International Standard Serial Number (ISSN): 2249-6807

International Journal of Institutional Pharmacy and Life Sciences 2(1): January-February 2012

INTERNATIONAL JOURNAL OF INSTITUTIONAL PHARMACY AND LIFE SCIENCES

Chemical Engineering **Research Article……!!!**

Received: 19-01-2012; Accepted: 20-01-2012

SOLUBILITY AND MASS TRANSFER COEFFICIENT ENHANCEMENT OF TRIPHENYL PHOSPHATE IN WATER THROUGH HYDROTROPY

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Keywords:

Hydrotropy, Solubilization, Enhanced solubility, Mass transfer co efficient

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ABSTRACT

An encompassing investigation of the solubility and mass transfer coefficient enhancement of triphenyl phosphate through hydrotropy has been undertaken. The solubility studies have been carried out with hydrotropes such as potassium xylene sulfonate, ammonium xylene sulfonate, calcium xylene sulfonate, for a wide concentration range from 0 to 3.0 mol/L along with system temperature from 303K to 333 K. The effectiveness of hydrotropes was measured by the determination of Setschenow constant “Ks”. The solubility of triphenyl phosphate increases with increasing hydrotrope concentration and also with system temperature. A minimum hydrotrope concentration (MHC) in the aqueous phase was required to initiate significant solubilization of triphenyl phosphate. Consequent to the increase in solubilization of triphenyl phosphate, the mass transfer coefficient was also found to increase with increasing hydrotrope concentration. A threshold value of MHC is to be affirmed to have an appreciable enhancement in the mass transfer coefficient. The maximum enhancement factor, which is the ratio of the solubility values in the presence and absence of a hydrotrope, has been determined for all sets of experiments.

1. INTRODUCTION

Hydrotropy is a unique and unprecedented solubilization technique in which specific chemical components termed as hydrotropes can be used to affect a number of fold increases in the solubility of sparingly soluble solutes under standard conditions [1-4].

Hydrotropic substances are a class of chemical combinations that are freely soluble in water. Hydrotropes are much effective at high concentrations which in turn enhance the aqueous solubility of organic compound, because of the opportunity of molecular solution structures probably in the form of stack-type aggregates. The solubilized solute will therefore precipitate out on dilution with water from most hydrotropic solutions. This process may be used to recover the solute in a pure form, and the remaining mother liquor may be used to concentrate the hydrotrope for recycle[5].

Instant investigation, we have established the aggregation behavior of common hydrotropes by several techniques [6-7]. The self-aggregation of the hydrotropes has been thought over to be a pre-requisite for a number of applications in various meadows such as drug solubilization [8-12], and boswellic acids from Boswellia serrata resins[13].

The existing work was commenced for the principal study of the global character of hydrotropes in the selective solubilization of a triphenyl phosphate. With particular attention on both the theoretical understanding of the mechanistic action and the experimental studies which demonstrate the utility of hydrotropes in the solubilisation of a triphenyl phosphate (molecular weight M =326.29 and solubility 1.9mg/L) was selected, for enhancing its solubility using several commercially available hydrotropes. Since triphenyl phosphate serves as a raw material/intermediate. and this makes its separation from any liquid mixture, which has been troublesome, until now. Hence, this hydrotropic technique can be adopted to increase the solubility as well as to separate such mixtures effectively.

For many binary systems entailing a sparingly soluble organic compound such as triphenyl phosphate, the mass transfer coefficient in the presence of a hydrotrope is probably due to the difference between binary diffusivity (solute + solvent) and the diffusivity of the solute in the solution (solute + solvent + hydrotrope).

The hydrotropes used in this work are freely soluble in water. All are nonreactive and nontoxic and do not produce any significant heat effect when dissolved in water. The easy availability and low cost are two other factors considered in the selection of these hydrotropes.

2. EXPERIMENTAL

2.1 Materials

All the chemicals used in this work were manufactured by the Loba Chemie Pvt. Ltd., Mumbai. With manufacturers stated purity of 99.9 %. The hydrotropes used in this work viz., potassium xylene sulfonate, ammonium xylene sulfonate, calcium xylene sulfonate are analytical grade. Double distilled water was used for the preparation of hydrotropic solutions.

2.2 Methods

The experimental setup for conducting a single-stage batch wise liquid-liquid extraction consisted of a thermostatic water bath and a separating funnel. Measurement of the solubility of triphenyl phosphate was carried out at temperatures of 303, 313, 323, and 333 K.

For each solubility test, an equal volume of triphenyl phosphate was comprehensively mixed with equal volume of hydrotrope solution make a single-phase solution using a mechanical shaker. The hydrotrope solutions of different known concentrations were prepared by dilution with distilled water. Following to this, 100 ml of triphenyl phosphate was taken and added to 100ml of hydrotrope solution of known concentration. The mixture was then made to mix consecutively for three hours. The mixture was then allowed to settle and was transferred to a separating funnel, which was immersed in a thermostatic bath with a temperature controller within ± 0.1 °C. The setup was kept overnight for equilibration. After equilibrium was attained, the organic phase was carefully separated and analyzed to determine the concentration using a high-performance liquid chromatography (HPLC). All the solubility trials were conducted in duplicate runs to check their reproducibility. The observed error was <2%.

2.3 Mass transfer co efficient

The experimental setup for the determination of the mass transfer coefficient consisted of a vessel provided with baffles, and a turbine impeller run by a motor to agitate the mixture. The speed of the impeller at 600 rpm was selected to achieve effective mixing, and was maintained at the same value for all experiments. The vessel used for mass transfer studies had a height of 40 cm and an inner diameter of 15 cm. The turbine impeller had a diameter of 5 cm, width of 1 cm and length of 1.2 cm. It had four blades and rotated at 600 rpm. The baffle has a height of 40 cm, diameter of 1.5 cm and four baffles arranged at 90° to each other. For each run, to measure the mass transfer coefficient, an excess amount of triphenyl phosphate was added to the aqueous solution of the hydrotrope of known concentration. The sample was then agitated for 600, 1200, 1800 or 2400 s and the mixture was transferred to a separating funnel. After allowing the sample to stand for some time, the solution was filtered. The concentration of the solubilized organic compound triphenyl phosphate in aqueous hydrotrope solutions at time t was analyzed in the same way as done for solubility determinations using HPLC.

3. RESULTS AND DISCUSSION

Hydrotropic Extracted triphenyl phosphate been shown in schematic comparative HPLC chromatogram in Fig.1.

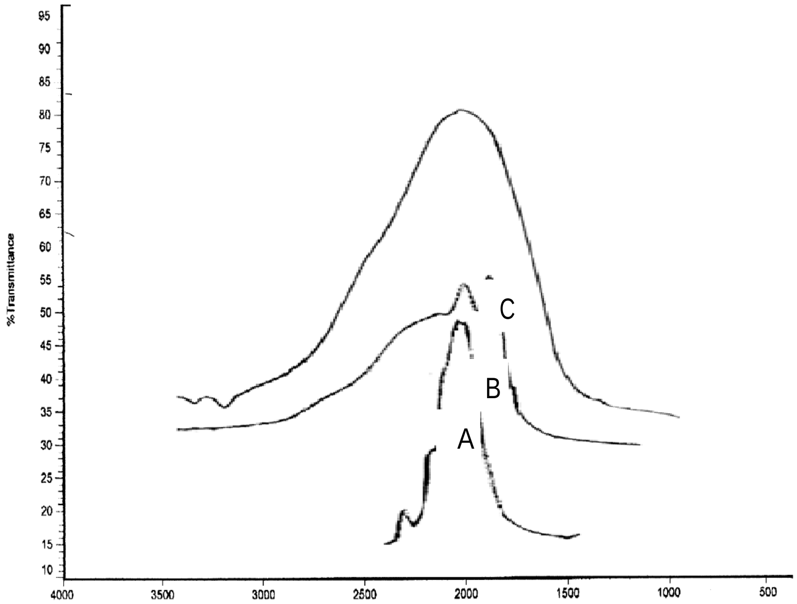

Fig.1, comparative HPLC chromatogram A. potassium xylene sulfonate B. ammonium xylene sulfonate C.calcium xylene sulfonate

Experimental data on the effect of hydrotropes, i.e potassium xylene sulfonate, ammonium xylene sulfonate, calcium xylene sulfonate on the solubility of triphenyl phosphate is displayed in Figs. 2–4.

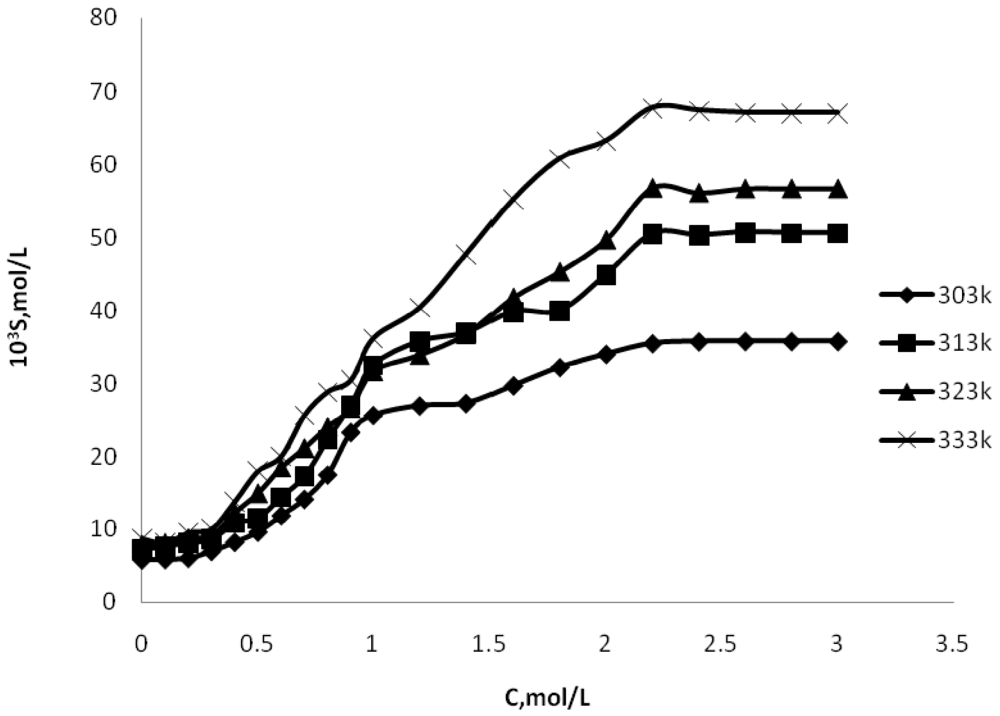

Fig-2 Effect of potassium xylene sulfonate concentration (C) on solubility of triphenyl phosphate

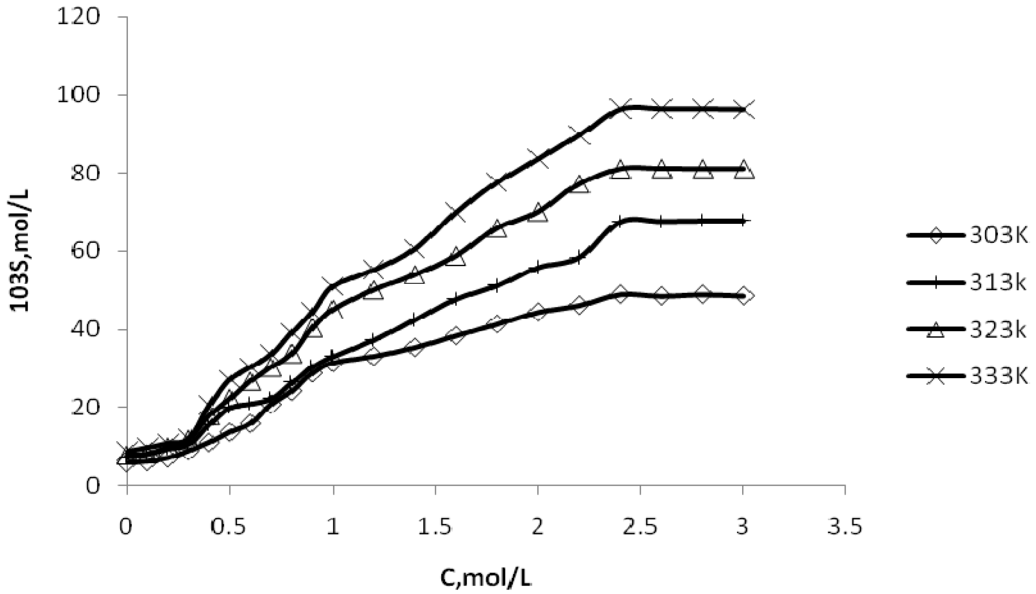

Fig-3 Effect of ammonium xylene sulfonate concentration (C) on solubility of triphenyl phosphate

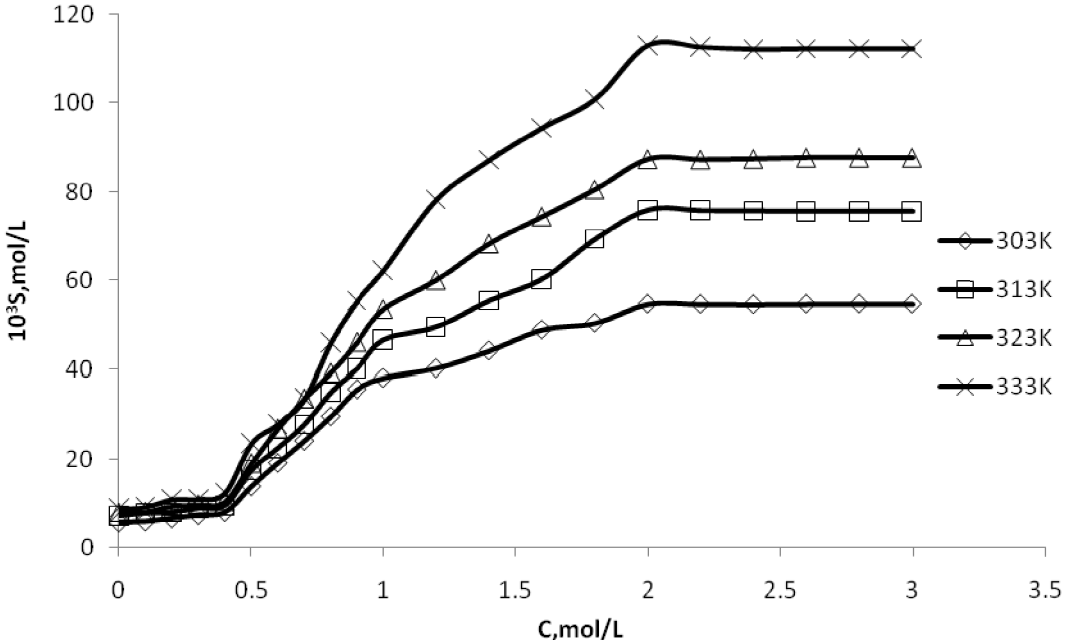

Fig-4. Effect of calcium xylene sulfonate concentration (C) on solubility of triphenyl phosphate

Calcium xylene sulfonate is one of the hydrotropes used in this research. It was observed that the solubility of triphenyl phosphate did not indicate any appreciable increase until 0.50 mol/L of calcium xylene sulfonate. However, upon a subsequent increase in the concentration of calcium xylene sulfonate, i.e., 0.50 mol/L, the solubility of triphenyl phosphate was found to increase significantly. This concentration of calcium xylene sulfonate in the aqueous phase, i.e., 0.50 mol/L, is termed as the Minimum Hydrotrope Concentration (MHC), which is the minimum required amount of calcium xylene sulfonate in the aqueous phase to commence a significant increase in the solubility of triphenyl phosphate. It was observed that the MHC of calcium xylene sulfonate in the aqueous phase does not modify even at increased system temperatures, i.e., 313, 323, and 333 K.

A related tendency in the MHC requirement has also been observed for other hydrotropes. Accordingly, it is manifest that hydrotropic separation is displayed only above MHC, irrespective of the system temperature. Hydrotropey does not seem to be functioning below the MHC, which may be a distinctive of a particular hydrotrope with respect to each solute. The solubility effect changes with concentration of the hydrotropes. In this case, a clear increasing trend in the solubility of triphenyl phosphate was observed above the MHC of calcium xylene sulfonate. This increase is affirmed only up to a certain concentration of calcium xylene sulfonate in the aqueous phase, i.e, 2 mol/L further than which there is no appreciable increase in the solubility of triphenyl phosphate. This concentration of calcium xylene sulfonate in the aqueous phase is referred to as the maximum hydrotrope concentration (Cmax). From the analysis of the experimental data, it is observed that further increase in the hydrotrope concentration beyond Cmax does not cause any considerable increase in the solubility up to 3.0 mol/L in the aqueous phase. Similar to the MHC values, the Cmax values of the hydrotropes also remained unaltered with the increase in system temperature. (Table. 1) The maximum enhancement factor of hydrotrope (fes) which is the ratio of the solubility value in the presence and absence of a hydrotrope respectively. It was determined and the highest value of(φ) 12.95 in the case of calcium xylene sulfonate at a system temperature of 333 K (Table.2).

Table -1 MHC and Cmax values of hydrotrops

Hydrotrope	MHC, mol/L	Cmax,mol/L
Potassium xylene sulfonate	0.4	2.2
Ammonium xylene sulfonate	0.4	2.4
Calcium xylene sulfonate	0.5	2

Table – 2 Maximum Enhancement factor (Φs)

	Temperature			
Hydrotrope	303K	313k	323K	333K
Potassium xylene sulfonate	6.11	6.97	7.22	7.77
Ammonium xylene sulfonate	8.41	9.29	10.32	11.05
Calcium xylene sulfonate	9.42	10.46	11.01	12.95

4. Effectiveness of hydrotrope

The effectiveness factor for each hydrotrope with respect to the solubility of triphenyl phosphate at different system temperatures was determined by applying the model suggested by Setschenow and later modified by Phatak and Gaikar as given by the equation.

$$\log (S/S_m) = K_s(C_s - C_m) \qquad \text{------------- } 1$$

Where S and Sm are the solubility values of triphenyl phosphate maximum hydrotrope concentration Cs (same as Cmax) and the minimum hydrotrope concentration Cm (same as MHC) respectively. The Setschenow constant (Ks) can be considered as a measure of the effectiveness of a hydrotrope at any given conditions of hydrotrope concentration and system temperature. The Setschenow constant values of hydrotropes, namely, potassium xylene sulfonate, ammonium xylene sulfonate, calcium xylene sulfonate for the solubility triphenyl phosphate different system temperatures are listed in Table. 3. The highest value was observed as 0.45 in the case of calcium xylene sulfonate as the hydrotrope at temperature 333K.

Table-3 Setschenow constant (*Ks*)

	Temperature			
Hydrotrope	303K	313k	323K	333K
Potassium xylene sulfonate	0.35	0.37	3.88	0.39
Ammonium xylene sulfonate	0.32	0.33	0.34	0.35
Calcium xylene sulfonate	0.39	0.42	0.44	0.45

Table - 4 Effect of hydrotrope concentration (C) on the mass-transfer coefficient (kLa) of triphenyl phosphate

Hydrotropes	C, mol/L	$10^3 K_L a, S^{-1}$
potassium xylene sulfonate	0	8.3±0.15
	0.2	9.7±0.16
	0.5*	12.8±0.22
	1	18.3±0.35
	1.4	23.2±0.47
	1.8	30.5±0.61
	2.2**	37.4±0.77
ammonium xylene sulfonate	0	8.3±0.15
	0.2	9.4±0.16
	0.4*	13.7±0.20
	0.8	25.5±0.47
	1.4	31.7±0.64
	1.8	40.2±0.80
	2.40**	46.3±0.95
calcium xylene sulfonate	0	8.3±0.15
	0.1	10.1±0.16
	0.5*	13.6±0.24
	1.4	26.7±0.45
	1.8	43.6±0.78
	2**	47.5±0.97
	2.2	63.4±0.21

*-MHC: **-C_{max}

5. Mass-Transfer Coefficient

The mass transfer coefficient of the triphenyl phosphate + water system in the absence of any hydrotrope is 8.3 x 10-3 s-1 at 303 K (Table. 4). The effect of different hydrotropes on the mass transfer coefficient of triphenyl phosphate at different hydrotrope concentrations is also given in the same table. It can be seen that a threshold value of 0.40 mol/L is required to affect significant enhancement in the mass transfer coefficient of triphenyl phosphate + water system, as observed in the case of solubility determinations. The mass transfer coefficient of triphenyl phosphate + water system increases with increase in calcium xylene sulfonate concentration. A similar trend in the mass transfer coefficient of triphenyl phosphate has been observed for other hydrotropes also, namely, potassium xylene sulfonate, ammonium xylene sulfonate.

6. CONCLUSIONS

The solubility of triphenyl phosphate which is practically insoluble in water has been increased to a maximum of 12.95 times in the presence of calcium xylene sulfonate as hydrotrope at a system temperature of 333 K with the corresponding increase in the mass transfer coefficient. This would be much useful in increasing the rate of output of the desired product made from triphenyl phosphate. The MHC and Cmax values of the hydrotrope with respect to triphenyl phosphate can be used for the recovery of the dissolved triphenyl phosphate and hydrotrope solutions at any hydrotrope concentration between MHC and Cmax by simple dilution with distilled water. This will eliminate the huge cost and energy normally involved in the separation of solubilized triphenyl phosphate from its solution. Hence calcium xylene sulfonate is found to be the best suitable hydrotrope for the enhancement of solubility and mass transfer coefficient of poorly soluble triphenyl phosphate within the framework of the present investigation.

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