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Enhancement of Aqueous Solubility of Corn Oil using Hydrotropes

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This paper presents a comprehensive study on the effect of hydrotropes on the solubility, mass transfer coefficients of corn oil in water using various hydrotropes such as sodium benzoate, sodium salicylate and sodium acetate trihydrate under a influence of wide range of concentrations 0-3.3 mol/L and system temperature of 303 K. It was found that the solubility and mass transfer coefficients increases with increase in the hydrotropic concentration. The performance of hydrotropes was measured in terms of setschenow constant, k_s. Effective mass transfer coefficient was found and reported for all the hydropes used in this study.

Key Words: Hydrotrope, Solubilization, Separation, Mass transfer coefficient.

INTRODUCTION

A hydrotrope is a compound that solubilizes hydrophobic compounds in aqueous solutions. Typically, hydrotropes consist of a hydrophilic part and a hydrophobic part (like surfactants). Hydrotropes are not surfactants. They do not absorb onto the surface or interface and do not form micelle. The increase in the solubility in the water is due to the formation of the organize assemblies of the hydrotrope molecule at critical concentrations. The phenomenon termed as hydrotropy, can be considered to be potentially and industrially attractive technique, since the absorbed increase in the solubility is generally higher than the effected by other known solubilization methods.

The hydrotropes used in this work are freely soluble in water and practically insoluble in sparingly soluble substances. All are non reactive and non toxic and do not produce any temperature effect when dissolved in water. Hydrotropes in general are water-soluble and surface-active compounds that enhances the solubility of organic solutes like acids, esters, alcohols, aldehydes, ketones, hydrocarbons and fats[1-4]. Hydrotropes have been widely used in drug solubilization[5-7], detergents formulation, health care, household applications[8,9] and also an extraction agent for fragrances. Each hydrotrope has a selective ability towards a particular component in the mixture to facilitate easy recovery of the hydrotrope solution by controlled dilution with the distilled water[10,11].

The solubility enhancement of the organic solute is due to the formation of molecular structures in the form of complexes[12-14]. The previous experimental findings concluded that hydrotropy is a process which goes beyond conventional solubilization methods, such as miscibility, co-solvency and the salting-in effect, since the solubilization affected by hydrotropy is higher and more selective compared to other solubilization methods[15,16]. The effect of hydrotropes on the solubility and the mass transfer coefficients of a series of the organic esters were studied was studied in earlier publications[17-20].

Besides the advantage of certain properties such as the solvent character being independent of pH, non-flammability, easy availability of hydrotropes, inexpensive aqueous phase makes this method superior to other solubilization methods. The hydrotropic technique can be adopted to increase the solubility as well as to separate such mixtures effectively. Easy recovery of the dissolved solute and possible reuse of the hydrotropic solution make this method the most effective one particularly at industrial levels.

EXPERIMENTAL

2 L of corn oil was obtained from retail shop, which contains 990 g of corn oil in 1 L. All the chemicals used in this experiment were bought from SD chemicals of 99 % purity.

For each run, to measure the mass transfer coefficient, an excess amount of corn oil 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 separated from the remaining solution. The concentration of the solubilized organic acid in aqueous hydrotrope solutions at time t was analyzed in the same way as for solubility determinations.

Detection method: For each solubility test, about 5 mL of corn oil was taken in a separating funnel and 100 mL of a solution of hydrotrope of known concentration was added. Separating funnel was sealed to avoid evaporation of mixtures at room temperatures. The solutions of different concentration were prepared by dilution with distilled water. The setup was kept overnight for equilibration. The aqueous layer was carefully separated from ester layer and transferred into a beaker. The oil concentration was estimated using UV carry-5E spectrophotometer.

RESULTS AND DISCUSSION

Solubility study: The solubility of the sodium salicylate in water was 3.10×10^{-3} mol/L at 303 K compared to insoluble as reported in previous work[21,22], sodium benzoate was 3.08×10^{-3} mol/L and sodium acetate trihydrate was 5.11×10^{-3} mol/L.

Experimental data representing the average of duplicate determinations on the effect of hydrotropes, *i.e.*, sodium salicylate, sodium acetate trihydrate and sodium benzoate on the solubility of corn oil are presented in Table-1 (Fig. 1). Sodium salicylate is one of the hydrotropes used in this study. The solubility of corn oil in water at 303 K in the absence of any hydrotrope is 2.02×10^{-3} mol/L. It has been observed that the solubility values increase significantly only after the addition of 0.20 mol/L of sodium salicylate in the aqueous phase. This concentration is referred to as minimum hydrotrope concentration (MHC).

TABLE-1
EFFECT OF HYDROTROPES CONCENTRATION(C) ON SOLUBILITY (S) OF OIL IN WATER

Hydrotrope concentration	Solubility S × 10^3 (mol/L)		
	Sodium salicylate	Sodium benzoate	Sodium acetate trihydrate
0.0	2.02	2.02	2.02
0.1	2.04	2.03	2.02
0.2	3.10	2.05	2.04
0.3	6.87	3.08	2.05
0.4	10.22	6.69	3.07
0.5	20.66	8.44	5.11
0.7	30.82	11.33	8.66
0.9	50.11	28.11	20.32
1.1	70.36	39.86	30.86
1.3	80.44	48.32	40.11
1.5	120.33	67.22	50.62
1.7	130.82	72.64	60.01
1.9	136.37	88.10	70.23
2.1	142.11	90.11	76.43
2.3	148.62	96.43	83.11
2.5	152.33	98.32	92.00
2.7	160.86	108	92.03
2.9	180.00	108.13	92.11
3.1	180.11	108.23	92.21
3.3	180.141	108.28	92.28

Therefore, it is evident that hydrotropic solubilization is displayed only above the minimum hydrotrope concentration, irrespective of system temperature. Hydrotropy does not seem to be operative below the minimum hydrotrope concentration, which may be a characteristic of a particular hydrotrope with respect to each solute. This minimum hydrotrope concentration value assumes greater significance in the context of recovery of hydrotrope solutions. Since hydrotropy appears to operate only at significant concentrations of hydrotrope in water, most hydrotropic solutions release the dissolved solute on dilution with distilled water below minimum hydrotrope concentration. The knowledge of minimum hydrotrope concentration values is necessary especially at industrial levels, as it ensures ready recovery of hydrotrope for reuse.

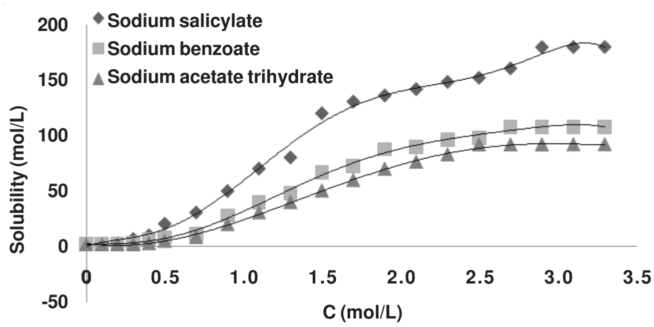

Fig. 1. Effect of hydrotropes on the solubility of corn oil

The solubilization effect varies with concentration of hydrotropes (Table-1). In the present case, a clear increasing trend in the solubility of corn oil was observed above the minimum hydrotrope concentration of sodium salicylate. This increasing trend is maintained only up to a certain concentration of sodium salicylate in the aqueous phase, beyond, which there is no appreciable increase in the solubility of corn oil. This concentration of sodium salicylate(hydrotrope) in the aqueous phase is referred to as the maximum hydrotrope concentration (C_{max}). From the analysis of the experimental data, it is observed that a further increase in hydrotrope concentration beyond C_{max} does not bring any appreciable increase in the solubility of corn oil even up to 3 mol/L of sodium salicylate in the aqueous phase.

It appears that the solute molecules after finding their way through the interface of hydrotrope aggregates are held hidden in the hydrotropic stock. However, this arrangement seems to be a purely temporary one, because the solute particles contained within the hydrotrope stack can be brought out by simple dilution with distilled water, which alters the solution properties of the hydrotrope stack. This causes the dissociation of hydrotropic molecules and the properties of hydrotrope solutions with decrease in hydrotrope concentration approach to that of water, similar to the situation below minimum hydrotrope concentration. This phenomenon was observed experimentally by release of the dissolved solute from the hydrotrope solution at any concentration between the minimum hydrotrope concentration and C_{max} by simple dilution with distilled water and hence possible reuse of the hydrotrope solution. This is the unique advantage of the hydrotropic solubilization technique.

In the concentration range of sodium salicylate between 0 and 3 mol/L, three different regions of sodium salicylate as hydrotrope were observed. It was inactive below minimum hydrotrope concentration value of 0.40 mol/L, above which an appreciable increase in the solubility of corn oil was found up to 2.40 mol/L and beyond which there is no further increase in the solubility even upto 3 mol/L. Hence sodium salicylate was found to be an effective hydrotrope in the concentration range between 0.40 and 2.40 mol/L towards corn oil. It has also been observed that the solubilization effect of sodium salicylate was not a linear function of the concentration of the sodium salicylate solution. The solubilization effect of sodium salicylate increases with increase in hydrotrope concentration.

A similar trend has been observed in the solubilization effect of other hydrotropes namely sodium salicylate, sodium acetate trihydrate and sodium benzoate. It has also been observed that the minimum hydrotrope concentration values of hydrotrope used in this work range between 0.2 and 0.5 mol/L (Table-2), which seem to depend on the hydrophilicity of a hydrotrope. The C_{max} values of hydrotropes range between 2.50 and 2.90 mol/L (Table-2) in most cases. The highest value of solubilization enhancement factors Φ_s, which is the ratio of solubility values in the presence and absence of a hydrotrope has been observed in case of sodium salicylate as 89.18 at 303 K (Table-3).

TABLE-2
MINIMUM HYDROTROPE CONCENTRATION (MHC) AND MAXIMUM HYDROTROPE CONCENTRATION (C_{max}) VALUES FOR HYDROTROPES

Hydrotrope	MHC (mol/L)	C_{max}
Sodium salicylate	0.2	2.9
Sodium benzoate	0.3	2.7
Sodium acetate trihydrate	0.5	2.5

TABLE-3
SOLUBILITY ENHANCEMENT FACTOR FOR OIL

Hydrotrope	Enhancement factor Φ_s
Sodium Salicylate	89.18
Sodium Benzoate	53.60
Sodium Acetate Trihydrate	45.68

Mass transfer coefficient: The mass transfer coefficient for the corn oil + water system in the absence of any hydrotrope was determined to be 0.89×10^{-4} S^{-1} at 303 K (Table-3). The effect of different hydrotropes on the mass transfer coefficient of corn oil at different hydrotrope concentrations is also presented in Table-3. It can be seen that a threshold value of 0.20 mol/L is required for significant enhancement in the mass transfer coefficient of the corn oil + water system, as observed in the case of the solubility determinations. The mass transfer coefficient of the corn oil + water system increases with an increase in the hydrotrope concentration. Beyond a C_{max} value of 2 mol/L, there is no appreciable increase in the mass transfer coefficient of corn oil as observed in the case of the solubility determinations. The observed increase of the mass transfer coefficient in presence of hydrotrope is probably due to the difference between the binary diffusivity (solute + solvent) and the diffusivity of the solute in the solution (solute + solvent + hydrotrope). A similar trend in the mass transfer coefficient enhancement (Φ_{mtc}) of corn oil has been observed for other hydrotropes also. The maximum enhancement factor for the mass transfer coefficient (Φ_{mtc}), ratio between the mass transfer coefficient (k_La) values (in the presence and absence of hydrotropes) values observed for the corn oil + water system in the presence of various hydrotropes at 303 K are reported in Table-4. The highest values of Φ_{mtc} (20.66) has been observed in presence of sodium salicylate as the hydrotrope at C_{max} value of 2.9 mol/L.

TABLE-4
EFFECT OF HYDROTROPE CONCENTRATION ON THE MASS TRANSFER COEFFICIENT OF OIL

Hydrotrope	Hydrotrope concentration (mol/L)	Mass transfer coefficient $k_La \times 10^4$ (S^{-1})	Enhancement factor for mass transfer coefficient Φ_{mtc}
Sodium salicylate	0.0	0.89	-
	0.2	1.72	1.93
	1.1	10.97	12.33
	1.9	14.12	15.86
	2.9	15.41	17.32
	3.3	18.39	20.66
Sodium benzoate	0.0	0.89	-
	0.3	1.27	1.46
	1.7	11.86	13.33
	2.1	13.10	14.72
	2.5	14.53	16.33
	3.3	16.12	18.11
Sodium acetate trihydrate	0.0	0.89	-
	0.3	1.12	1.26
	0.5	4.16	4.67
	1.5	11.23	12.62
	2.1	11.85	13.32
	2.5	14.26	16.02
	3.3	14.92	16.76

Effectiveness of hydrotropes: The effectiveness factor of each hydrotrope with respect to corn oil at 303 K was determined by analyzing the experimental solubility data for each case, applying the model suggested by Setschenow and later modified by Gaikar and Sharma[23] as given by the equation below:

$$\log(S/S_m) = Ks(C_s - C_m)$$

where, S and S_m are the solubility values of salicylic acid at any hydrotrope concentration (C_s) and the minimum hydrotrope concentration (C_m) (the same as minimum hydrotrope concentration), respectively. The Setschenow constant (K_s) can be considered to be a measure of the effectiveness of a hydrotrope in any given conditions of hydrotrope concentration and system temperature. The Setschenow constant values of the hydrotropes, sodium salicylate, sodium acetate trihydrate and sodium benzoate for the corn oil + water system at different system temperatures are listed in Table-5. The highest value observed was 0.696, in the case of sodium acetate as the hydrotrope at 303 K.

TABLE-5
SETSCHENOW CONSTANT (K_S) OF HYDROTROPES WITH RESPECT TO HYDROTROPES AT 303 K

Hydrotrope	K_s
Sodium salicylate	0.653
Sodium benzoate	0.644
Sodium acetate trihydrate	0.628

Conclusion

From the literature, the solubility data for corn oil show that the fatty acid is practically insoluble in water, which has been increased to a maximum value of 17.32 in the presence of sodium salicylate as the hydrotrope with a corresponding increase in the mass transfer coefficient. This would be useful in increasing the rate of output of the desired product made from corn oil. The minimum hydrotrope concentration and C_{max} values of the hydrotrope with respect to corn oil can be used for the recovery of the dissolved corn oil and hydrotrope solutions at any hydrotrope concentration between minimum hydrotrope concentration and C_{max} by simple dilution with distilled water. This will eliminate the huge cost and energy normally involved in the separation of the solubilized corn oil from its solution. The unprecedented increase in the solubilizing effect of hydrotropes is attributed to the formation of organized aggregates of hydrotrope molecules at a particular concentration.

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