Stabilization of Asphaltenes by Phenolic Compounds Extracted from Cashew-Nut Shell Liquid

LUIZ FERNANDO BANDEIRA MOREIRA,[1] ELIZABETE FERNANDES LUCAS,[1] GASPAR GONZÁLEZ[2]

[1] Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, bloco J, P.O. Box: 68525, 21945-970, Rio de Janeiro, RJ, Brazil

[2] PETROBRAS Research Center, Ilha do Fundão, quadra 7, Cidade Universitária, 21949-900, Rio de Janeiro, RJ, Brazil

ABSTRACT: The liquid extracted from cashew-nut shell is composed almost completely of phenolic compounds containing 15-carbon chains with variable unsaturation degrees, *meta*-substituted in the aromatic ring. The similarity of these compounds with the structures described as efficient peptizing agents for asphaltenes, the crude oil polar fraction, induced us to evaluate cashew-nut shell liquid (CNSL) and its derivatives, cardanol and polycardanol, as asphaltene stabilizing agents. The results confirm that CNSL and cardanol have a performance comparable to nonylphenol. Polycardanol was not only less efficient than its monomer, but, instead, enhanced the precipitation of asphaltenes. This effect may be ascribed to the large number of phenol groups present in the polymer that may flocculate the asphaltene particles or increase its polarity, reducing its solubility in aliphatic solvents. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 29–34, 1999

Key words: asphaltenes; natural phenolic compounds; crude oil; organic deposition

INTRODUCTION

Asphaltenes are the heavier, more polar, and nonvolatile components of petroleum or crude oil. This fraction is usually composed of condensed polyaromatic rings containing aliphatic and naphthenic side chains and sulfur, oxygen, and nitrogen as heteroelements or functional groups. Metals such as vanadium and nickel are also present in this fraction as part of porphyrinic or nonporphyrinic groups.[1] Yen[2] classified asphaltenes as multipolymers, that is, a combination of a random polymer and an intrinsic mixture of structurally related homologous compounds associated by physical bonds. Under favorable conditions, asphaltenes in crude oil or in aromatic solvents may be considered to be dissolved as a liophilic (macromolecular) colloid or dispersed as a stable liophobic colloidal dispersion.[3] Due to their complex molecular structure, asphaltenes tend to associate to form aggregates called micelles, clusters, or particles, and as an extreme case, when the solvent (or dispersing) properties of the medium are unfavorable, precipitation and deposition of the asphaltic fractions may occur. Massive separation of asphaltenes will, obviously, cause very serious operational problems; however, irrespective of the amount of solids formed, for all the oil production, treatment, and movement operations, it is advantageous to maintain the asphaltic fraction as stable or well peptized.

The use of chemical additives to avoid the deposition of asphaltenes has been highly recommended in recent years.[4] In this context, alkylbenzene derivatives and other amphiphiles were assayed in laboratory tests by González and Middea[5] and Chang and Fogler.[6] They concluded that

alkylphenols with a medium-to-long hydrocarbon tail exhibit fairly good performance as asphaltene stabilizing agents. This effect has been ascribed to acid–base interactions between the asphaltenes and the amphiphile molecules and to steric stabilization provided by the hydrocarbon tail. It was also observed that the stabilization capability may be improved by the presence of additional polar groups, notably OH, in the aromatic ring.[6]

Cashew-nut shell liquid (CNSL) obtained from *Anacardium occidentale* or *Anacardium anum* which are native trees from northeastern and north of Brazil,[7] is a dark, viscous fluid constituted almost completely by phenolic compounds with long linear alkyl chains containing 15 carbons with variable unsaturation degrees, *meta*-substituted in the aromatic ring. Anacardic acid is the major component of raw CNSL material; however, the composition of a particular CNSL preparation depends on the process used to extract the material from the cashew-nut shell.[8,9] It seems interesting, therefore, to note that these phenolic compounds have chemical structures very similar to the amphiphiles studied as asphaltene-stabilizing agents. Furthermore, the side-chain unsaturation allows one to obtain, by addition polymerization, polymers containing various free phenol groups in the same molecule, which, in principle, seems an attractive possibility to improve the efficiency of phenolic compounds to disperse asphaltic dispersions. The objective of this work was to assess the performance of CNSL, cardanol, and their derivatives as asphaltene-stabilizing agents.

EXPERIMENTAL

Materials

Technical CNSL was obtained from Usibrás Ltda. (Rio Grande do Norte, Brazil). The asphaltene residue was obtained from the PETROBRAS Research Center. Borontrifluoridediethyletherate ($\sim$ 48% BF_3) was purchased from Fluka Chemicals (Neu-Ulm, Germany). Toluene and *n*-heptane were purchased from Vetec Química Ltda. (Rio de Janeiro, Brazil). *p*-(*n*-Nonyl)phenol was kindly supplied by Henkel Indústrias Químicas S.A. (São Paulo, Brazil). All these materials were used as received.

Methods

Cardanol was obtained by vacuum distillation of technical CNSL, carried out at 3–4 mmHg and 228–235°C, with a weak nitrogen current to improve the rising of steam through the column. The cardanol obtained presented a transparent yellowish color that changed to amber with time. Similar color changes were observed for nonylphenol by Preston and Reed[10] and ascribed to the antioxidant property of this type of molecule.[11] After distillation, the product was stored under nitrogen at a temperature of 0°C.

The polymerization of cardanol was based on the studies reported by Antony et al.[12] They carried out reactions at different temperatures and showed that at 140°C 30 min is enough to obtain 80% conversion and polymers with higher molecular weights. In this work, polycardanol was synthesized in a bulk process via cationic polymerization at 140°C using (1% wt) $BF_3O(CH_2CH_3)$ as an initiator. Part of this polycardanol was purified using heptane to remove the smaller molecular weight fractions.

The asphaltene fraction was precipitated from an asphaltic residue, by the addition of heptane, and filtered and Soxhlet-extracted to remove all the heptane-soluble material. The solid material was dissolved in toluene and filtered and Soxhlet-extracted to remove the toluene-insoluble material. Subsequently, the asphaltene–toluene solution was evaporated and dried to get a solid asphaltene which was crushed in a mortar to give a fine powder of asphaltenes.

GPC data were obtained using Waters 600 equipment with a 10^5, 10^4, 10^3, and 500 Å Ultra-styragel column series calibrated with monodispersed polystyrene standards. THF was used as a solvent at a flow rate of 1 mL/min and Waters 410 and 991 detectors. Infrared spectra (FTIR) were recorded on Perkin–Elmer spectrophotometer, Model 1720-X, as film on NaCl or KBr windows.

An absorption scanning using UV-vis (200–800 nm) was carried out for asphaltene, cardanol, and CNSL samples, each one solved in toluene, using a Camspec spectrophotometer, Model M330. The dispersion of asphaltenes by nonylphenol, cardanol, and CNSL samples was measured at 780 nm using a Celm digital spectrophotometer, Model E205D. A calibration curve of absorbance versus concentration of the asphaltenes dissolved in toluene was used to extrapolate the amount of asphaltenes dispersed.

The ability of CNSL and cardanol to stabilize asphaltene was studied using two different methods:

(a) *Peptization test*. Sixty milligrams of asphaltene was added into several flasks containing 10 mL of heptane and different amounts of the peptizing agent. The amount of asphalt-

Figure 1   FTIR spectrum of CNSL.

enes dispersed was subsequently measured using the procedure described above.

(b) *Precipitation test.* Different amounts of heptane were added into flasks containing a solution of asphaltenes in toluene and 0.0, 0.5, and 1.0% of the stabilizer or peptizing agent. The flasks were sealed and stirred for 24 h at 24°C. After this period, they were centrifuged at 3000 rpm for 30 min and the absorbance of the particle-free supernatant was measured at 780 nm. Since polycardanol and purified polycardanol are insoluble in heptane, they were tested only by the second procedure. Nonylphenol was used as a reference in all assays.

RESULTS AND DISCUSSION

The FTIR spectrum of CNSL is shown in Figure 1. It shows a large band of axial stretching of O—H in the region around 3400 cm^{-1}. The peak at 3010 cm^{-1} is related to the C—H axial stretching of olefin. The peaks at 2925 and 2856 cm^{-1} are related to the axial stretching of the C—H bond. The peak at 1487 cm^{-1} is related to the C=C bond of the aromatic ring. Axial stretching of C—O may be observed at 1262 cm^{-1}. These results confirm the presence of unsaturated phenolic compounds in the CNSL, as previously described[9] by other authors.

The cardanol sample was separated from CNSL by distillation following details described by previous workers.[13] GPC analysis indicated a number-average molecular weight of 311, which is close to the average molecular weight of 301 estimated from the composition of cardanol presented in Figure 2.[14]

Polycardanol was obtained by cationic polymerization of cardanol using $BF_3 \cdot O(CH_2CH_3)_2$ as an initiator, according to the mechanism shown in the Figure 3.[15] The chain mechanism for the polymerization was confirmed by the crossing data from the IR spectra, H-NMR, and polymerization rates. It is important to remember that in the cardanol composition there is around 12% saturated compounds, which are not able to react with the initiator used. It was not necessary to have any solvent to promote the separation of the ions when the initiator was added, because the monomer reacted immediately: The reaction medium became a reddish color and it became highly viscous after cooling down. This observation suggests that the reactive centers formed are easily attainable in these conditions and the energy involved in the process is enough to make the reaction possible. Polycardanol was purified by an extraction process using heptane as a residual cardanol solvent.

The infrared spectra of cardanol shows peaks at 3007 and 1589 and three peaks at 988, 945, and 912 cm^{-1} which are related to unsaturated bonds. For polycardanol, these last three peaks are no longer present, suggesting that, as expected, the polymerization occurred through the double bound of the side alkyl chain of cardanol.[12] GPC analysis of polycardanol shows the complete disappearance of the monomer peak in the purified sample. Furthermore, the number-average molecular weight ($\bar{M}_n$) increased from 900 ($\bar{M}_w$ = 4600) to 2300 ($\bar{M}_w$

Figure 2   Components and composition of cardanol.

$$BF_3 \cdot O(CH_2CH_3)_2 \; + \; H_2O \; \rightleftharpoons \; H^+(BF_3OH)^- \; + \; O(CH_2CH_3)_2$$

Figure 3 Polymerization of monounsaturated component of cardanol.

Figure 4 Infrared spectrum (FTIR) of the asphaltene sample.

= 6900), after the heptane extraction. These results confirm previous studies reported by other authors.[14]

The infrared spectrum for the asphaltene sample is presented in Figure 4. It shows a peak related to N—H axial stretching (3583 cm^{-1}), a large band corresponding to O—H bonds (3369 cm^{-1}), sharp peaks for C—H axial stretching (2924 and 2853 cm^{-1}), peaks of C=O bond axial stretching (1733 cm^{-1}), and a C=C bond for aromatic rings (1612 cm^{-1}). These results illustrate the complex nature of the asphaltene fraction in which several types of functional groups are present in the asphaltene molecule.[16] The GP chromatogram for the asphaltene sample presents a wide molecular weight distribution. Similar diagrams were presented in the literature for asphaltene samples from other sources.[17] The number-average molecular weight obtained was 2000 and the corresponding weight average was 11,300, with a polydispersity of 5.6.

The peptization of asphaltenes by CNSL, cardanol, and nonylphenol is shown in Figure 5. Both cardanol and CNSL showed good performance when compared to nonylphenol, which has been described as an efficient peptizing agent for this fraction.[5] The chemical structure of these compounds containing polar phenol groups capable of undergoing relatively strong interactions with the functional groups of the asphaltenes par-

ticles[6] may account for these results. The shape of the curves that denote an improved peptization for higher concentrations of the peptizing agent may be ascribed to the complex nature of the asphaltene particles that must present functional groups of different polarities on their surface.

Figure 5 Graphic concentration of asphaltene stabilized (C_{asp}) versus concentration of the stabilizing agent for the peptization tests. (×) Nonylphenol, (◆) cardanol, and (△) CNSL were used as stabilizing agents.

Figure 6 Graphic asphaltene dispersed (C_{asp}) versus heptane added for the precipitation tests using (+) 0.0, (□) 0.5, and (■) 1.0% (wt) of nonylphenol.

Figure 8 Graphic asphaltene dispersed (C_{asp}) versus heptane added for the precipitation tests using (+) 0.0, (○) 0.5, and (●) 1.0% (wt) of cardanol; (-) 0.5 and (×) 1.0% (wt) polycardanol; and (◆) 1.0% (wt) purified polycardanol.

The results obtained in the *precipitation test* using nonylphenol and CNSL are presented in Figures 6 and 7. Figure 8 presents the results corresponding to cardanol, polycardanol, and purified polycardanol. This test really measures the effectiveness of the additives to maintain the asphaltene particles dispersed in an adverse solvent condition created by the addition of heptane. As in the previous sets of results obtained using the *peptization test,* CNSL and cardanol present a performance similar to that obtained using nonylphenol. However, a rather surprising result was obtained for polycardanol and purified polycardanol: These polymeric forms of cardanol are not only less efficient as dispersants than are their respective monomers or is nonylphenol, but, instead, they enhance the precipitation of the asphaltene particles.

In a very simplistic model to account for the dispersing effect presented by amphiphilic molecules, it may be assumed that the asphaltene particles present a nonpolar, hydrocarbon surface containing discrete, isolated polar groups responsible for their instability in aliphatic solvents. In this scheme (Fig. 9), a good peptizing amphiphile should adsorb on the particles, occluding the polar groups and turning the surface more nonpolar and, hence, increasing its capacity to interact with aliphatic solvents. CNSL, cardanol, and nonylphenol follow this model [Fig. 9(a)]. The bad performance of polycardanol may be ascribed to its structure in which the phenol groups, which represent the active sites for the peptization process, may be relatively separated in the polymer and could interact with more than one particle, causing the flocculation and subsequent aggregation of the asphaltene dispersion, as shown in Figure 9(b). An alternative mechanism would be related to the relatively large number of phenol groups in the polymer. If the amphiphile interacts with the asphaltene particles, leaving in this process various of its phenol groups exposed to the

Figure 7 Graphic asphaltene dispersed (C_{asp}) versus heptane added for the precipitation tests using (+) 0.0, (△) 0.5, and (▲) 1.0% (wt) of CNSL.

Figure 9 Suggestions of models of interaction between stabilizing and asphaltene particles: (a) molecules of cardanol, CNSL, and nonylphenol are able to stabilize particles of asphaltene; (b) molecules of polycardanol are not able to stabilize particles of asphaltene; and (c) the asphaltene particle has its polarity increased after interacting with molecules of polycardanol and then it precipitates in the medium.

solution, the overall polarity of the amphiphile particle would increase, enhancing the separation of the asphaltene fraction [Fig. 9(c)].

REFERENCES

1. Yen, T. F. In Encyclopedia of Polymer Science and Engineering; Mark, H. M.; Bikales, H. F.; Overberger, C. G.; Menges, G., Eds.; Wiley: New York, 1990; Index, pp 1–10.
2. Yen, T. F. Energy Sources 1974, 1, 447–463.
3. Hunter, R. J. Foundations of Colloid Science; Clarendon: Oxford, 1989; Vol. I, p 7.
4. Groffe, P.; Volle, J. L.; Ziada, A. In 2nd International Symposium on Colloid Chemistry in Oil Production, Rio de Janeiro, 1997; paper 18.
5. González, G.; Middea, A. Colloids Surf 1991, 52, 207–217.
6. Chang, C.; Fogler, H. S. Langmuir 1994, 10, 1749–1757.
7. Mothé, C. G.; Milfont, W. N. Rev Quim Ind 1994, 695, 15–19.
8. Mothé, C. G.; de Castro, S. M.; Ganem, M.; da Silva, T. C. Rev Quim Ind 1996, 708/709, 19–23.
9. Tyman, J. H. P. Chem Soc Rev 1979, 8, 499–536.
10. Preston, R. W.; Reed, H. W. B. In Encyclopedia of Chemical Technology; Mark, H. M.; McKetta, J. J.; Othmer, D. F., Eds.; Wiley: New York, 1963; Vol. 1, pp 908–915.
11. Tychopoulos, V. T.; Tyman, J. H. P. J Sci Food Agric 1990, 52, 71–83.
12. Antony, R.; Pillai, C. K. S.; Scariah, K. S. J Appl Polym Sci 1990, 41, 1765–1775.
13. Murthy, B. G. K.; Menon, M. C.; Aggarwal, J. S.; Zaheer, S. H. Paint Manuf 1961, 31, 47–50.
14. Anthony, R.; Pillai, C. K. S. J Appl Polym Sci 1990, 41, 1765.
15. Odian, G. Principles of Polymerization; 2nd ed.; Wiley: New York, 1981.
16. Antony, R.; Pillai, C. K. S.; Scariah, K. S. J Appl Polym Sci 1990, 41, 1765–1775.
17. Travalloni, M.; Freire, N. O. In 1st International Symposium on Colloid Chemistry in Oil Production: Asphaltenes and Wax Deposition, Rio de Janeiro, 1995; pp 252–262.