CHAPTER 2

LITERATURE REVIEW

2.1 HYDROTROPES-ORIGIN

Neuberg (1930) was the first to report hydrotropy when he dissolved a variety of organic compounds in aqueous solution containing hydrotropes. After this, there is hardly any publication in this promising field for three decades. The emphasis on chemical engineering and industrial applications of hydrotropes started with an article by Mckee (1946). Badwan et al. (1983) made a significant contribution to hydrotropy during the last decade.

2.2 SOLUBILISING EFFECT OF HYDROTROPE SOLUTIONS

The literature available on the effect of hydrotropes on the solubility of solutes is rather limited.

Neuberg (1930) showed a substantial increase in the solubilities of cyclohexanone, cyclohexanol and furfural in the presence of hydrotropes such as urea and sodium toluene sulfonate in aqueous solutions.

Mckee (1946) demonstrated that solubilities of many sparingly soluble compounds like amyl chlorides could be increased 10-100 times using aqueous hydro trope solutions of sodium xylene sulfonate. They visualised the easy recovery of the dissolved solute and the hydrotrope solutions by dilution with water.
Booth and Everson (1948) have found that increase in concentration of hydrotropes in aqueous solutions can increase the solubility of many sparingly soluble compounds by several fold. They were the first to show that the solubility increase in hydrotrope solution does not occur in a linear fashion with the concentration of the hydrotrope. They determined the solubility of a variety of solutes such as amyl alcohol, benzoic acid, butyl alcohol and chloroform in aqueous 40% sodium xylene sulfonate solutions at 25°C. They observed a pronounced increase in the solubility of solutes in hydrotrope solutions.

In further investigations, Booth and Everson (1949, 1950) observed a substantial increase in the solubility of solutes such as acetophenone, aniline and benzaldehyde in hydrotrope solutions of sodium-benzene sulfonate and sodium-xylene sulfonate. Their objective in this effort was to determine the relative effectiveness of these salt solutions as hydrotrope solvents at two different temperatures of 25° and 60°C. The results obtained by them indicated that in general, sodium-xylene sulfonate was found to be effective for use even at lower temperatures.

The solubility of benzoic acid at 40°C in hydrotrope solutions of homologous series of derivatives of sodium benzene sulfonate was determined by Licht and Wiener (1950). They observed a dramatic increase in the effect of hydrotrope with increase in temperature. Among the various salts used as hydrotropes for benzoic acid as the solute, sodium-p-cymene sulfonate was found to be most effective. These researchers also compared and analysed the hydrotropic effects of the various salt solutions on the solubility of benzoic acid.

Poochikian and Cradock (1979) have shown a significant increase in the solubility of ‘water-insoluble’ cytotoxic agent namely chartreusin in the presence of various hydroxy benzoates as hydrotropes. A significant
increase in the solubility of chartreusin in aqueous phase was observed by them in the case of sodium-tri-hydroxy benzoate hydrotrope.

Badwan et al. (1983) determined the solubility of poorly soluble benzodiazipine derivatives in the presence of sodium salicylate and sodium benzoate as hydrotropes in the aqueous phase. They were the first to point out the requirement of minimum hydrotrope concentration in the aqueous phase to initiate significant solubilisation of the solute.

Later Saleh et al. (1985) made an attempt to extend the definition of the term hydrotrope to include cationic and non-ionic organic compounds. They also pointed out that this hydrotropic phenomenon is independent of pH.

Pandit and Sharma (1987) found that potassium salts of butyl monoglycol sulfate, p-cumyl phenol as hydrotropes were able to enhance the solubilities of sparingly soluble organic compounds such as phenyl benzoate even to 100 fold. They exploited the solubilisation efficiency of hydrotropes to increase the rates of heterogeneous reactions, involving such solutes.

Pathak and Gaikar (1992) carried out a study on the solubility of chlorobenzoic acids at the temperatures of 303, 313 and 323K in the presence of hydrotropes such as sodium-p-toluene sulfonate and sodium-butyl monoglycol sulfate. They also reported Setschenow constant for these solute-hydrotrope systems. They observed a substantial enhancement in the solubility of o-chlorobenzoic acid. As per their view, this effect may be due to the lower melting point of o-chlorobenzoic acid.

2.3 OTHER EFFECTS OF HYDROTROPE SOLUTIONS

The work of Janakiraman and Sharma (1985) shows that the rates of heterogeneous reactions can be enhanced considerably in the presence of
hydrotropes. They studied the hydrotropic action of urea on the solid-liquid
oxidation of cyclododecane.

A report on possible extractive separations using hydrotrope
solutions was published by Gaikar and Sharma (1986).

Gaikar and Sharma (1993) reviewed the field of separations using
hydrotrope solutions.

Dhananjay S.Rane and Man M.Sharma (1994), Vikas G.Sadvilkar
et al. (1995) obtained significant enhancement in the rates of some
heterogeneous reactions due to the consequent solubilisation effect of
hydrotropes.

2.4 COMPARISON WITH OTHER SOLUBILISATION METHODS

In the light of some similarities in the behaviour of hydrotropes and
other solubilisers particularly micellar surfactants, this comparison is
unavoidable.

Srinivas et al. (1991) observed that the behaviour of hydrotropes
differ from that of micelles in displaying a higher and somewhat more
selective ability to solubilise solutes.

Gaikar and Sharma (1993) pointed out that the problem of
emulsification normally encountered with micellar solutions is not found
with hydrotrope solution.

However, a clear and undisputed distinction between hydrotropy
and other solubilisation methods was brought to light by Balasubramanian
et al. (1989). For this purpose, they have compared the increase in the
solubility of the solute, perylene, brought about by sodium-p-toluene
sulfonate, a hydrotrope with that of guanidinium thiocyanate, a salting-in agent and in the presence of poly-ethylene glycol, a cosolvent or phase mixing agent.

The solubility increase of perylene was seen to be monotonic and gradual in the case of salting in and cosolvency process. In neither case was seen the sigmoidal pattern of solubility increase of perylene observed with sodium-p-toluene sulfonate, a hydrotrope. Based on their experimental findings, they concluded that hydrotropy is a process which goes beyond miscibility or cosolvency or salting-in or any other solubilisation methods. They have also shown that the solubilisation effected by hydrotrope was higher and more selective compared to other solubilisation methods.

The requirement of minimum hydrotrope concentration in the aqueous phase to show significant increase in the solubilities of solutes was observed by them. However, they demonstrated that the MHC of a hydrotrope is not analogous to the critical micellar concentration required in the case of micellar surfactants.

A list of previous works done on the effect of hydrotropes on the solubility of various solutes is given in Table 2.1.

2.5 SUMMARY

From Table 2.1, it can be seen that a certain amount of work has been carried out on the hydrotropic effect on the solubility of some organic and inorganic compounds.

However, a comprehensive study on the effect of different hydrotropes on the solubility of a series of solutes like organic esters has not been carried out so far.
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Author(s)</th>
<th>Year</th>
<th>Particulars</th>
<th>Solutes studied</th>
<th>Hydrotrope(s) used</th>
<th>Parameters varied</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Neuberg</td>
<td>1930</td>
<td></td>
<td>Cyclohexanone, Cyclohexanol, Furfural</td>
<td>Urea, sodium toluene sulfonate</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>McKee</td>
<td>1946</td>
<td></td>
<td>Amyl chlorides</td>
<td>Sodium xylene sulfonate</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>Booth and Everson</td>
<td>1948</td>
<td></td>
<td>Amyl alcohol, benzoic acid, bromoform, butyl alcohol, chloroform</td>
<td>40% Sodium xylene sulfonate</td>
<td>25°C</td>
</tr>
<tr>
<td>4.</td>
<td>Booth and Everson</td>
<td>1949</td>
<td></td>
<td>Acetophenone, Aniline, Benzaldehyde, Benzene</td>
<td>Na-benzene sulfonate</td>
<td>-</td>
</tr>
<tr>
<td>5.</td>
<td>Booth and Everson</td>
<td>1950</td>
<td></td>
<td>Hexane, Carbon-tetrachloride, Cotton seed oil, O-cresol, Cyclohexanol</td>
<td>Na-o-xylene sulfonate Na-m-xylene sulfonate Na-p-xylene sulfonate</td>
<td>25°C and 60°C</td>
</tr>
<tr>
<td>6.</td>
<td>Licht and Wiener</td>
<td>1950</td>
<td></td>
<td>Benzoic acid</td>
<td>Na-p-cymene sulfonate Na-p-bromobenzene sulfonate Na-m-benzene disulfonate</td>
<td>40°C</td>
</tr>
<tr>
<td>7.</td>
<td>Poochikian and Cradock</td>
<td>1979</td>
<td></td>
<td>Cytotoxic agent, 'chartreusin'</td>
<td>Na-mono, di and tri hydroxy benzoates</td>
<td>-</td>
</tr>
<tr>
<td>8.</td>
<td>Badwan et al.</td>
<td>1983</td>
<td></td>
<td>Benzodiazepine derivatives</td>
<td>Sodium salicylate Sodium benzoate</td>
<td>25°C</td>
</tr>
<tr>
<td>9.</td>
<td>Pandit and Sharma</td>
<td>1987</td>
<td></td>
<td>Phenyl benzoate</td>
<td>Potassium salts of butyl mono-glycol sulfonate and p-cumyl phenol.</td>
<td>-</td>
</tr>
</tbody>
</table>
It is therefore necessary to study the effect of a particular hydrotrope towards a series of solutes like organic esters.

Data on the effect of hydrotrope under a wide range of hydrotrope concentrations is absent. Hydrotropic study at increased system temperatures will be an additional information in the selection of a hydrotrope with respect to a particular solute.

Special emphasis need to be given to the easily available chemical compounds in the selection of hydrotropes.

The literature provides some information on the requirement of certain Minimum Hydrotrope Concentration (MHC) in the aqueous phase to show significant increase in the solubility of solutes. However, this aspect requires extensive experimental investigations for different solute-hydrotrope systems to gather additional information on MHC.

It is beneficial to ascertain the hydrotropic effect on the mass transfer coefficient of esters in order to explore the possibility of using them as a suitable reaction medium/component. This aspect is totally lacking in literature.