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Partitioning of *o*/*p*-Nitrophenols in the Presence of Hydrotropes in Aqueous Solutions

Aalok S. Negi[a]; Vilas G. Gaikar[a]
[a] Institute of Chemical Technology, University of Mumbai, Mumbai, India

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Partitioning of *o*/*p*-Nitrophenols in the Presence of Hydrotropes in Aqueous Solutions

Aalok S. Negi and Vilas G. Gaikar
Institute of Chemical Technology, University of Mumbai, Matunga,
Mumbai, India

Abstract: Partitioning of *o*/*p*-nitrophenols between organic solvents and water in the presence of hydrotropes such as sodium toluene sulfonate, sodium xylene sulfonate, and sodium cumene sulfonate, has been experimentally investigated and modelled in terms of co-aggregation of the hydrotrope and nitrophenols in aqueous solutions. The phenol-hydrotrope and hydrotrope-hydrotrope interactions are characterized by an aggregation model. The experimental data for a series of hydrotropes are further used to predict the partitioning behavior of *p*-nitrophenol in the presence of sodium butyl benzene sulfonate (Na-NBBS). The aggregation number of NaNBBS, (~30) obtained from the partitioning data, matches well with that obtained by small angle neutron scattering.

Keywords: Aggregation, alkylbenzene sulfonates, hydrotrope, nitrophenol, partition coefficient, selectivity

INTRODUCTION

Hydrotropes are highly water soluble organic salts which, when present at a sufficiently high concentration, increase solubility of sparingly water-soluble or almost water-insoluble organic substances in aqueous solutions (1–4). Alkali and alkaline metal salts of short chain alkyl substituted aromatic carboxylic and sulfonic acids, phenols and glycol sulfates are

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Address correspondence to Vilas G. Gaikar, Chemical Engineering Department, Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai-400019, India. Tel.: 91-22-21445616; Fax: 91-22-24145614. E-mail: v.g.gaikar@udct.org

commercially available hydrotropes. These are conventionally used in detergent formulations and drug solubilization (4) and in recent years in chemical reactions and separations (5–13). In principle, a highly water-soluble amphiphilic compound having a polar/ionic group and a short hydrophobic hydrocarbon group can function as a hydrotrope (4). Hydrotropes are structurally similar to surfactants with a difference only in size of hydrophobic groups. The hydrophobic chain in a hydrotrope is much shorter, i.e. C_1 to C_6 carbon atoms as compared to C_8 and above in case of surfactants (14) Because of their amphiphilic structure, hydrotropes reduce surface tension of aqueous solutions and are now considered to self-associate forming non-covalent micro-assemblies of reduced polarity in aqueous solutions, in a manner analogous to the micelle formation of a surfactant, beyond a characteristic minimum hydrotrope concentration (MHC) (4). The hydrotropic effect in solubilization and several other applications is a strong function of hydrotrope concentration and can be reversed by dilution of the hydrotropic solution by water to recover the solubilized compound from the aqueous solution (9). Easy recovery of dissolved solute by mere dilution by water and absence of emulsification of the hydrotrope solutions with organic solvents provide the major advantages in using hydrotropes in some of the recent applications (4–11).

Although, micellar solubilization of water insoluble organic substances in aqueous solutions is well known, the capacity of a surfactant solution to dissolve an organic compound in micelles is reportedly often lower as compared to that of a hydrotrope aggregate (4,13). Aromatic hydrotropes form planer but open layer structures in such self-aggregates (1,4,10,13). Not all hydrophobic compounds are dissolved by hydrotropes thus giving high selectivity in the hydrotropic solubilization (4,9). Due to their weak hydrophobic nature, the MHCs of hydrotrope, however, are in a molar concentration region and a very high concentration of hydrotrope is usually required for significant solubilization.

Using hydrotropes for extractive separations, even differentiating between isomeric organic compounds, was pioneered in this laboratory with selectivity sometimes surpassing that obtained with reactive extractants (8–12). Since hydrotropes are completely water soluble and show poor affinity towards organic solvents without emulsification, their application in extractive separations deserves better attention.

In this paper, we model the aggregation behavior of alkyl benzene sulfonates with a carbon chain up to butyl group, using partitioning data of nitrophenol isomers between organic solvents of different polarities and the aqueous hydrotropic phase at different concentrations of the hydrotropes. The aggregation of a hydrotrope is presumably necessary for the enhanced solubilization of a solute in aqueous solutions (1,4,9,12). The approaches which have addressed earlier the hydrotropic solubilization and extractive separations fall into two categories. The most common approach treats these organic salt solutions as inorganic salt solutions (15) while the other approach treats them as micellar aggregates of conventional surfactants (1,4). The former approach, however, completely neglects the self assembly of these molecules which is contrary to the now well-established aggregation behavior of hydrotropes (1,4). Any theory of hydrotrope solutions should take into account the aggregation of the hydrotrope molecules in bulk phase. We had earlier proposed an association model for hydrotropic solubilization of organic compounds which explicitly considered the aggregation of hydrotrope molecules and the subsequent co-aggregation of solute molecules with the hydrotrope aggregates as the mechanism of hydrotropic solubilization (10). The model, however, leads to dimers of hydrotrope as the predominant species in the aqueous hydrotrope solutions which is unlikely. The model, therefore, has been further modified in this work by considering an optimum size of the aggregates.

MODELING AGGREGATION OF HYDROTROPE

In the case of amphiphilic molecules, the formation of aggregates is due to conflicting effects of repulsion between the similarly charged ionic head-groups and the attractive hydrophobic effect that pulls the hydrocarbon chains of neighboring molecules together to minimize their contact with water in an aqueous solution (4,14). The latter effect is a result of entropic contribution from the release of structured water from overlapping hydration shells of individual organic hydrocarbon structures on their aggregation (14). The disorder generated by water structure-breaking on bringing the hydrocarbon chains together provides the necessary impetus for aggregation of these molecules. This effect is relatively poorer in case of hydrotropes because of a much smaller hydrocarbon chain while the strong ionic character of these molecules pulls these molecules apart from each other, particularly in solvents of high dielectric constant such as water. In the case of a hydrotrope, a shorter hydrocarbon chain and completely dissociating ionic head-groups warrant stronger repulsion between the similarly charged head groups of adjacent molecules which should make the hydrotrope aggregates somewhat open and less co-operative as compared to the surfactant micelles (4). Unlike surfactant solutions, therefore, the macroscopic properties of hydrotrope solutions, such as surface tension, conductivity, etc.,

$$H_1 + H_1 \overset{K_2}{\longleftrightarrow} H_2$$

$$H_2 + H_1 \overset{K_3}{\longleftrightarrow} H_3$$

…………………

…………………

$$H_{n-1} + H_1 \overset{K_n}{\longleftrightarrow} H_n$$

Scheme 1.

show a gradual variation with hydrotrope concentration (1,9). This variation in different properties of the hydrotrope solutions indicates that the hydrotrope aggregation is a stepwise process rather than a highly cooperative process like micelle formation of a surfactant at its critical micellar concentration (4,10). The process of hydrotrope aggregation, therefore, can be represented by mass action law as shown in Scheme 1.

The general case with individual values of K_i's for each of the aggregation steps is much more complex. It would almost be impossible to evaluate all these constants unless they are related to each other in some way.

The tendency of aggregation of amphiphilic substances is due to the short-range hydrophobic and dispersive forces between the hydrophobic parts and is opposed by the long range electrostatic forces between the charged head groups (14).

$$-\mathrm{RT}\ln(\mathrm{K_n}) = \Delta\mathrm{G_n} = \Delta\mathrm{G}_{el,n} + \Delta\mathrm{G}_{hy,n} \tag{1}$$

The first term in eq (1) is due to repulsive electrostatic interaction which keeps the charged molecules away from each other while the second term is the result of hydrophobic effect because of the hydrocarbon structure which attracts the molecules towards each other in water. The free energy of the aggregative process will be decided by the number of molecules in an aggregate. It is, therefore, proposed that there must be an optimum aggregation number, *m*, such that it will be the stable aggregate in the population. For planer dyes, the aggregation constant has been shown to be inversely proportional to the number of molecules in the aggregate (16). It is, therefore, assumed that *K* is related to the aggregation number (*n*) of the aggregate and optimum aggregation number (*m*) as follows (10,16):

$$K_n = \frac{mK_2}{n} \tag{2}$$

such that

$$K_n > K_2 \qquad \text{for } n < m$$
$$K_n > K_2 \qquad \text{for } n > m$$

where, K_2 is the hydrotrope dimerization constant. The association constant (K_n) for an *n-mer*, therefore, increases up to formation of an m-mer and then decreases with further increase in the aggregation number leading the aqueous solution to be more populated in m-mers of the hydrotrope.

The total concentration of the hydrotrope, $[C_S]$, and the monomer concentration $[H_1]$ can then be related by the following equation:

$$[C_s] = \sum_{n=1} n[H_n] = 2\frac{[H_1]}{m}\left[\left(\frac{m}{2} - 1\right) + \exp(mK_2[H_1])\right] \tag{3}$$

The hydrotrope aggregates presumably dissolve the organic solutes by trapping them within the aggregates (10). This solute association with the hydrotrope aggregate can be governed by specific interaction of the solute with the hydrotropic assemblies and the geometrical constraints on the final structure of the aggregates because, unlike micelles, there is no fluid like core for the solubilization of organic solutes in the hydrotrope aggregates. There is no definite answer on the aggregate structure of hydrotrope yet but the experimental results do indicate the formation of non-polar assemblies of these molecules and the non-polar environment the dissolved solute experiences in the hydrotrope solutions (1,13,17). The small angle neutron scattering studies have indicated the presence of ellipsoidal assemblies with significant charge ($\sim$45%) on the surface (18).

Since the spectroscopic studies indicate the presence of a dissolved probe in a nonpolar environment (4), the solute probably intercalates between hydrotrope molecules in an aggregate. With a hydrotrope n-mer ($n \geq 2$) assembly, the solute association with the hydrotrope is, therefore, considered in Scheme 2 as stepwise addition to a hydrotrope n-mer.

The term H_nS_p indicate a $n =$ mer with p molecules of the solute while H_{n0} indicates an n-mer without any solute. The above scheme is related to the hydrotrope-solute interaction parameter (K_{Sp}) through equation (4) if the intercalation of a solute with a hydrotrope aggregate is to follow a mass action law:

$$[H_nS_p] = K_{Sp}\left[H_nS_{p-1}\right][S_1] \tag{4}$$

$$H_{no} + S_1 \xleftrightarrow{K_S} H_nS_1$$

$$H_nS_1 + S_1 \xleftrightarrow{K_{S2}} H_nS_2$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$H_nS_{p\text{-}1} + S_1 \xleftrightarrow{K_{Sp}} H_nS_p$$

Scheme 2.

In most cases, the solubility curve of an organic compound reaches to a plateau showing saturation solubility at higher hydrotrope concentrations (1,4). In the absence of an organic solute, the hydrotrope molecules are repelled by the electrostatic interaction between their same ionic head groups. The presence of a nonpolar organic solute between the hydrotrope molecules, can reduce local dielectric constant of the medium. This in turn increases the counter-ion association with the head-groups of the aggregates and reduces the electrostatic repulsion between the charged head groups of the adjacent hydrotrope molecules. The SANS studies indicate almost 50% of the aggregated molecules in an assembly have counter-ion association (18). The assembly now packs relatively more closely and thus provides constraint to the incorporation of the additional solute molecule(s) into the same aggregate. It is thus assumed that K_{Sp} decreases with the number of the solute molecules (p) in the co-aggregated state.

$$K_{Sp} = \frac{K_S}{p} \tag{5}$$

where, K_S is the association constant characterizing the hydrotrope-solute interaction of a solute free *n*-mer with the first solute molecule. K_s is taken independent of the aggregation number of an aggregate, i.e., the solute's preference for a solute-free hydrotrope aggregate is not affected by the size of the aggregate.

The amount of a solute associated with an *n*-mer, therefore, can be shown to be:

$$\begin{aligned} S_n &= [H_nS_1] + 2[H_nS_2] + 3[H_nS_3] + \ldots \\ S_n &= [H_{n0}]K_S[S_1]\exp(K_S[S_1]) \end{aligned} \tag{6}$$

where, S_1 is the concentration of free solute in the aqueous phase and $[H_{\mathrm{n}0}]$ is the concentration of solute free n-mer at equilibrium conditions and subjected to the condition

$$\begin{aligned}[H_n] &= [H_{n0}] + \sum_{i=1}^{p}[H_nS_i] \\ &= [H_{n0}]\exp(K_S[S_1]) \qquad (7)\end{aligned}$$

From equations (6) and (7), the concentration of the solute with the n-mer will be

$$[S_n] = K_S[S_1][H_n] \qquad (8)$$

The total amount of the solute associated with the hydrotrope aggregates can be shown to be

$$\begin{aligned}[S_T] &= \sum_{n=2}^{\infty}[S_n] \\ &= 2\frac{K_S}{m^2K_2}\{[S_1](\exp(mK_2[H_1]) - (1 + mK_2[H_1]))\} \qquad (9)\end{aligned}$$

Equations (3) and (9) with parameters K_2 and K_S characterize the hydrotrope-hydrotrope and solute-hydrotrope interactions while explicitly accounting for the aggregation behavior of a hydrotrope in the aqueous solutions. These equations now also include an optimum aggregation number (m) of a given hydrotrope.

The amount of a solute associated with the hydrotrope (Eq. 9) can be related to the total concentration of the hydrotrope (Eq. 3). These two equations can be used to estimate the interaction parameters, K_S and K_2, from a solute's partitioning data. The partitioning data gives an estimate of free solute concentration in the hydrotrope solutions along with the amount associated with the hydrotrope assemblies which is otherwise difficult to obtain from solubilization experiments. The partition coefficient of a free solute is assumed to be the same as that in the absence of the hydrotrope. It is also worthwhile to investigate the effect of the presence of the solvent on the ability of a hydrotrope to selectively extract an organic molecule from the organic solutions. The organic solvent is expected to compete with the hydrotrope solution to solvate the solute. This selectivity effect becomes still more attractive while dealing with isomeric compounds. It is reasonable to assume that the solvent's own solubilization into the hydrotrope solution is not appreciable as compared to that of the solutes.

MATERIALS AND EXPERIMENTAL METHODS

Sodium *p*-toluene sulfonate (NaPTS), sodium xylene sulfonate (NaXS), and sodium cumene sulfonate (NaCS) were purchased from Navdeep Chemicals Ltd., Mumbai. *o*/*p*-Nitrophenols were purchased from Loba Chemicals having a purity of 98%. The phenols were purified before use by repeated crystallization. Toluene, chloroform, and dichloroethane, were supplied by Merck (I) Limited.

Standard solutions of known concentrations of the phenols were prepared in different solvents and used as stock solutions. A mixture of an aqueous solution of a hydrotrope and an equal volume of organic solution of one of the NPs was equilibrated on a magnetic stirrer in a constant temperature water bath at 30°C. After sufficient time (~2 hr) was given for equilibration, the organic phase was separated from the aqueous phase by decantation. The organic and aqueous phases were analyzed by UV-Absorption Spectroscopy at respective wave lengths of nitrophenols ($\lambda_{\mathrm{max,\ o\text{-}NP}} = 369\,\mathrm{nm}$ and $\lambda_{\mathrm{max,\ p\text{-}NP}} = 332\,\mathrm{nm}$) (17). The regression values for the calibration line were 98–99%.

Results and Discussions

The effect of hydrotropes on partitioning of nitrophenols was studied at different hydrotrope concentrations. The solvents, toluene (slightly polar), chloroform (polar), and dichloroethane (polar) covered a reasonable range of polarity. The partition coefficient, K_p is defined as the ratio of concentration of the solute in organic phase (moles/dm^3) to its concentration in the aqueous hydrotrope phase (moles/dm^3).

Single Component Partitioning Study for *p*-NP

Figure 1 shows single component partitioning of *p*-NP in three solvents in the presence of NaCS at different concentrations. With the increase in NaCS concentration, the partitioning coefficient of *p*-NP towards the organic phase decreases almost exponentially. The decrease in the partition coefficient was very large even before reaching the reported MHC of NaCS (0.1 kmol/m^3). At concentrations, beyond MHC, the hydrotrope supposedly forms self aggregates and these aggregates are considered to be responsible for the increased concentration of the solute in the aqueous hydrotrope solutions (1,4). The decrease in the partition coefficient of the phenol, however, starts well below the reported MHC of the hydrotrope (4). If the aggregation of the hydrotrope is responsible

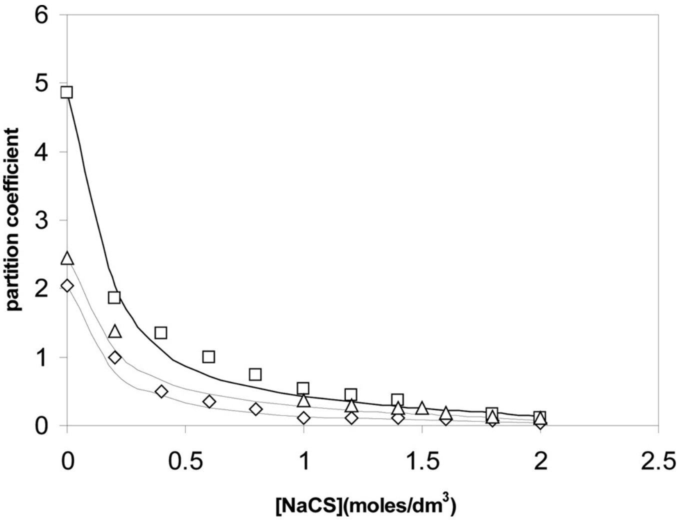

Figure 1. Partition coefficient of *p*-NP in different solvents using aqueous NaCS solutions ◇, toluene; □, chloroform; Δ, dichloroethane (the lines are the fitted curves).

for solubilization of the phenol and, therefore, reducing its partitioning towards the organic phase, then the aggregation of the hydrotrope seems to have started well before the MHC is reached. Pre-aggregation structures of hydrotrope in aqueous solutions, particularly in the presence of a solute therefore, are not ruled out.

On increasing the hydrotrope concentration, the number of hydrotrope aggregates in the solution is expected to increase. This should then also increase the amount of the phenol associated with the hydrotrope aggregates. At intermediate concentrations, the hydrotrope aggregates should cover a wide range of aggregation number in the solution. At increasingly higher hydrotrope concentrations, the hydrotrope should mostly be present in aggregates of optimum size but with an increasing number of the aggregates in the solution. The presence of a large number of such charged species might force the aggregates to have increased counter-ion condensation on their surface, with the formation of more compact structures and reducing the ability of the aggregates to associate with more amount of the solute. Increasing the number of hydrotrope aggregates, however, leads to more and more amount of the phenol transferred to the aqueous phase, resulting in reduced partitioning of the phenol towards the organic phase. The formation of compact aggregate structures on the other hand limits the phenol-hydrotrope aggregate association and thus the system shows a limiting value of partition coefficient of the phenol.

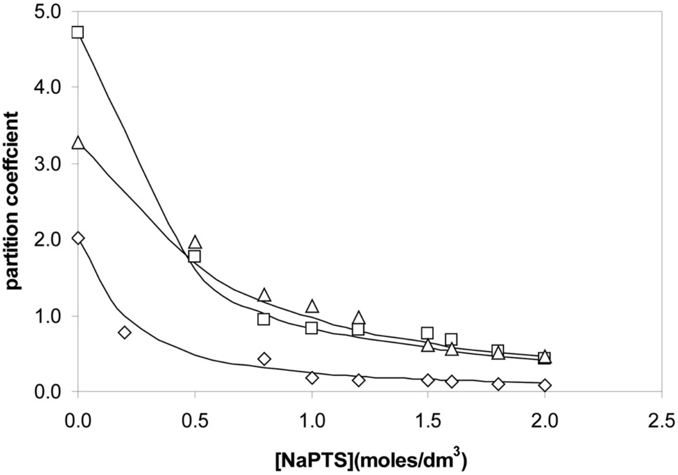

Figure 2. Partition coefficient of *p*-NP in different solvents using aqueous NaPTS solutions ◇, toluene; □, chloroform; Δ, dichloroethane (the lines are the fitted curves).

The partition coefficient of *p*-NP reached to a value as low as 0.03 with toluene as solvent. *p*-NP has a strong tendency to form intermolecular H-bonding. It is also sparingly soluble in toluene as the solvent can not break the intermolecular H-bonding in *p*-NP to solvate it. The poor solvation of *p*-NP in the toluene phase results in its greater tendency to move out of the toluene phase. Figures 2 and 3 show similar partitioning behavior of *p*-NP towards different solvents in the presence of other two hydrotropes.

The partitioning coefficient of *p*-NP, at a given hydrotrope concentration, decreased more for Na-CS as compared to NaPTS. It is clearly apparent from these data that with the increased hydrophobic structure of a hydrotrope, its capacity to associate with the organic solute increases. The solubilization experiments in the absence of organic solvent also point to a similar effect of solubilization capacity of the hydrotropes. A hydrotrope with large and bulky hydrocarbon structure is more effective in solubilization of water insoluble organic compounds (4). Thus, the stronger is the hydrophobic character of a hydrotrope, the more effective is its ability to extract a solute from an organic phase. Hence, the lower is the partition coefficient of the phenol. Na-CS showed, therefore, the largest decrease in the partition coefficient of *p*-NP. It reduced the partition coefficient of *p*-NP by factor of 57 in toluene, while the phenol partitioning was reduced by 44 and 22 fold with chloroform and dichloroethane, respectively, as solvents. The solvent, therefore, also

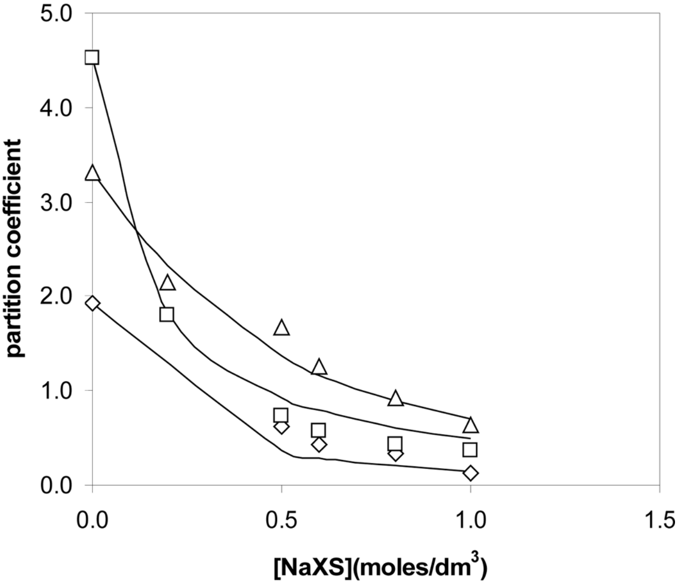

Figure 3. Partition coefficient of *p*-NP in different solvents using aqueous NaXS solutions ◇, toluene; □, chloroform; Δ, dichloroethane (the lines are the fitted curves).

has a significant effect on the phenol partitioning in the presence of a hydrotrope. In polar solvent(s), the partition coefficient of p-NP is affected to a lesser extent as the phenol gets solvated better in these solvents. Even then there is a significant decrease in the partition coefficient of *p*-NP.

Single Component Partitioning Study of *o*-NP

Figure 4 shows the single component partitioning of *o*-NP in the same three solvents at different concentrations of NaCS. With the increase in NaCS concentration, the partitioning of *o*-NP towards the organic phase decreases in the same manner as that of *p*-NP. The partition coefficient of *o*-NP is much higher than that of *p*-NP in all the three solvents. For example, the partition coefficient of *o*-NP in toluene/water system is ≈180 times of partition coefficient of *p*-NP. o-Nitrophenol, unlike *p*-NP, is a relatively non-polar solute because of *intra*molecular H-bonded structure and, therefore, prefers the organic phase than the aqueous phase. *o*-NP is soluble in most of the organic solvents including non-polar solvents such as hexane.

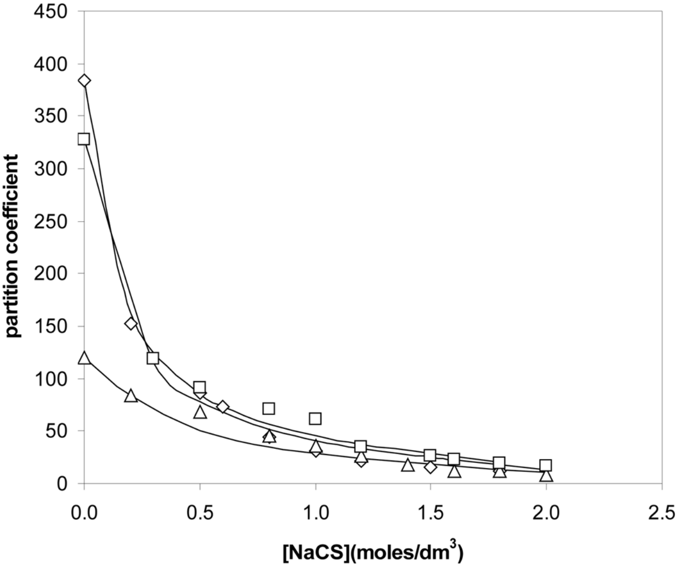

Figure 4. Partition coefficient of *o*-NP in different solvents using aqueous NaCS solutions ◇, toluene; □, chloroform; Δ, dichloroethane (the lines are the fitted curves).

Figures 5 and 6 show partitioning behavior of *o*-NP in different solvents using the other two hydrotropes in aqueous solutions. The decrease in the partition coefficient of o-NP was of the same order for the three hydrotropes as that in case of *p*-NP. It was also observed that the decrease in the partition coefficient of *o*-NP was less than that observed with *p*-NP, i.e., the decrease was only 18-fold in the NaCS-toluene system as compared to 57 fold with *p*-NP in the same system.

Parameters of the Association Model of Hydrotrope Extraction

The association model uses free solute concentration $[S_1]$ in the aqueous phase, which the partitioning data did not provide directly. To fit the partitioning data in the model, it was assumed that the free solute in the aqueous phase and the solute in the organic phase are in equilibrium with each other. It was observed that partition coefficient of the free solute between water and the solvent is a function of the solute's organic phase concentration. Figures 7 and 8 show the dependence of the partition coefficient of both the phenols on their organic phase concentration, in the absence of a hydrotrope. Using this dependence, the *free* solute

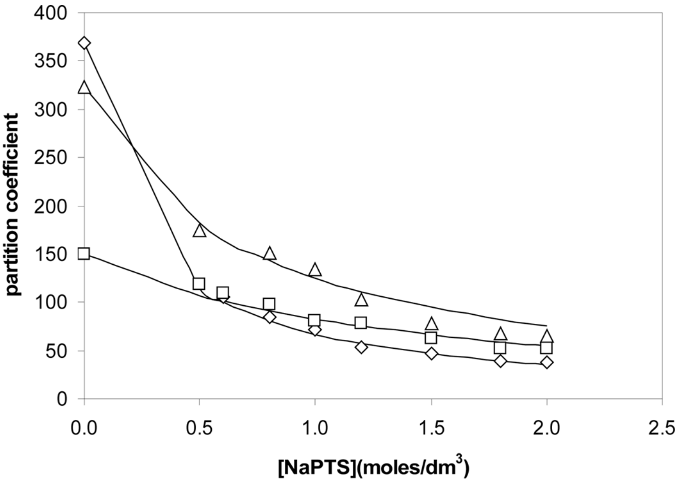

Figure 5. Partition coefficient of *o*-NP in different solvents using aqueous NaPTS solutions ◇, toluene; □, chloroform; Δ, dichloroethane (the lines are the fitted curves).

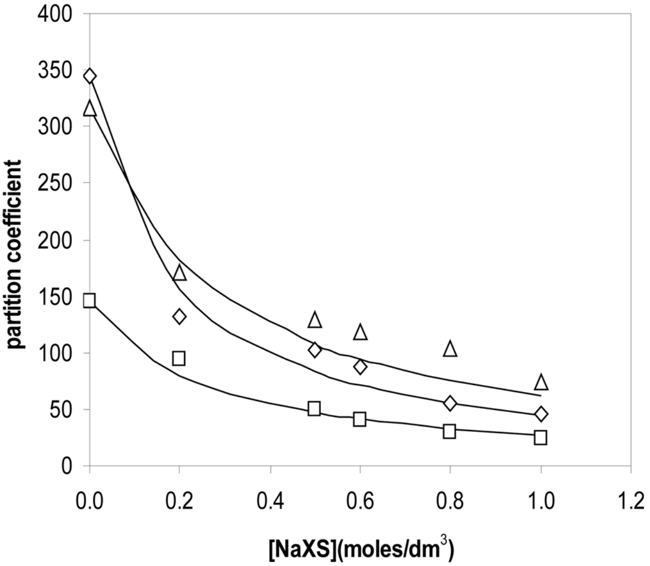

Figure 6. Partition coefficient of *o*-NP in different solvents using aqueous NaXS solutions ◇, toluene; □, chloroform; Δ, dichloroethane (the lines are the fitted curves).

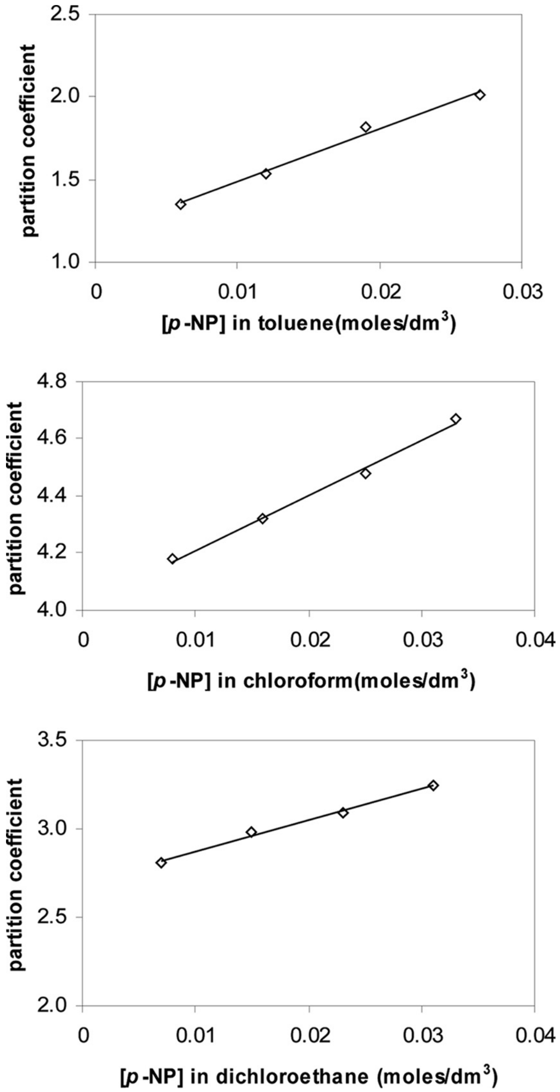

Figure 7. Effect of organic phase concentration on partition coefficient of *p*-NP.

concentration in the aqueous phase can be estimated assuming that the partition coefficient of the *free* solute is not affected by a hydrotrope. Subtracting $[S_1]$ from the aqueous phase total solute concentration, the amount of the solute associated with the hydrotrope can be calculated.

The partitioning data were fitted in the model equations (Equations (3) and (6)) using the least squares method to evaluate the hydrotrope-solute

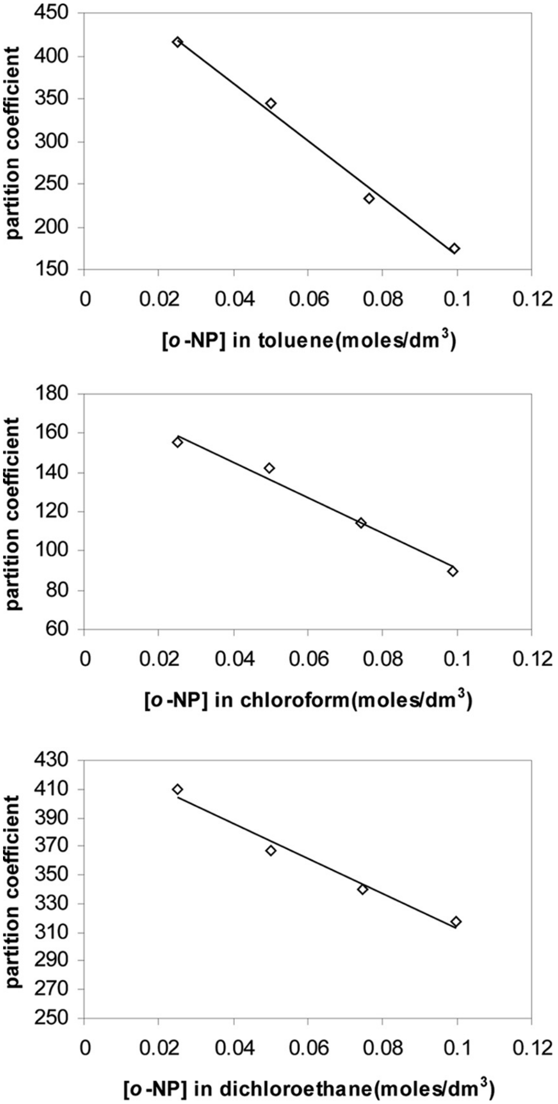

Figure 8. Effect of organic phase concentration on partition coefficient of *o*-NP.

interaction parameter (K_S), hydrotrope-hydrotrope interaction parameter (K_2), and optimum aggregation number (m) for all the systems. There was no change in these parameters for a pair of solute and hydrotrope, with different solvents. Since, it is an aqueous phase based model, no effect of the organic phase was expected once the effect of the organic phase

Table 1. Interaction parameters for *o*/*p*-NPs and hydrotropes using modified Association model

solute	Hydrotrope	m	K_2	K_S
p-Nitrophenol	NaCS	23	0.06	42
	NaXS	20	0.05	36
	NaPTS	18	0.025	20
o-Nitrophenol	NaCS	23	0.06	32
	NaXS	20	0.05	18
	NaPTS	18	0.025	13

concentration on the free solute concentration in the aqueous phase was taken into account.

Table 1 lists the interaction parameters and optimum aggregation number for different systems of phenols and hydrotropes. The lines in Figs. 1–6 indicate the fitted curves. The parameters, K_2 and *m*, do not change substantially with the solute or its concentration as these two characterize intrinsic aggregation behavior of the hydrotrope. The K_S values of *p*-NP are higher than the corresponding K_S values for *o*-NP suggesting that *p*-NP associates better with the hydrotropes as compared to *o*-NP. It is also observed that all the three parameters i.e., K_S, K_2, and *m* increase gradually from NaPTS to NaCS. This indicates that the solute-hydrotrope and hydrotrope-hydrotrope interactions are decided by the structure of the hydrotrope. As the number of $–CH_2–$ groups in the hydrotrope structure increases, the hydrophobicity of the hydrotrope also increases (1,15) and this results in an increased solubility of the solute or its partitioning towards the hydrotropic solution by its association with the hydrotrope.

The three parameters (for *p*-NP) were plotted with the number of carbon atoms attached to the benzene sulphonate ring (N) (Fig. 9). These dependencies were extrapolated to predict the parameters for sodium butyl benzene sulfonate (NaNBBS) as the hydrotrope and *p*-NP as the solute. The estimated aggregation number of NNBBs is 27 while its dimerization constant is 0.0706. The estimated solute interaction parameter with NaNBBS aggregate is 48.73. It is worth noting that the SANS studies on NaNBBS have given an aggregation number of 30 for Na-NBBS at high concentrations (18). The parameters were used further to predict the partition coefficient of *p*-NP in the presence of Na-NBBS in the aqueous solutions. Figure 10 shows that the prediction of partition coefficient of *p*-NP was quite satisfactory with the new hydrotrope.

The proposed model has a fair degree of accuracy useful for prediction of partition coefficient of the phenols in the presence of hydrotropes.

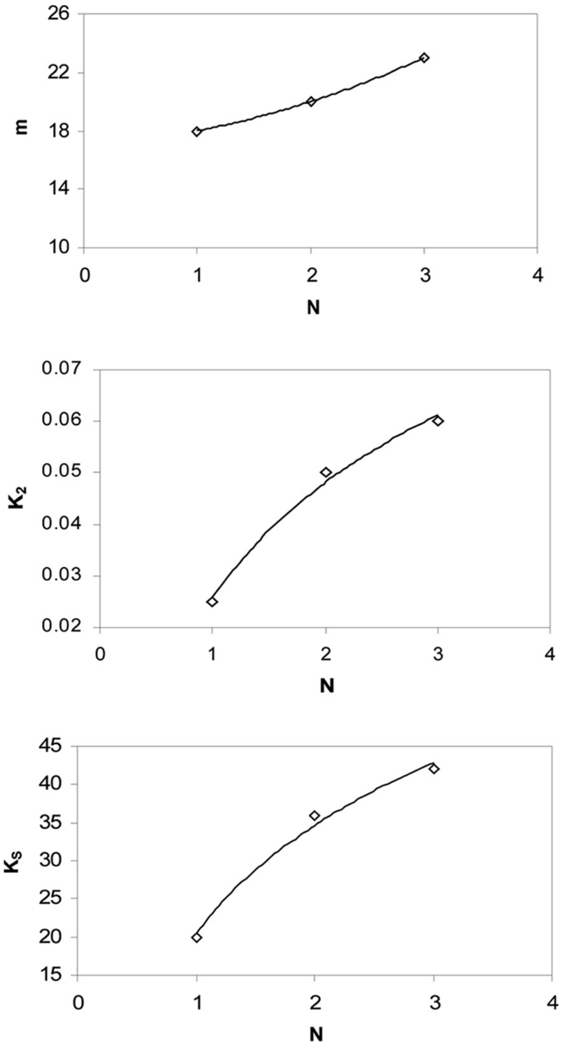

Figure 9. Plot of association model parameters with number of carbon atoms attached to the benzene sulphonate ring.

In addition, the model gives an indirect measurement of the aggregation number of the hydrotrope apart from the parameters that characterize the aggregation behavior of the hydrotrope. It is also satisfying that the aggregation number so estimated is very close to that reported by small angle neutron scattering for NaNBBS (18). The model, however, does not provide any details on the type and the shape of the hydrotrope

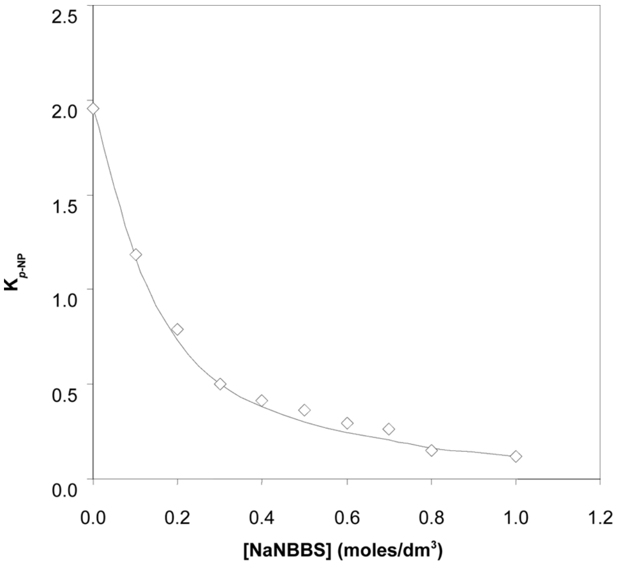

Figure 10. Predicted partitioning for NaNBBS and *p*-NP system with modified association model (the line is the predicted curve).

aggregates. Similarly, it cannot give any information about the way the solute interacts with the hydrotrope aggregates. The step-wise aggregation seems to be a reasonable assumption in this analysis, but the size distribution of hydrotrope aggregates can be and indeed is very wide in the present case. The pre-MHC aggregation of hydrotrope in the aqueous solutions has also been taken into account by the model without explicitly considering the aggregate formation at or beyond the MHC of the hydrotrope.

CONCLUSION

The aggregate formation of the hydrotrope molecules in aqueous solutions and the interaction between the solute and hydrotrope aggregates are explained by a step-wise Association model. Hydrotrope aggregates exist at an optimum aggregation number in the solution depending upon the hydrotrope's hydrophobic structure. The partition coefficient of phenols decreases with increase in hydrotrope concentration and with increasing non-polarity of the organic solvent. It is also possible to predict the partitioning coefficient of nitrophenols between the organic and hydrotropic phases on the basis of hydrophobicity of the hydrotrope.

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