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# ***Atomic Force Microscopy Investigation of Interaction Forces Between Polyethylene and Asphaltene Surfaces in Nonaqueous Systems***

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*Many petroleum-derived asphalts used for road construction exhibit poor rheological properties. These properties of asphalt can be improved by addition of various polymer fillers to the asphalt blend. Recycled polyolefines, especially polyethylene and polypropylene have been used as the asphalt modifying fillers. Unfortunately the polyolefine-asphalt mixtures are not stable and have a tendency to separate because of the chemical incompatibility of the components. In our research, surfactants were used to improve polymer-asphalt compatibility. Interaction forces between a polyethylene particle and a polyethylene surface and between a polyethylene particle and an asphaltene-surface were measured in surfactant solutions in n-tetradecane and pyridine using the atomic force microscopy colloidal probe technique. Dodecylamine, lauric acid and tetraethoxylated lauric alcohol ( $C_{12}E_4$ ) were used as surfactants. The most pronounced change in the interactions was observed for polyethylene-polyethylene surfaces in the solution of lauric acid. At the same conditions polyethylene-asphaltene interactions were decreased. The most pronounced increase was the increase in the repulsion range (to 26 nm) between the spherical PE probe and flat polyethylene surface for  $10^{-3}$  M n-tetradecane solution of ethoxylated lauryl alcohol ( $C_{12}E_4$ ). In the case of lauric acid the interaction range extended to 24 nm and for dodecylamine to 21 nm. The interaction between the polyethylene sphere and flat asphaltene surface extended to 16 nm for dodecylamine, to 18 nm for lauryl alcohol ethoxylated ( $C_{12}E_4$ ) and to 14 nm for lauric acid.*

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## INTRODUCTION

A wide spectrum of modifying polymers has been used for asphalt fillers. In order for a polymer to be effective, it must blend with the bitumen and improve the flow resistance at higher temperature without making the bitumen too viscous at the mixing temperature or too brittle at low temperature. If used in road asphalt, the polymer should be capable of being processed by conventional equipment. In any case it must be easily available and inexpensive. Recycled polyolefines satisfy all the mentioned concerns. The addition of dispersed polyolefines to the asphalt blends helps to retard the low-temperature thermal stress cracking as well as rutting of the pavement at elevated temperatures. Other benefits include: greater fatigue resistance, reduced temperature susceptibility, increased tire traction and greater adhesion to the aggregate. Polymonoolefine polymers (e.g., polyethylene) do not contain double bounds and therefore have good thermal and aging resistance [1]. The major obstacles to widespread application of polyolefines for asphalt modification is low stability of the polymer dispersion in asphalt at elevated temperature, which results in separation of the polymer phase from the asphalt blend [2, 3]. The understanding of interaction forces existing between the polyolefine particles in the asphalt matrix and between the polyolefine particles and asphalt itself may help in further modification of these forces in order to improve the stability of the polymer-asphalt blends.

## THEORETICAL CONSIDERATIONS

Hydrocarbons and other apolar solvents have low dielectric constants, and a very small surface-charge density is usually developed at the surface in apolar solution. Thus the thickness of Debye's layer is very high. These facts account for a relatively weak electric double layer interaction force. For this reason, the van der Waals attractions in pure solvents cause coagulation. To prevent this phenomenon from occurring, surfactants can be used for steric stabilization. The van der Waals attractions are reduced on account of steric interaction between adsorbed polymer and surfactants chains [4, 5].

The relationship for attractive potentials, originating from the London-van der Waals dispersion forces for two equally sized spheres interacting in vacuum as derived by Hamaker, is as follow [4, 6]:

$$\Delta G_S^{att.} = -\frac{A_{11}}{6} \left[ \frac{2}{s^2 - 4} + \frac{2}{s^2} + \ln \frac{s^2 - 4}{s^2} \right] \quad (\text{EQ 1})$$

where:

$$s = a/R$$

$a$  = the distance between the particle centers

$R$  = the particle radius

$A_{11}$  = the Hamaker constant for the particles.

For small interparticle distances compared to the particle diameters, this relationship reduces to [4, 7]:

$$\Delta G_S^{att.} = -A_{11} \frac{R}{12h} \quad (\text{EQ 2})$$

where:

$h$  = the surface to surface distance between the particles

The above relationships are only valid for two spheres interacting in vacuum. In dispersion medium, which attenuates the interaction, an effective Hamaker constant should be used:

$$A^* = A_{11} + A_{22} - A_{12} \approx \left( A_{11}^{\frac{1}{2}} - A_{22}^{\frac{1}{2}} \right)^2 \quad (\text{EQ 3})$$

where:

$A_{11}$  = the Hamaker constant for the particles,

$A_{22}$  = the Hamaker constant for the solvent,

$A_{12}$  = the Hamaker constant for particle-solvent interaction

The repulsive interaction energy can be calculated from following equation:

$$V_R = 2\pi\epsilon R\xi^2 \ln[1 + \exp(-\kappa h)] \quad (\text{EQ 4})$$

where:

$\epsilon$  = the medium permittivity

$\xi$  = zeta potential of the emulsion

$\kappa$  = the Debye-Hückel parameter

The total interacting energy is:

$$V_T = V_A + V_R = -A^* \frac{a}{12h} + 2\pi\epsilon a\xi^2 \ln[1 + \exp(-\kappa h)] \quad (\text{EQ 5})$$

The classical DLVO theory cannot predict exactly the stability of the systems where the molecular structure and heterogeneity of the medium in which the particles are dispersed must be considered [8, 9, 10]. This is the case of the asphalt dispersions where asphalt matrix has a complicated structure.

The repulsive forces in sterically stabilized colloidal systems are often divided into those with enthalpic origin and those origin with an entropic or volume restriction origin. The domination of the enthalpic or entropic force determines parameters like: the interparticle distance in relation to the steric layer thickness, the particle size, the concentration of steric stabilizer and the interaction between the stabilizer and the continuous phase.

Fischer [11] first derived equation (6) for the interaction free energy due to enthalpic or mixing effects when interparticle distances are less than two times the steric layer

thickness. This relation gives the enthalpic or mixing contribution to the interaction energy as function of the interparticle distance.

$$\Delta G_S^{mix} = \frac{4\pi}{3V_1} \varphi_2^2 \left( \frac{1}{2} - \chi_1 \right) \left( L - \frac{h}{2} \right)^2 \left( 6R + 2L + \frac{h}{2} \right) \quad (\text{EQ 6})$$

where:

$V_1$  = the molar volume of the continuous phase

$\varphi_2$  = the polymer volume fraction in the steric layer

$\chi_1$  = the Flory-Huggins polymer-solvent interaction parameter

$L$  = the steric layer thickness

$R$  = the particle radius

$h$  = the surface-to-surface interparticle distance

The elastic or entropic contribution to the steric stabilization mechanism for two spherical particles covered with polymer or surfactants tails is obtained from equation (7), as reported in the literature [12].

$$\Delta G_S^{el} = 4L\nu\pi RKT \left( \frac{2}{3} - \frac{\delta_o}{2} - \frac{\delta_o^3}{6} + \delta_o \ln \delta_o \right) \quad (\text{EQ 7})$$

where:

$\nu$  = the total number of chains per unit area

$\delta_o = h/L$

$L$  = the steric layer thickness

With these equations we can estimate the total interaction free energy in an elastically stabilized system:

$$\Delta G_S^{tot} = \Delta G_S^{att} + \Delta G_S^{el} \quad (\text{EQ 8})$$

It is also possible to obtain a better understanding of how the surface coverage (stabilizer concentration) and steric layer thickness influence the colloidal stability.

## EXPERIMENTAL

### Materials

The polyethylene (PE) powder was a low-density PE (Scientific Polymer Product, Inc.) with a molecular weight (MW) of 1,800 and a melting point (mp) of 117°C. The spherical particles of PE were prepared using the method described by Nalaskowski et al. [13]. Powdered polymer was mixed with glycerol to form a 0.1% wt suspension. The suspension was agitated using an Ultra-Turrax type homogenizer (Silverson L4R) at 2,000 rpm

and heated above the melting temperature of the suspended material, i.e., 130°C for PE (mp 117°C). The temperature and stirring were maintained for about 10 min and then the homogenizer's head was removed and the suspension was left to cool for about 15 min until the temperature reached 50°C. The suspension was then diluted about ten times with cold water and left for another 5 min. The spherical particles were filtered from the suspension using 0.2  $\mu\text{m}$  pore size filter unit with a cellulose acetate membrane (Sigma Chemical Co.). The filter with separated particles was then rinsed with water several times to remove any residual traces of glycerol. Finally, the filter unit was dried at room temperature in a dust-free environment. The membrane with spherical particles was removed from the filtration unit. The spherical particles were eventually dried again in an oven at 75°C for 24 h in nitrogen at ambient pressure and subsequently stored in an evacuated (66.5 Pa) desiccator for 1 h.

The spherical particles of asphaltene were prepared in similar way. Because of the very high melting point (above 280°C) of asphaltenes and decomposition of polycondensed aromatic rings at high temperature, melting of asphaltene in glycerol (boiling point about 200°C) is impossible. Therefore, asphaltene powder was dissolved in toluene to form 30% wt. mixture and next mixed with glycerol to form a 0.1% wt suspension. The suspension was agitated at 2,000 rpm and heated above 150°C. The temperature and stirring were maintained for about 15 min and then the homogenizer's head was removed and the suspension was cooled to 50°C. The suspension was then diluted about ten times with cold water and the particles were filtered from the suspension using 0.2  $\mu\text{m}$  pore size filter. The filter with separated particles was then rinsed with water several times to remove any residual traces of glycerol. Finally, the asphaltene particles were dried at 130°C temperature in an evacuated (60 Pa) desiccator to a constant weight. The asphaltene particles had regular spherical shape and roughness was measured using atomic force microscope (see Figure 1).

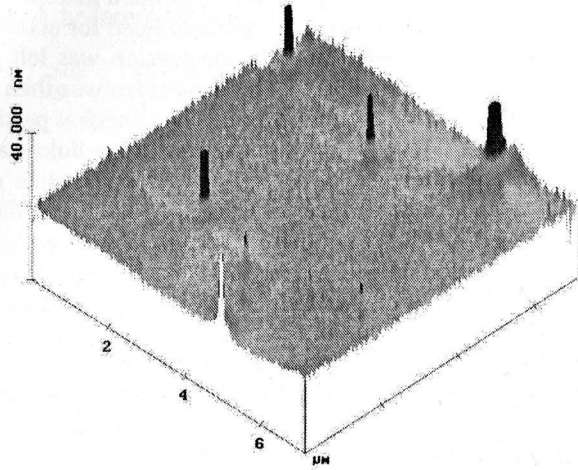
The asphaltene was extracted from an asphalt sample (D50 Rafineria Gdanska Ltd.). Small samples of asphalt (about 10 g) were dissolved in toluene, centrifuged and the mixture was filtered for removal of mineral precipitates. After that, n-heptane was added, the asphaltene was filtered from the suspension, and then rinsed 3 times by n-heptane. Finally, the filter unit was dried at elevated temperature (40°C) and stored in an evacuated desiccator.

For preparing a flat surface of asphaltene the spin-coating method was used. Small amounts of asphaltene (0.2 g) were dissolved in 3  $\text{cm}^3$  volume of toluene and several drops of the mixture were deposited at the surface of a glass disk rotating at 300 rpm. After evaporation of toluene, the disk with the film of asphaltene was dried in a desiccator to a constant weight.

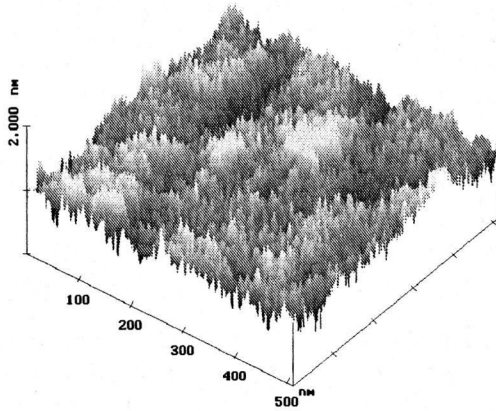
The disc of PE was prepared by melting powdered PE in a vacuum oven. The melt was casted onto a freshly cleaved mica surface. After cooling the PE disc was separated from mica under water. The obtained PE disc had very smooth surface as was determined by AFM imaging (see Figure 2).

## Methods

Topography features of the prepared asphaltene disc and PE spherical particles were measured using a Veeco Nanoscope III E AFM. Measurements were done in the contact mode (in air) by means of triangular oxygen-sharpened silicon nitride cantilevers (spring constant 0.12 N/m). Topographic images were obtained from the "height"



**FIGURE 1** Surface of asphaltene sphere prepared using the technique described in materials section



**FIGURE 2** Surface of the PE disc as measured by the AFM method

channel with relatively high values of integral and proportional gain. Images were planarized using a third-order planarization algorithm. Roughness measurements were performed using the Veeco Nanoscope III E software for  $2.5 \mu\text{m}^2$  areas of the sample.

Force measurements for the different systems were done using silicone nitride tipless cantilevers obtained from Veeco. A triangular cantilever ( $205 \mu\text{m}$  width,  $195 \mu\text{m}$  length,  $36 \mu\text{m}$  thickness) with a nominal spring constant  $0.12 \text{ N/m}$  were used. Before measurements, the spring constant was measured by Cleveland's method [14]. A small sphere of PE or asphaltene was glued to a cantilever using a two-component epoxy glue. The radii of the spheres were measured from the SEM photos [15].

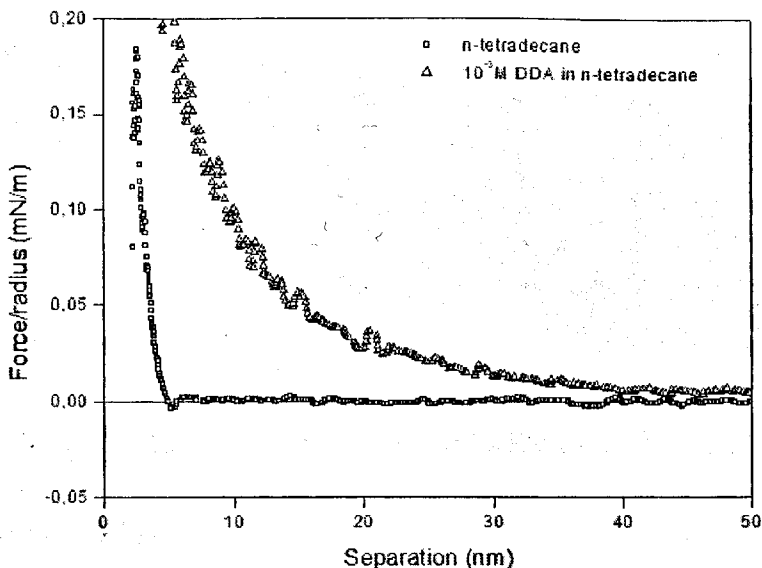


FIGURE 3 Force of interaction between polyethylene particle and smooth polyethylene surface in n-tetradecane and  $10^{-3}$  M dodecylamine solution in n-tetradecane

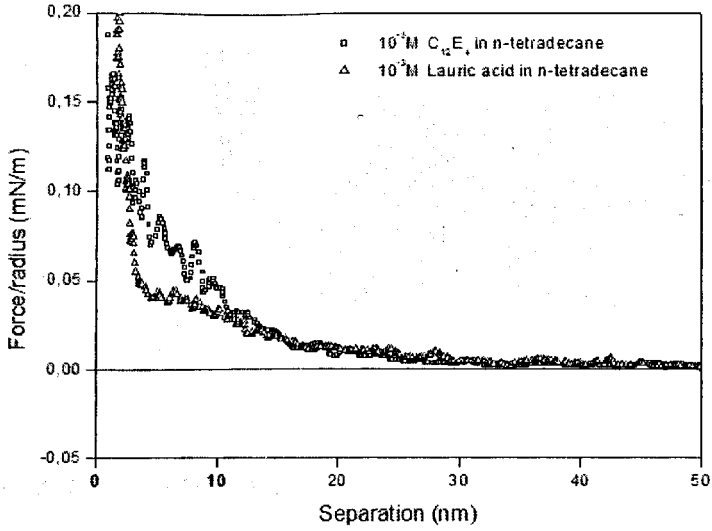
## RESULTS AND DISCUSSION

Interactions between polyethylene particles and the smooth polyethylene surface in n-tetradecane and dodecylamine solution at 23°C are shown in Figure 3. It can be seen from the curve for the polyethylene-polyethylene interaction in n-tetradecane a small minimum at a distance of 5 nm. In such a case the polyethylene particles may flocculate or coalesce. In the case of the dodecylamine solution the attraction force between polyethylene surfaces is not observed and the repulsive force has a range almost ten times greater than in pure n-tetradecane.

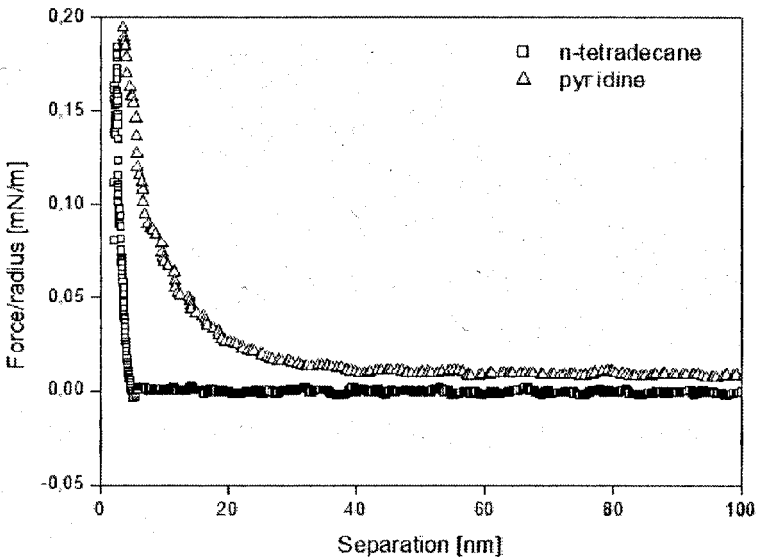
In the case of polyoxyethylene-4-lauryl ether and lauric acid solution in n-tetradecane we have observed an increase of the repulsive interaction (Figure 4). In both cases the force range increases about six times when compared to pure n-tetradecane. On the curve for the lauric acid solution a step at the 5–10 nm range can be seen which is most probably due to the interpenetration of absorbed surfactant chains.

The interaction between polyethylene surfaces in polar (pyridine) and apolar (n-tetradecane) solvents has also been studied (see Figure 5). In polar solution (pyridine) the interaction range is about six times greater than in n-tetradecane. The local short-range attractive minimum, which was visible in n-tetradecane case, was not detected. These differences can be explained by swelling of the polyethylene chains as well as a stronger electric double layer contribution in pyridine. In the case of polyethylene interactions in pyridine/surfactant solutions the increase in the repulsive force is not as evident as it was in the case of n-tetradecane solutions.

The steric stabilization in pyridine by surfactants is less effective than in n-tetradecane. The largest steric layer thickness was in  $10^{-3}$  M polyoxyethylene-4-lauryl ether solution and

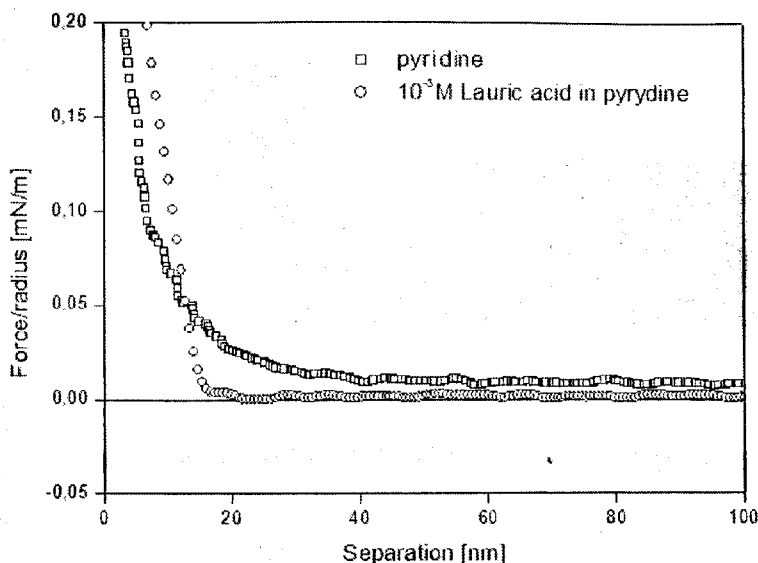


**FIGURE 4** Force of interaction between a polyethylene particle and a smooth polyethylene surface in  $10^{-3}$  M polyoxyethylene-4-lauryl ether and  $10^{-3}$  M lauric acid solution in n-tetradecane



**FIGURE 5** Force of interaction between a polyethylene particle and a polyethylene surface in n-tetradecane and pyridine





**FIGURE 6** Force of interaction between a polyethylene particle and polyethylene surface in pyridine and  $10^{-3}$ M lauric acid in pyridine solution

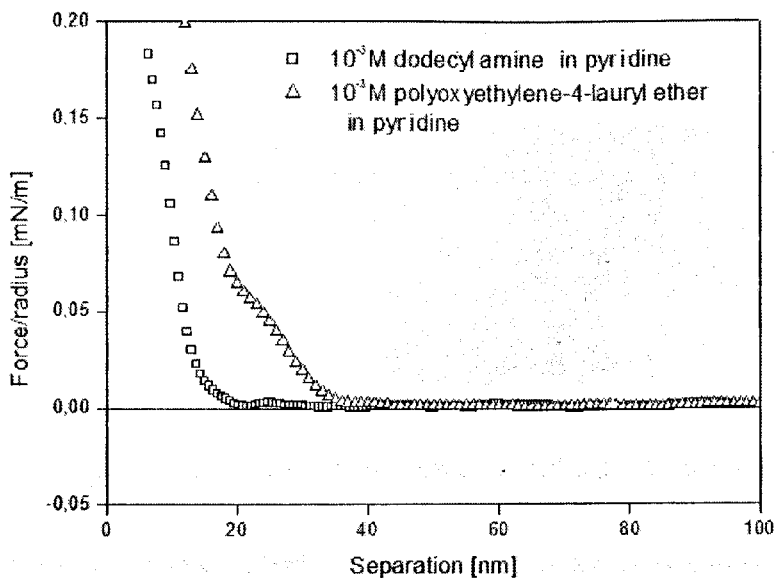
almost the same range for dodecylamine and lauric acid (about 20 nm). The repulsive interaction in pure pyridine increases gradually but in the case of dodecylamine and lauric acid (in spite of a smaller range) increases suddenly (Figure 6 and Figure 7).

The interaction force between polyethylene particles and an asphaltene surface are presented on Figure 8 and Figure 9 in various solutions. In all cases the interaction is repulsive. Because of very complicated structure of asphaltene molecules, that have many polar groups, the adsorption of the surfactants at the asphaltene surface is difficult to describe.

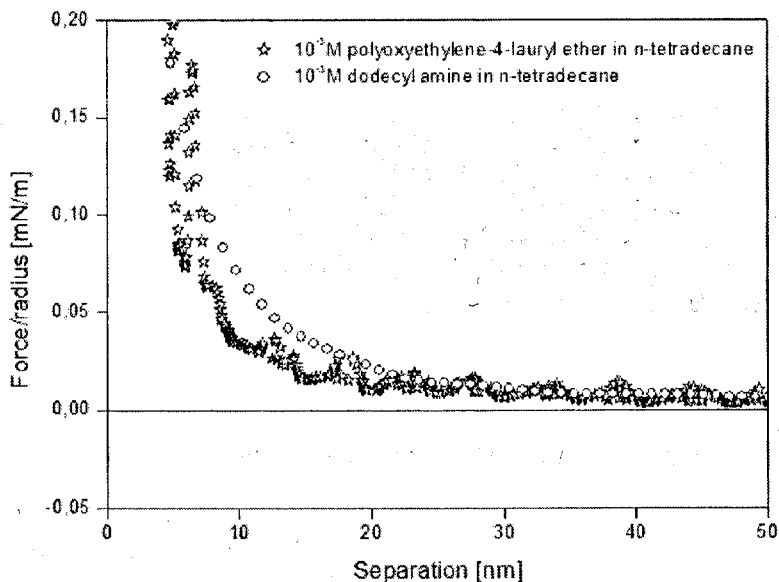
The repulsive force for these systems was found to increase with increasing temperature. At high temperature the adsorbed surfactant chains can move more easily, so the steric layer thickness increases (Figure 10 and Figure 11). Additional swelling of the polymer or asphaltene is also possible.

## CONCLUSIONS

Surfactant molecules in nonaqueous systems can significantly increase the repulsion between PE filler particles. Despite the small size of surfactant molecules the repulsion can be sufficient to provide for an increase in the stability of PE filler suspended in asphalt blends. At the same time the interaction between PE and asphaltene surfaces was found to be much less affected by the presence of surfactants.



**FIGURE 7** Force of interaction between a polyethylene particle and a polyethylene surface in  $10^{-3}\text{M}$  dodecylamine and  $10^{-3}\text{M}$  polyoxyethylene-4-lauryl ether in pyridine solution



**FIGURE 8** Force of interaction between a polyethylene particle and a flat surface of asphaltene in  $10^{-3}\text{M}$  dodecylamine and  $10^{-3}\text{M}$  polyoxyethylene-4-lauryl ether in n-tetradecane solution

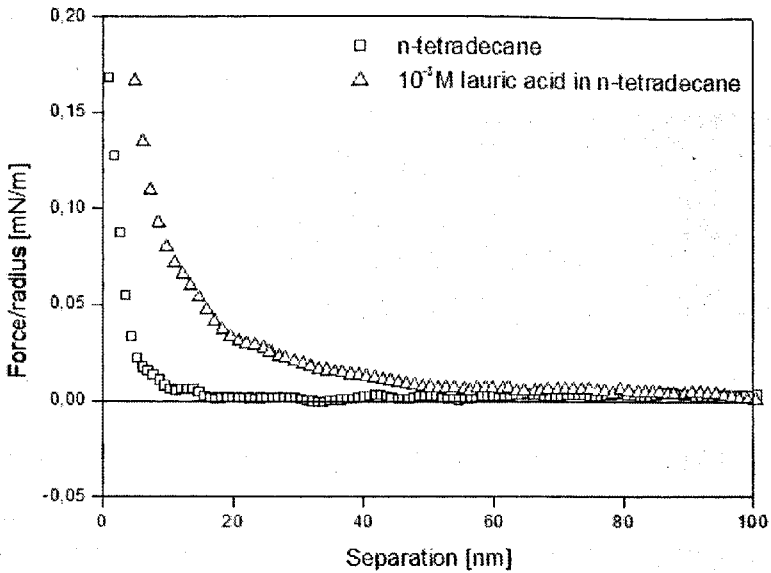


FIGURE 9 Force of interaction between a polyethylene particle and an asphaltene surface in n-tetradecane and 10<sup>-3</sup> M lauric acid n-tetradecane solution

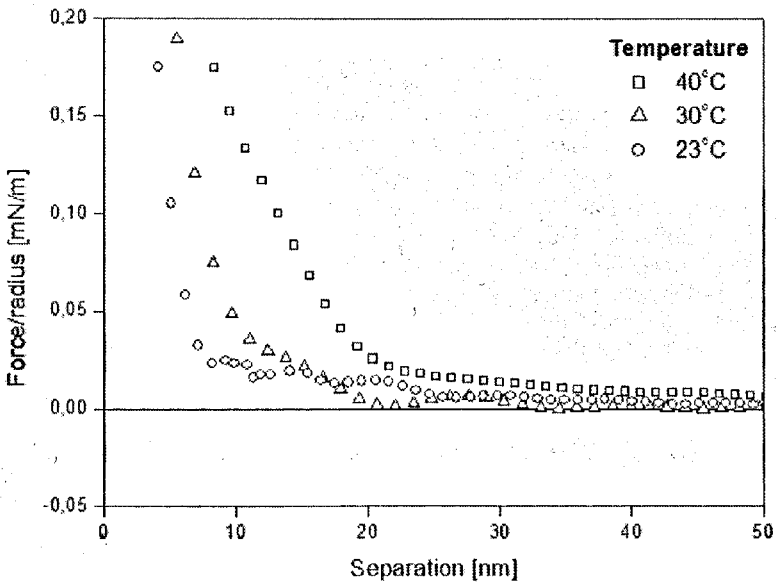
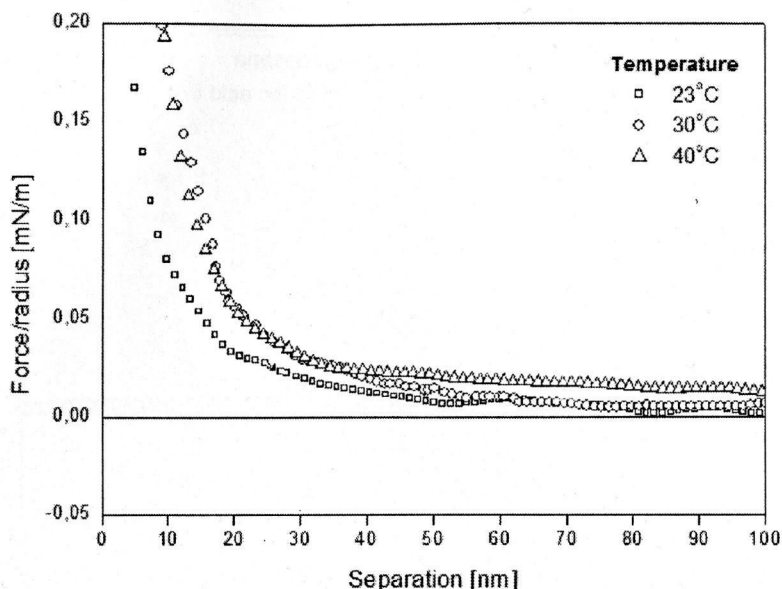


FIGURE 10 Force of interaction between a polyethylene particle and a polyethylene surface in 10<sup>-3</sup> M lauric acid in n-tetradecane solution at different temperatures



**FIGURE 11** Force of interaction between an asphaltene particle and an asphaltene surface in n-tetradecane at different temperatures

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