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Molecular Characterization of *p*-Alkyl Phenol−*n*-Heptane Interactions and Their Implication as Asphaltene Dispersants

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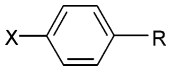
The interaction between a series of *p*-alkyl phenols with the solvent *n*-heptane (*n*-C_7) is studied by means of theoretical methods. The solvation energies of these molecules are computed using quantum mechanical methods in which the solvent is considered as a dielectric medium. Accordingly, the interaction of a solute molecule with the reaction field of the solvent yields a solvation free energy. The electrostatic, dispersion, and repulsion contributions to the solvation energies are analyzed as a function of the alkyl chain length and the relationship with the electronic structure of the molecules, as accounted for by the properties of the quantum topological atoms defined within the formalism of the atoms in molecules theory, is also discussed. Implications of the solvation energies, computed at the microscopic level, on the efficiency of *p*-alkyl phenols as asphaltene dispersants are discussed. The quantitative aspects of the solubility of these amphiphiles are correlated with their experimentally reported dispersing power of an asphaltene of a given oil source in *n*-C_7. These observations support the hypothesis that the relative ability of a series of *p*-alkyl phenols to dissolve a given asphaltene in *n*-C_7 is dominated by the amphiphile−solvent interactions, which are sufficient to offset the repulsion and cavitation contributions.

1. Introduction

Asphaltene is an oil component operationally defined as the fraction soluble in benzene or toluene and insoluble in *n*-heptane, *n*-C_7.[1,2] The presence of asphaltene in crude oil is responsible for pipeline obstruction problems that occur during petroleum extraction and processing, with concomitant high economic losses. Asphaltene is a complex mixture of polycyclic aromatic hydrocarbons with heterocyclic rings and alkyl side chains. Although it has been established that the aromatic core involves from 4 to 10 aromatic rings,[3,4] little is known about the precise molecular structures of the components of such a complex mixture. This situation explains the limitations of using a single average molecule as a characteristic model to simulate the microscopic and macroscopic behavior of asphaltenes, although reasonable results can often be obtained using such an approximation.[5,6] In addition, resins are mixtures of complex molecules that make up another component that performs as natural asphaltene stabilizers in the crude oil. From the theoretical point of view, attempts have been made to understand the structure and interactions of these components. García-Cruz et al.[7,8] analyzed the reactivity indices of species related to asphaltenes and resins, such as carbazol, dibenzothiophene, and dibenzofurane, in an effort to gain theoretical insight into the mechanism of asphaltene formation. Despite the lack of precise knowledge of the molecular structure of these two heavy oil fractions, dipole moment measurements of the oil components have been carried out which suggest the following order of polarity: oil < resin < asphaltene.[9] On the other hand, the understanding of the mechanisms of asphaltene stabilization during petroleum processing by means of either resins or synthetic dispersants is a technologically relevant issue in the oil industry. In particular, the latter compounds are highly desirable, and the design of more effective molecules is currently an important research topic in this field.

A number of studies on the use of surfactants (amphiphiles) as asphaltene stabilizers have been reported. Amphiphiles often used are of the type



Examples of common amphiphiles are *p*-alkyl phenols and *p*-alkyl benzensulfonic acids, for which X = OH or SO_3H, respectively, and R = *n*-alkyl groups. There are a number of experimental studies that analyze, among other topics, the effect of the R and X groups on the ability of these dispersants to

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stabilize asphaltenes in the crude oil. The following techniques have been used: spectroscopic (UV, FTIR, SAXS, fluorescence), thermodynamic (calorimetric titrations, thermogravimetric analysis, adsorption isotherms), and other methods which yield physical properties such as dielectric constant, refractive index, or mass density.[10−18,19] Two aspects discussed in those works refer to the X group acidity and to the nature (length and degree of branching) of the R alkyl chain. Because of its high acidity, *n*-dodecylbenzene sulfonic acid (DBSA) is one of the most effective asphaltene dispersants, and *p*-alkyl phenols are also used. For example, it has been found that the shortest chain length of a *p*-alkyl phenol should contain at least 6 C atoms[10] (although a chain length of greater than 9 C atoms has also been mentioned as being required)[17] so that *p*-alkyl phenols could act as effective asphaltene dispersants. Of these, *p*-nonyl phenol in the presence of *n*-C_7 is often used in order to assess the asphaltene−amphiphile interactions.

Thermodynamic studies indicate that adsorption enthalpies can be used as a criterion for the selection of an appropriate amphiphile.[12,14] However, it is known that the effect of dispersing agents does not depend only on their structure but that the composition of the crude oil is also important.

The nature of the interactions involved during asphaltene solubilization has also been mentioned in the literature. It has been usually assumed that surfactants operate by means of acid−base reactions with a given asphaltene and that the effect of the alkyl chain is only to provide steric stabilization[10] to prevent the asphaltene molecules from aggregating. From theoretical calculations, it has also been proposed that the interaction energies are proportional to the amphiphile's polarizability[12,20] and dipole moment.[20] These findings suggest that the role of amphiphiles could be explained in terms of the molecular properties that determine the nature of the interactions. For example, molecular dynamics calculations of the adsorption energies of *p*-alkylphenol ethoxylated amphiphiles on an average asphaltene model structure yield values that relate to dipole moment and molecular polarizability for several amphiphile concentrations.[20]

The asphaltene−amphiphile interactions have also been interpreted from experimental results in terms of intermolecular arrangements. Experimental adsorption isotherms can be rationalized in terms of the orientation of the amphiphile on the asphaltene surface. In the case of *p*-alkyl phenols, it has been suggested that the molecules orient parallel to the asphaltene surface (probably because of dispersion interactions). On the other hand, DBSA stands perpendicular to the surface (probably because of the strong interaction of the polar head with the asphaltene molecules, while the alkyl chain remains extended toward the solvent).[14] Molecular dynamics calculations[20] involving adsorption of alkyl-phenol-ethoxylated amphiphiles or DBSA on an asphaltene surface corroborate these findings and also propose from the distribution of atoms of the ethoxylated head groups that the larger the size of the polar head, the larger the atomic density near the asphaltene surface.

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It has also been proposed that up to 6−8 amphiphile molecules could interact with an asphaltene molecule during micelle formation.[15] From the previous discussion, it can be understood why it has been proposed that the asphaltene−amphiphile interaction is an important parameter for the stabilization of the asphaltene micelles in the crude.

From the point of view of theoretical physical chemistry, a few reports exist which resort mostly to the use of phenomenological thermodynamic models, and a small number of molecular simulation studies of the asphaltene−amphiphile interactions exist. It has also been proposed that the specific interactions, which take place during the process of asphaltene solubilization, can be properly characterized by means of quantum mechanical calculations provided that the asphaltene−amphiphile interactions with a solvent (such as *n*-C_7) are considered. Such studies could contribute to the understanding of the mechanism through which the solubilization process occurs.

Clearly, the detailed analysis of the mechanism by which a given amphiphile dissolves an asphaltene should involve consideration of the specific molecular interactions among the components involved, but such an approach can be hardy carried out with the use of quantum chemical tools. Nevertheless quantum theory provides the means for analyzing individual components of such complex interactions which certainly contribute to the collective behavior of this type of systems. It is also known that *p*-alkyl phenols can redissolve an asphaltene that was previously solubilized in *n*-C_7. Hence, it is worthwhile to analyze the amphiphile−solvent interactions on the grounds that the extent of asphalthene resolubilization should dependent on the amphiphile's capacity to solubilize itself in *n*-C_7 first; otherwise the asphalthene phase would never be attained. Therefore, the present contribution is focused on the analysis of the nature of the amphiphile−solvent interactions between members of the family of *p*-alkyl phenols with *n*-C_7. On the basis of reported experimental results,[10] the basic assumption made is that once the asphaltene of a given oil source has been selected, the trend observed for the ability of a family of amphiphiles to disperse it in a given solvent can be explained in terms of the solvation energy of the dispersant alone. This is a sound hypothesis considering that, even though present, the other interactions should remain nearly constant because only one of the factors involved is changed along the series, namely, the length of the amphiphile's alkyl chain. In particular, the solvation energies, computed by means of quantum mechanical methods, are analyzed and the changes on the properties of the molecular charge distribution are discussed as well. These theoretical tools are used to shed light on the nature of one of the relevant interactions that are active during the solubilization of asphaltenes.

2. Theoretical Basis: Continuum Treatment of Solute−Solvent Interactions

Within this molecular approach, rather than accounting for the specific interactions occurring in solution, the solvent is treated as a continuum dielectric medium, usually characterized with a bulk dielectric constant, which interacts with a charge distribution that represents a solute molecule. In this manner, the molecular detail of the solvent is not included explicitly. Such a simplification can be justified by the lack of important local structure of the solvent *n*-C_7. Also, because the interaction between solute molecules is not accounted for either, the results obtained by such an approach correspond to the infinite dilution case. Among others, Onsager

pioneered this type of approach,[21] proposing a classical model for the interaction between a point dipole immersed in a spherical cavity of a dielectric. Further developments have taken into account the quantum mechanical nature of the interactions. Detailed reviews on the fundamentals, the refinements of the computational implementations, and applications of the continuum solvation models have been published elsewhere.[22−25,26] In these types of models, the solute−solvent interactions can be split[27] into electrostatic, van der Waals, and repulsion interactions. In particular, the electrostatic contribution arises as a polarization of the solvent in response to the field of the molecular charge distribution. In this process, the solute becomes polarized by an amount dependent on its molecular polarizability. Another effect also included is the cavitation energy, the work necessary to create a cavity within the solvent where the solute is placed and the van der Waals term is computed as a classical long-range dispersion energy.

The quantum mechanical models usually rely on the Born−Oppenheimer approximation for the separation of the nuclear and electronic motions, and the reaction field effect is explicitly included in the solute electronic Hamiltonian. According to electrostatics, the response of a homogeneous dielectric continuum to the presence of a solute consists on a charge distribution on the solute−solvent interface. The effect of this reaction field can be replaced by a set of induced polarization charges located on the surface of the cavity in such a manner that appropriate boundary conditions are satisfied for the potential included in the solute Hamiltonian. This approach is called the polarized continuum model (PCM)[28] and has been applied to describe a number of systems. A PCM calculation involves a self-consistent procedure to obtain both the polarization charges and the solute molecular wavefunction. A related approach, called the conductorlike screening model (COSMO),[29] takes advantage of the numerically easier to handle boundary conditions for a cavity in a conductor. In a self-consistent field step (SCF), the polarization charges of the reaction field are scaled with the factor $(\epsilon - 1)/\epsilon$, so that the actual charges correspond to a dielectric continuum. CPCM, a PCM implementation of the COSMO model, has been reported[30] and made available within the Gaussian98 quantum chemical program.[31] In this implementation, the nonelectrostatic contribution of the dispersion interaction between the solvent and the dielectric is also computed after the SCF procedure. In addition, the cavity of the surface is partitioned into small domains called tesserae in such a way that the molecular shape is represented by interlocking spheres centered at the solute atoms or functional groups. This procedure has been tested for a number of molecules and a set of optimal parameters which minimize the numerical errors resulting from discretization of the polarization charges and the radii of the interlocking spheres, among others, have been defined in the literature[30] and are used here as suggested.

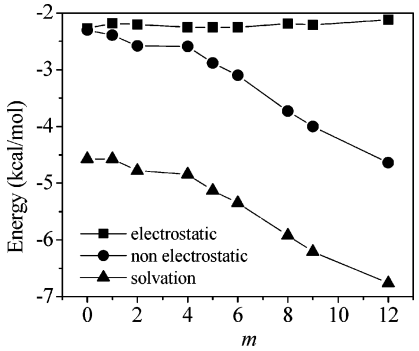

Figure 1. Solvation free energy of *p*-alkyl phenols in *n*-C_7 and electrostatic and nonelectrostatic contributions as a function of the chain length, *m*.

Table 1. Contributions to the Solvation Free Energy (kcal/mol) of *p*-alkyl Phenols as a Function of the Chain Length, *m*

m	ΔG_{solv}	ΔG_{elec}	ΔG_{nelec}
0	−4.57	−2.27	−2.30
1	−4.57	−2.18	−2.39
2	−4.78	−2.20	−2.58
4	−4.84	−2.25	−2.59
5	−5.13	−2.25	−2.88
6	−5.35	−2.25	−3.10
8	−5.92	−2.19	−3.73
9	−6.21	−2.21	−4.00
12	−6.76	−2.12	−4.64

The calculations of the *p*-alkyl phenols studied in this work were performed using density functional theory and the B3LYP exchange-correlation gradient corrections[32,33,34] with the 6-31++G** orbital basis set[35] and *n*-C_7 as a solvent. It is well-known that approximate exchange-correlation potentials, like those used in this work, fail to account for van der Waals interactions because of their incorrect long-range behavior. Nevertheless, because this nonelectrostatic term is accounted for by means of an implementation that uses classical dispersion formulas,[36] such a limitation of the density functional approach does not affect the calculation of this contribution to the solvation energy. The amphiphile geometry relaxation due to the solute−solvent interaction was also included at the same level of theory. Local minima on the potential energy surface were located after a nonexhaustive search over the standard conformations that yielded the all-staggered alkyl chains with the OH group lying on the aromatic ring plane. It is worth mentioning that the molecular geometry optimization involves the application of analytical gradient methods, considering the contributions from both for the SCF reaction field and for the dispersion term. To perform appropriate comparisons, gas-phase calculations were also performed using the same density functional and basis set.

3. Results and Discussion

3.1. Solvation Energies of *p*-Alkyl Phenols in *n*-C_7. The solvation free energies (ΔG_{solv}) of a series of *p*-alkyl phenols in *n*-C_7 were calculated with the CPCM density functional at 25 °C. The values obtained are reported in Table 1, with the corresponding electrostatic and nonelectrostatic contributions, and are plotted in Figure 1 as a function of alkyl chain length, *m*. These results indicate that the electrostatic contribution

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Table 2. Molecular Dipole Moments (debye) of *p*-Alkyl Phenols as a Function of Alkyl Length, *m*

	dipole moment	
m	gas phase	*n*-C_7
0	1.394	1.579
1	1.419	1.588
2	1.445	1.617
4	1.455	1.632
5	1.444	1.618
6	1.459	1.632
8	1.460	1.630
9	1.447	1.621
12	1.455	1.648

remains nearly constant with a value of -2.21 ± 0.04 kcal/mol and that the nonelectrostatic energy dominates the behavior of the solvation free energy. This latter contribution cannot be interpreted as arising from the dispersion interaction only because the cavitation and repulsion energies are also important. For example, for *p*-nonylphenol, the values for the cavitation, dispersion, and repulsion contributions are 22.07, −32.69, and 6.61 kcal/mol, which yield a neat stabilizing nonelectrostatic free energy of −4.00 kcal/mol. These values, along with the electrostatic energy, show the relevant role of all the solvent−amphiphile interactions. It can be concluded that, since the electrostatic solvent−solute interaction energy does not change significantly along the series, the difference in the nonelectrostatic energy, dominated by the attractive van der Waals interactions, is responsible for the relative solubilities of the studied *p*-alkyl phenols in *n*-C_7.

As a comparison, we also computed the solvation energies of these *p*-alkyl phenols in toluene. In this case, no definite trend is obtained along the series, and only a small variation in the values is observed. The average electrostatic and nonelectrostatic contributions along the series are -2.74 ± 0.05 and -0.06 ± 0.22, respectively, indicating that the former dominates the solvation energies, -2.80 ± 0.19. However, these values should be improved because of the known specific aromatic−aromatic interactions that take place in this type of system, which are expected to be more significant than those taking place with *n*-C_7.

3.2. Electronic Structure of *p*-Alkyl Phenols in Solution. Further insight into the solvation process can be obtained from the molecular information available from the quantum mechanical calculations. For example, the magnitude of the dipole moment of *p*-alkyl phenols, both in the gas phase and in solution, calculated with the same density functional, are given in Table 2. As can be observed from this table, because of the reaction field of the solvent, the values in solution are in all cases larger than in the gas phase. Although not monotonous, the trend displayed by the dipole moment along the series of *p*-alkyl phenols roughly reaches a constant value from *p*-pentyl phenol. However, the variation is not very large, and its contribution to the electrostatic interaction with the solvent might not be enough to have a significant effect on the solvation energies, in line with the discussion given above for Figure 1 where the small variation of the electrostatic contribution to the solvation energies along the series is displayed.

Additional information can be obtained from the analysis of the properties of the electron distribution with a partitioning formalism that allows the identification of the individual atoms making up the solvent molecules. In this work, we use the quantum theory of atoms in molecules (QTAIM),[37] an approach that relies on the topological properties of the electron density, a property that can be obtained from the molecular wave function and also from X-ray experiments. The analysis of the gradient vector field of the electron density allows partitioning of the three-dimensional space into open sets that in general contain one atomic nucleus each. Abundant evidence leads one to identify these subsets with the atoms and functional groups of chemistry.[38] The properties of these atoms, such as the atomic charges and energies, can be calculated, in this case, from the molecular densities by means of the integration of the appropriate quantum mechanical operators over a given open set. This formalism has been used successfully in the analysis of the electronic structure of aromatic molecules[39,40] and has also been applied in combination with continuum solvation models to explain the acidities of many types of compounds including phenols.[41,42] In this work, the atomic charges and energies of the atoms in the amphiphiles reported were calculated with the AIMPAC set of programs.[43]

Table 3. Charge and Energy of the Hydroxyl Group H Atom (in atomic units) as a Function of Alkyl Chain Length, *m*, for *p*-Alkyl Phenols in the Presence of *n*-C_7

m	charge	energy
0	0.602	−0.35370
1	0.601	−0.35412
2	0.602	−0.35409
4	0.601	−0.35414
5	0.601	−0.35445
6	0.601	−0.35445
8	0.601	−0.35470
9	0.601	−0.35470
12	0.601	−0.35450

The charge of the O atom and the average value of this property for the aromatic and aliphatic C and H atoms of the *p*-alkyl phenols were analyzed. Although some of the atoms (aromatic C and H) show slight differences with respect to the gas-phase values, the tendencies are comparable in both cases. A similar situation is observed for their atomic energies. The aromatic C atoms become more stable at expense of the aromatic H atoms when the solvent is included in the calculation (that is, their atomic energies decrease relative to the gas-phase values for which no solvent is considered). Nevertheless, comparable trends along the series of alkyl phenols are also obtained both in the gas phase and in *n*-C_7. This constancy of the electronic structure along the series of *p*-alkyl phenols for cresol and beyond is in keeping with the long-range nonelectrostatic nature of their interaction with *n*-C_7.

The values of the H atom charge and energy in the OH functional group are presented in Table 3. As can be seen, these properties remain virtually unchanged along the *p*-alkyl phenol series. The average atomic charge is 0.6012 ± 0.0004, for which the uncertainty is close to the numerical error involved in the calculation of this property, and the average energy is -0.35431 ± 0.00031 au (1 au = 627.507 kcal/mol). Interestingly, the corresponding average charges and atomic energies for the same atom in the gas phase are 0.5882 ± 0.0004 and -0.36259 ± 0.00028 au, respectively, showing that the H atom of the OH group becomes more positive and its energy becomes less negative in solution.

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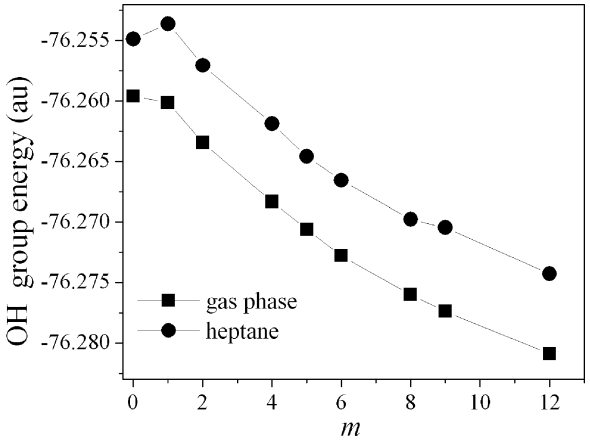

Figure 2. OH functional group energy as a function of alkyl chain length in the gas phase and in *n*-C_7.

Table 4. Energy of the Hydroxyl Group (in atomic units) as a Function of Alkyl Chain Length, *m*, for *p*-Alkyl Phenols in the Gas Phase and in the Presence of *n*-C_7

m	gas phase	*n*-C_7
0	−76.25961	−76.25486
1	−76.26015	−76.25361
2	−76.26346	−76.25706
4	−76.26833	−76.26187
5	−76.27061	−76.26461
6	−76.27279	−76.26657
8	−76.27601	−76.26978
9	−76.2774	−76.27045
12	−76.2809	−76.27427

The pK_a values of a range of compounds, including phenol, have been reported[41] to be proportional to the energy of the acidic H atoms. That work shows that the larger the pK_a value, the more negative (stable) the acidic proton. In the case of the Hammet constant of phenol, the pK_a value is usually accepted to be the result of electron delocalization between the OH group and the aromatic ring, but for the the homologous series studied in the present contribution, going from one *p*-alkyl phenol to the next yields a negligible change on the electron density of the OH group. For example, the analysis shows that the most important changes in the atomic or functional group electronic charges occur from phenol to *p*-cresol and remain nearly constant for greater alkyl chain lengths. Instead, the charge of the C_6H_4 group becomes less positive by 0.044 electrons along the series (from +0.543 in phenol to +0.499 for $m = 12$), whereas the charge of the alkyl group displays an increasing trend which compensates the corresponding decrease for the C_6H_4 group.

The energy of the OH functional group is also available from the QTAIM calculation. The values obtained are reported in Table 4, both for the gas phase and in solution in *n*-C_7, and are plotted in Figure 2. Because the contribution of the H atom of the OH group remains nearly constant along the series of compounds analyzed, the trend observed for the OH energy values is dictated by contribution of the O atom. It should be observed that, apart from phenol, the functional group energies for $m > 0$ display a definite trend: the OH group energy becomes more negative for larger molecules. However, the same behavior is observed both in the gas phase and in solution (although more negative values are obtained in the former case because of the H atom contribution), and hence, it does not explain alone the trends obtained for the solvation energy.

On the basis of this behavior, the results presented suggest that the acid character of the *p*-alkyl phenols in *n*-C_7 remains nearly constant from $m = 0$ to 12, as expected. Rather than resulting from a strong charge redistribution, the results of this work indicate that the long-range contribution, accounted for by the dispersion interaction, explains the trend in solvation energies.

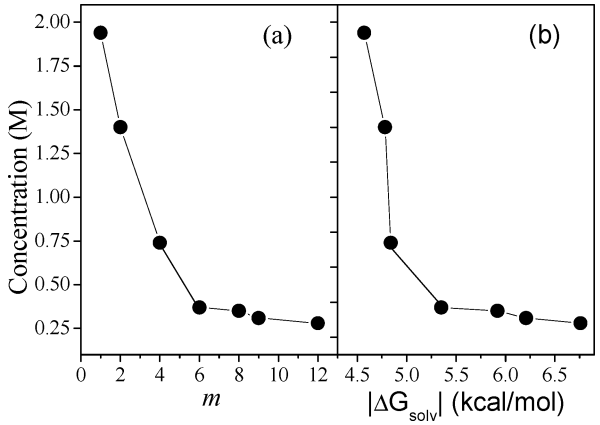

Figure 3. Minimum *p*-alkyl phenol concentration necessary to dissolve an asphaltene as a function of (a) alkyl chain length and (b) absolute value of solvation free energy computed from CPCM density functional calculations (concentrations obtained from information in ref 10).

3.3. *p*-Alkyl Phenols as Asphalthene Dispersants. We turn now to the ability of the *p*-alkyl phenols to dissolve asphaltenes in *n*-C_7. It can be reasonably assumed from the results of section 3.2 that the proton acidity of the OH functional group remains nearly constant along the homologous series. Even though scarce, there are some experimental indications that such assumption is a valid one. For example, the Hammet σ^- constants of substituted *p*-cresol and *p*-pentyl phenol are −0.10 and −0.19, respectively, showing a small variation of the acidity constants of these compounds with respect to phenol; the negative values are a consequence of the electron-donating nature of these substituents.[44] It can be argued that these values, obtained from aqueous solution, might not be representative of the behavior of *p*-alkyl phenols in *n*-heptane, but indications of the feasibility of preserving this behavior in *n*-C_7 are obtained from available activity coefficients at infinite dilution, γ^∞, of phenol in *n*-hexane and water. The value of γ^∞ for phenol in *n*-hexane, obtained from differential ebulliometry at 320 K, is ∼45, a value that only decreases about 20% when water is used as a solvent instead of *n*-hexane.[45] Interestingly, this variation is to be compared with the observed 50% decrease if benzene is used instead as a solvent.

The contribution of the interactions occurring between the acidic H atom and the asphaltene aromatic core in the presence of *n*-C_7 can be considered to be nearly constant along the series of *p*-alkyl phenols, whenever an asphaltene of same oil source is used. We propose that the trend observed for dissolving this asphaltene in *n*-C_7 by means of *p*-alkyl phenols can be explained by the alkyl chain−solvent interactions and quantified by the free energy of solvation; this hypothesis is tested in the present investigation.

According to Figure 1, a change in the slope in the trend of computed amphiphile solvation energy in *n*-C_7 as a function of alkyl chain length is observed at approximately $m = 5$, *p*-pentylphenol, a behavior that mirrors the experimental measurements for asphaltene dispersion in *n*-C_7 with *p*-alkyl phenols. This can be seen in Figure 3a where the experimental

(44) Corwin, H.; Leo. A. *Substituent Constants For Correlation Analysis in Chemistry and Biology*; John Wiley and Sons: New York, 1979

(45) Dobrjakov, Y. G.; Balashova, I. M.; Maurer, G. *Fluid Phase Equilib.* **2001**, *181*, 59.

minimum concentration of *p*-alkyl phenols necessary to dissolve an asphaltene in *n*-C_7 as a function of alky chain length is shown and in Figure 3b in which the same concentration versus the theoretically computed ΔG_{solv} values are plotted.

In particular, Figure 3 shows the importance of the solvation energy of the dispersant itself, in this case a *p*-alkyl phenol, on the solubilization of a given asphaltene. Moreover, the analysis of ΔG_{solv} given in Figure 1 shows the factors involved, in this case, the relevance of van der Waals forces that counteract the effect of repulsion energies.

4. Conclusions

In agreement with experimental observations, the computed solvation free energies of the series of *p*-alkyl phenols studied in this work allow us to anticipate that *n*-pentyl phenol has the shortest alkyl chain necessary to efficiently dissolve an asphaltene in *n*-heptane. The nonelectrostatic contribution to ΔG_{solv} is the leading factor that differentiates the relative solubility of these compounds. From the dissection of the nonelectrostatic term, which has been calculated classically, it is determined that the repulsive contribution is offset in an important manner by the stabilizing effect of the van der Waals forces included in the long-range dispersion interaction. Accordingly, the leading stabilizing effect comes from the van der Waals interaction because of the minor variance of the electron distribution, as explained by the molecular dipole moments and by atomic charges and energies of the atoms making up the molecules. Moreover, the trend observed along the series of molecules analyzed is the result of the long-range stabilization of the alkyl chain while the electrostatic term remains nearly constant. From these results, the amphiphile−solvent interaction explains the ability of *p*-alkyl phenols to disperse an asphaltene in *n*-C_7. The amphiphile solvation energies computed by means of a dielectric polarization model provide detailed insight on the nature of one of the stabilizing factors involved (the amphiphile−solvent interactions) when *p*-alkyl phenols are used as asphaltene dispersants in *n*-C_7. These results should not be understood to imply that the amphiphile−asphaltene interactions are not relevant in the solubilization process; on the contrary, these interactions, as well as the amphiphile−solvent and solvent−solvent contributions, are clearly involved in the global process. However, once a given asphaltene and a solvent are selected, the main variation should come from contributions from the alky chains of varying length along the amphiphile series, and this factor should explain the trend observed for their asphaltene dissolving power. A theoretical justification for this hypothesis was tested in this work and its plausibility was confirmed, as discussed.

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