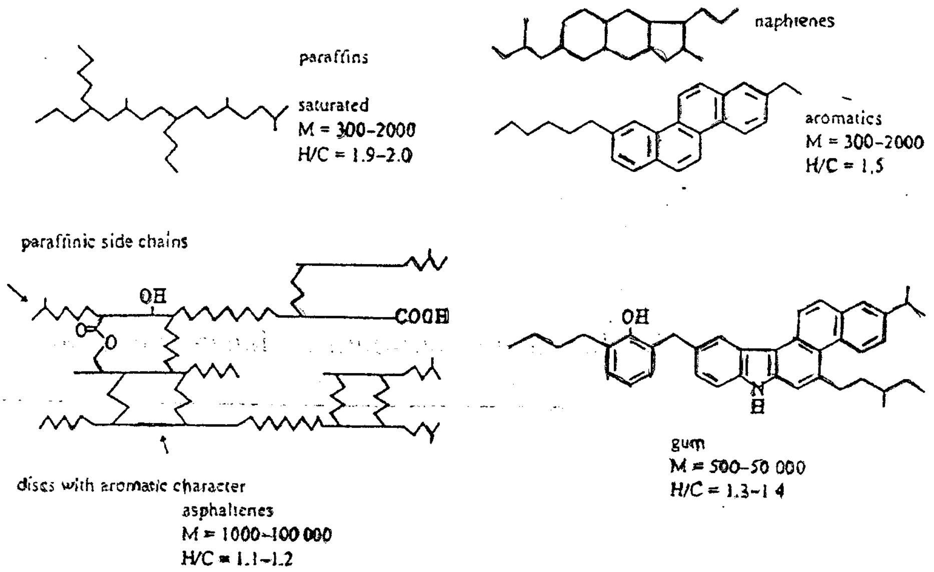


Fig.1: *Colloidal system made of four groups of components.*

The stability of colloidal system increases as the content of aromatic hydrocarbons increases (about 50%). The parafines help the precipitation of asphaltenes that destroy the colloidal system. A good bitumen has a maximum content of about 10% asphaltenes.

Because Romanian bitumens have the aromatic hydrocarbons content between 24-36%, and that of asphaltenes is increased (16-18%), the introduction of some adhesives is necessary and this leads to a change of the colloidal balance of the bitumen.

This change doesn’t have a negative influence on the stability of colloidal system and doesn't lead to a fast separation of the phases, or to a temperature at which all the components are in liquid state.

An important role in the preparation of bitumen emulsions has the emulsifier that besides the stability can ensure the improvement of the emulsion and the bonding capacity of the inorganic aggregates, by the modification of surface tension. The distribution of the emulsifier between the two phases (aqueous and bitumen) acts on the breaking speed of emulsion. This distribution of the emulsifier is extremely important, being correlated to the time of the emulsifier, to the concentration of surface tension and to the micelle critical concentration (CMC) [4].

Is very important to know and anticipate the evolution of these characteristics during a period of time because an emulsion has to keep its stability in time and carry out the role of ligand inside the asphalt mixture.

Experimental Methods and Materials

A bitumen from Crisana (Suplacu de Barcau) was used having the following composition:

– asphaltenes	16÷17%
– saturated hydrocarbons	42÷44%
– cyclic hydrocarbons	32÷36%
– resins	12÷13%
– colloidal stability index (IC)	1.0÷1.4

The following emulsifiers were tested:

- anionic type sodium dodecyl sulphate, CH_3-$(CH_2)_{11}OSO_3Na$ (SDS) (from Merck) M=288.3 with CMC=$8.2\div9.0\times10^{-3}$ mol/L;
- cationic type, cetyl trymethylammonium $CH_3(CH_2)_{15}NBr(CH_3)_3$ (CTAB) M=364.5 with CMC=4.0×10^{3} mol/L;
- cationic polyelectrolyte, PONILIT CS_2, polymer produced by Macromolecular Chemistry Institute “P.Poni” Jassy, obtained by the polymerisation-polycondensation of dimethylamine with 1,3 diaminepropane and epyclorhydrine.

The concentration of the solution: 346%, M=80.000.

Surface tensions were determined with a tension - meter by drop volume method.

Critical micelle concentration (CMC) was determined from the variation of surface tension with the concentration of the emulsifier. The solutions were prepared with distilled water, at working concentration of about 1%.

Results and Discussions

It is known that the polyelectrolytes have a lower hydrophobicity in general and an adsorption capacity and lower surface activity compared to classic emulsifiers.

The surface tension curves vs. the concentration of polyelectrolyte solutions (curve 1) and for the two types of emulsifiers: anionic SDS (curve 2) and CTAB (curve 3) are presented in Fig. 2.

The values of critical micelle concentration experimentally determined are according to the data reported in the literature. It can be noticed that the surface tension of water at 25°C=70 dyne/cm, of anionic emulsifier for a 1% solution, the concentration in the bitumen emulsion is 37 dyne/cm and for the cationic emulsifier is 34 dyne/cm. This proves that the capacity of surface-active compound of two emulsifiers for the reduction of the surface tension during the process for forming the emulsion.

The addition of small and variable amounts of surface active compounds with opposite ionic charge (SDS) in PE solution up to constant working concentration (Fig. 3) produces a synergetic effect on surface tension decrease. This can be explained by the formation of some aggregates with strong surface activity and the formation of a surfactant-polyelectrolyte complex (SPECOM).

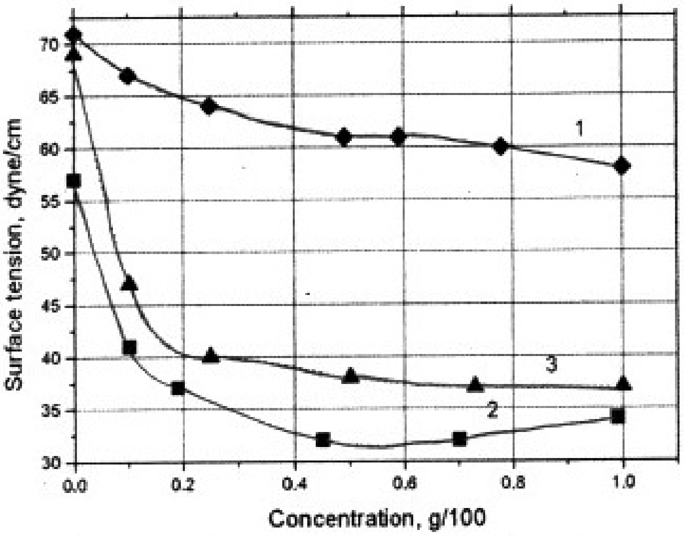


Fig. 2: *The variation of surface tension with the concentration for:*
cationic polyelectrolyte PONILIT CS_2-curve 1, anionic emulsifier SDS-curve 2 and cationic CTAB-curve 3.

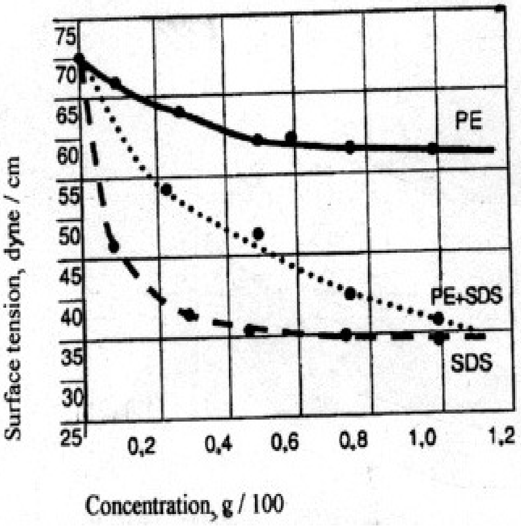


Fig. 3: *The variation of surface tension with concentration for PE-SDS (1:1) complex, compared to PE and SDS.*

In case of the addition of surfactant with the same ionic charge (CTAB), surface tension of the mixture with PE doesn't decrease that much (Fig. 4).

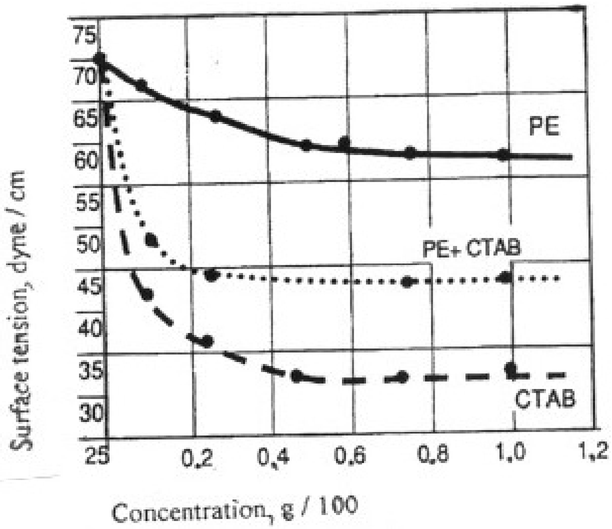
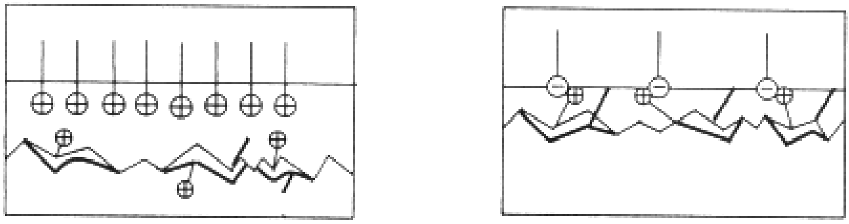


Fig. 4: *The variation of surface tension with concentration for complex, PE-CTAB compared to PE and CTAB.*

The two situations can be represented schematic as it follows (Fig. 5)



(a) (b)

Fig.5: a) cationic surfactant and cationic polyelectrolyte (having the same ionic charge) does not form a complex; b) anionic surfactant and cationic polyelectrolyte (having opposite ionic charge) forms a complex.

At the formation of bitumen emulsion, in the case of ionic opposite charge of PE and surfactant, the synergetic effect manifests by forming a complex SPECOM adsorption layer at the interface with bitumen drops and mutual rejection of these layers inside the emulsion. Stronger stabilisation effect can be explained by greater surface activity of the complex SPECOM in which the alkyl-hydrophobic chain of surfactant molecules acts as an "anchor" that stops the complex desorption and its removal with a liquid medium [2,3].

The steric stabilisation of microscopic liquid film (bitumen emulsion) with SPECOM complex, compared to polyelectrolyte is schematically presented in Fig. 6.

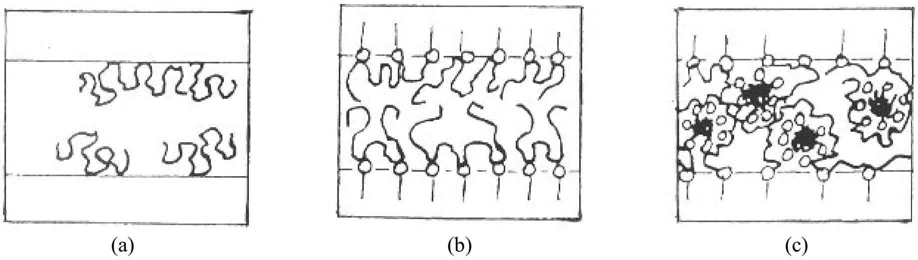

(a) (b) (c)

Fig. 6: *Schematic representation of steric stability of SPECOM complex, compared to PE.*
a) polyelectrolyte; b) lower critic micelle concentration (CMC); c) greater critic micelle concentration

Polymer adsorption capacity at bitumen surface and the creation of some "adhesion centres", respectively, were tested. The addition of 1% of SPECOM complex to Crisana bitumen leads to an increase of adhesion values [5]:

Table 1

Sample	Adhesion
Crisana Bitumen	74
Crisana Bitumen + 1% SPECOM	84

Conclusions

The influence of anionic type (sodium dodecyl sulphate) and cationic type (trymethyl cetyl-ammonium bromide) emulsifiers on the stability of bitumen emulsion shows a weaker influence of the cationic one compared to the anionic one.

The use of a mixture of emulsifier and polyelectrolyte in the ratio 1:1, at the working concentration of about 1%, a remarkable surface tension decrease in the case of emulsifier with an electric opposite charge (CTAB) can be seen, underlining the synergetic effect of SPECOM complex formed between PE and surfactant. This complex is strongly adsorbed at the surface of bitumen particle: the alkylhydrophobic chain of surfactant acts as an "anchor" that stops the complex desorption and its removal from liquid medium.

This polyelectrolyte also increases bitumen adhesion.

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