Articles

Effect of Hydrotropes on Solubility and Mass-Transfer Coefficient of Butyl Acetate

N. Nagendra Gandhi, M. Dharmendira Kumar, and N. Sathyamurthy*

Department of Chemical Engineering, Alagappa College of Technology, Anna University, Chennai-600 025, India

This paper presents a comprehensive study on the effect of citric acid, sodium benzoate, sodium salicylate, and urea (hydrotropes) on the solubility and mass-transfer coefficient for the extraction of butyl acetate in water. The influence of a wide range of hydrotrope concentrations (0–3.0 mol/L) and different temperatures (303 K to 333 K) on the solubility of butyl acetate has been studied. The influence of different hydrotrope concentrations on the mass-transfer coefficient for the butyl acetate +water system has been ascertained. The Setschenow constant, K_s, a measure of the effectiveness of hydrotrope, has been determined for each case. The solubility of butyl acetate increases with increase in hydrotrope concentration and also with temperature. Consequent to the increase in the solubility of butyl acetate, the mass-transfer coefficient was also found to increase with increase in hydrotrope concentration. A minimum hydrotrope concentration was found essential to show a significant increase in the solubility and mass-transfer coefficient for the butyl acetate + water system. The enhancement factor, which is the ratio of the value in the presence and absence of a hydrotrope, is reported for both solubility and mass-transfer coefficient.

Introduction

Hydrotropes are a class of chemical compounds that effect a severalfold increased aqueous solubility to certain solutes that are sparingly soluble in water under normal conditions (Neuberg, 1916; Saleh and El-Khordagui, 1985). This increase in solubility in water is probably due to the formation of organized assemblies of hydrotrope molecules at critical concentrations (Badwan et al., 1983; Balasubramanian et al., 1989). This phenomenon termed as hydrotropy can be considered to be a potentially and industrially attractive technique since the observed increase in solubility is generally higher than that effected by other known solubilization methods. Hydrotropes have been used to solubilize various sparingly soluble organic compounds and drugs and recently in heterogeneous reactions (Booth and Everson, 1948, 1949, 1950; Korenman, 1974; Janakiraman and Sharma, 1985; Pandit and Sharma, 1987). Hydrotropes have been effectively used in the development of extractive separations and in distillation as extractive solvents for the separation of close boiling point mixtures (Gaikar and Sharma, 1986; Mamta Agarwal and Gaikar, 1992; Mahapatra et al., 1988). Easy recovery of the dissolved solute and the possible reuse of hydrotrope solutions make this method the most effective one particularly at industrial levels (McKee, 1946).

Besides, the advantage of certain properties, such as the solvent character being independent of pH, high selectivity, and absence of emulsification, makes this technique superior to other solubilization methods. Because of the solubilizing effect of these hydrotropes, the mass-transfer coefficient of two-phase systems can considerably be enhanced.

It has been observed that in many two-phase reaction systems involving a sparingly soluble organic compound like butyl acetate, the mass-transfer coefficient was found to be very low solely due to the poor solubility of butyl acetate in the aqueous phase. Since butyl acetate serves as a raw material/intermediate for a wide variety of chemicals and allied products and the separation of butyl acetate from any liquid mixture seems to be difficult, this hydrotropic technique can be adopted to increase the solubility as well as to separate such mixtures effectively. Data on various aspects of hydrotropic study on the solubility and mass-transfer coefficient for the butyl acetate +water system have been provided for the first time.

Experimental Section

The purity of butyl acetate was found to be 99.99%. Hydrotropes used in these exprimentations, i.e., citric acid, sodium benzoate, sodium salicylate, and urea, were of Analar grade. Double distilled water was used for the preparation of hydrotropic solutions. The hydrotropes used in this work are freely soluble in water and practically insoluble in butyl acetate. All are nonreactive and nontoxic. The easy availability and cheapness of hydrotropes are the other factors considered in the selection of hydrotropes.

The experimental setup for the determination of solubility values consists of a thermostatic bath and a separating funnel, which was thermostated in all experiments. For each measurement test, about 100 mL of butyl acetate, previously saturated with distilled water, was taken in a separating funnel and 100 mL of a solution of the hydrotrope of known concentration was added. The solutions of different concentrations of the hydrotrope were prepared by dilution with distilled water. The separating funnel was

* Author to whom correspondence should be addressed.

Table 1. Effect of Citric Acid Concentration [C] on the Solubility [S] of Butyl Acetate in Water and the Maximum Enhancement Factor for Solubility (ϕ_s)

C, mol/L	$10^2 S$, mol/L			
	T = 303 K	T = 313 K	T = 323 K	T = 333 K
0.00	5.74	5.85	6.12	6.19
0.10	5.79	5.88	6.09	6.26
0.20 MHC	5.85	5.90	6.18	6.31
0.30	7.86	7.84	8.01	9.82
0.40	8.02	9.04	9.75	13.12
0.50	8.98	10.44	13.16	16.84
0.60	10.47	14.06	19.98	22.05
0.70	12.11	17.12	22.24	24.13
0.80	13.76	18.07	28.13	32.08
0.90	15.30	24.03	30.04	41.94
1.00	16.87	26.31	55.37	56.69
1.20	25.95	47.89	62.63	77.63
1.40	28.06	52.63	84.11	102.49
1.60	32.89	66.14	107.89	136.17
1.80	42.01	82.31	149.42	151.88
2.00 c_{max}	56.02	105.48	171.12	193.19
2.25	56.65	106.19	171.10	193.55
2.50	56.79	107.05	171.55	193.68
2.75	56.69	107.05	171.59	194.75
3.00	56.67	106.98	171.63	194.83
ϕ_s	9.88	18.29	28.07	31.47

Table 2. Effect of Sodium Benzoate Concentration [C] on the Solubility [S] of Butyl Acetate in Water and the Maximum Enhancement Factor for Solubility (ϕ_s)

C, mol/L	$10^2 S$, mol/L			
	T = 303 K	T = 313 K	T = 323 K	T = 333 K
0.00	5.74	5.85	6.06	6.19
0.10	5.74	5.81	5.93	6.24
0.20	5.79	5.81	5.99	6.29
0.30	5.71	5.89	6.03	6.35
0.40	5.77	5.94	6.09	6.47
0.50	5.80	6.03	6.05	6.50
0.60 MHC	5.85	6.01	6.17	6.54
0.70	6.98	7.03	7.88	8.14
0.80	7.87	9.87	12.05	10.36
0.90	8.74	7.73	18.16	13.85
1.00	12.06	12.65	21.91	19.97
1.20	12.19	16.73	34.36	21.53
1.40	12.15	17.48	45.54	41.09
1.60	22.62	19.10	59.22	46.49
1.80	22.81	24.92	78.04	58.20
2.00	26.59	41.84	95.08	72.39
2.25 c_{max}	33.64	53.70	132.23	106.22
2.50	33.39	53.78	133.09	106.75
2.75	33.58	53.86	133.15	106.75
3.00	33.67	54.37	133.67	106.63
ϕ_s	5.87	9.29	22.06	17.23

Table 3. Effect of Sodium Salicylate Concentration [C] on the Solubility [S] of Butyl Acetate in Water and the Maximum Enhancement Factor for Solubility (ϕ_s)

C, mol/L	$10^2 S$, mol/L			
	T = 303 K	T = 313 K	T = 323 K	T = 333 K
0.00	5.74	5.85	6.06	6.19
0.10	5.65	5.63	5.91	6.19
0.20	5.62	5.69	5.91	6.25
0.30	5.69	5.74	5.96	6.20
0.40	5.78	5.76	6.05	6.22
0.50	5.82	5.79	6.09	6.28
0.60	5.82	5.85	6.15	6.35
0.70	5.84	5.88	6.18	6.42
0.80 MHC	5.80	5.90	6.22	6.46
0.90	6.97	7.03	8.96	9.08
1.00	7.39	8.72	10.53	10.57
1.20	7.88	9.57	16.59	18.69
1.40	8.69	14.11	19.49	23.47
1.60	9.52	16.23	22.87	30.29
1.80	10.08	18.81	27.24	39.53
2.00	11.55	22.07	36.74	49.50
2.25 c_{max}	13.67	28.11	49.69	67.53
2.50	13.79	28.29	49.79	67.79
2.75	13.75	28.34	49.88	67.68
3.00	13.88	28.41	49.83	67.84
ϕ_s	2.42	4.80	8.23	10.96

immersed in a constant-temperature bath fitted with a temperature controller, which could control the temperature within ±1 °C. The setup was kept overnight for equilibration. After the equilibrium was attained, the aqueous layer was carefully separated from the ester layer and transferred into a beaker. The concentration of the solubilized organic ester in aqueous hydrotrope solution was analyzed by back-titration of unconsumed NaOH using standardized HCl solution and phenolphthalein as indicator.

The experimental setup for the determination of mass-transfer coefficient consists of a vessel provided with baffles and a turbine impeller run by a motor to agitate the mixture. The speed of the impeller in rpm was selected in such a way to get effective mixing, which was maintained in the same value for all experiments.

For each run, to measure the mass-transfer coefficient, 250 mL of the ester previously saturated with distilled water was added to the aqueous solution of the hydrotrope of known concentration. The sample was then agitated for a known time of 600, 1200, 1800, and 2400 s. After the end of fixed time "t", the entire mixture was transferred to a separating funnel. After being allowed to stand for some time, the aqueous layer was carefully separated from the ester layer (C_b). The concentration of the solubilized organic ester in aqueous hydrotrope solutions at time t was analyzed as done for solubility determinations. A plot of $-\log_{10}[1 - C_b/C^*]$ vs t was made where C^* is the equilibrium solubility of butyl acetate at the same hydrotrope concentrations (taken from the solubility determinations part). The slope of the graph gives $k_L a/2.303$, from which $k_L a$, the mass-transfer coefficient, was calculated. Duplicate runs were made to check the reproducibility. The observed error was less than 2%.

Results and Discussion

(a) Solubility. Experimental data on the effect of hydrotropes, i.e., citric acid, sodium benzoate, sodium salicylate, and urea, on the solubility of butyl acetate are presented in Tables 1−4 and are plotted in Figures 1−4. Citric acid is one of the hydrotropes used in this study. The solubility of butyl acetate in water at 303 K in the absence of any hydrotrope is 5.74×10^{-2} mol/L (Table 1). It was observed that the solubility of butyl acetate in water has not shown any appreciable increase even after the addition of 0.20 mol/L of citric acid in the aqueous phase. But on subsequent increase in the concentration of citric acid above 0.20 mol/L, the solubility of butyl acetate in water was found to increase significantly. This concentration of citric acid in the aqueous phase, i.e., 0.20 mol/L, is termed as the Minimum Hydrotrope Concentration (MHC), which is the minimum required citric acid (hydrotrope) concentration in the aqueous phase above which the solubility of butyl acetate in water increases significantly. It has been observed that the MHC of citric acid in the aqueous phase is unaltered even at increased system temperatures. A similar trend in MHC requirement in the aqueous phase has been observed for other hydrotropes also.

Therefore it is evident that hydrotropic solubilization is displayed only above MHC, irrespective of temperature. Hydrotropy does not seem to be operative below MHC, which may be a characteristic of a particular hydrotrope
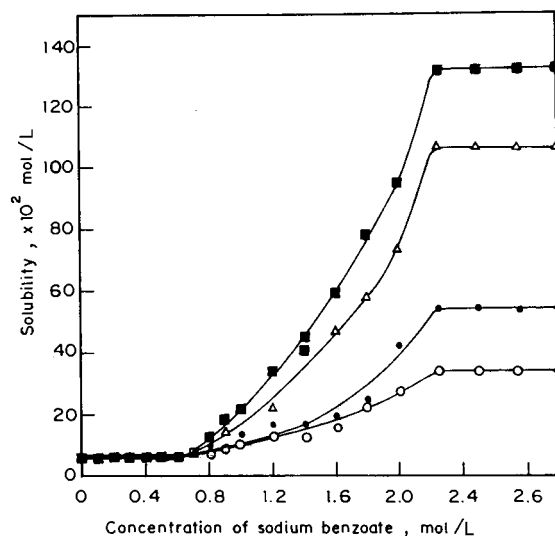
Table 4. Effect of Urea Concentration [C] on the Solubility [S] of Butyl Acetate in Water and the Maximum Enhancement Factor for Solubility (ϕ_s)

C, mol/L	$10^2 S$, mol/L			
	$T = 303$ K	$T = 313$ K	$T = 323$ K	$T = 333$ K
0.00	5.74	5.85	6.12	6.19
0.10	5.72	5.81	6.15	6.31
0.20	5.75	5.84	6.20	6.35
0.30 MHC	5.79	5.90	6.28	6.54
0.40	6.28	8.16	9.95	10.16
0.50	8.19	10.89	18.13	14.73
0.60	10.12	14.26	20.08	20.27
0.70	12.08	18.07	30.32	32.20
0.80	15.43	21.88	37.44	39.87
0.90	18.14	30.12	46.22	42.18
1.00	21.77	31.78	49.84	61.94
1.20	35.94	37.43	61.94	86.37
1.40	46.68	72.17	108.59	110.66
1.60	53.24	83.86	134.49	140.68
1.80	68.19	98.10	158.35	205.51
2.00 c_{max}	86.67	134.02	213.89	241.10
2.25	87.05	134.10	214.18	241.82
2.50	86.02	134.15	214.25	241.98
2.75	86.89	134.18	214.29	241.95
3.00	86.95	134.20	214.29	242.10
f_s	15.15	22.95	35.01	39.11
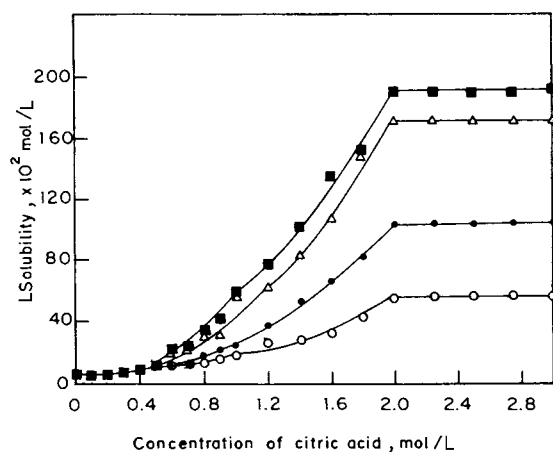
Figure 1. Effect of citric acid concentration on the solubility of butyl acetate in water (■, 333 K; ▲, 323 K; ●, 313 K; ○, 303 K).

Figure 2. Effect of sodium benzoate concentration on the solubility of butyl acetate in water (●, 333 K; ▲, 323 K; ●, 313 K; ○, 303 K).

Figure 3. Effect of sodium salicylate concentration on the solubility of butyl acetate in water (■, 333 K; ▲, 323 K; ●, 313 K; ○, 303 K).

with respect to each solute. This MHC 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 butyl acetate on dilution with water below MHC. The knowledge of MHC values is necessary especially at industrial levels as it ensures ready recovery of the hydrotrope for reuse.

The solubilization effect varies with concentration of hydrotropes (Table 1). In the present case, a clear increasing trend in the solubility of butyl acetate was observed above MHC of citric acid. This increasing trend is maintained only up to a certain concentration of citric acid in the aqueous phase, beyond which there is no appreciable increase in the solubility of butyl acetate. This concentration of citric acid (hydrotrope) in the aqueous phase is referred to as the maximum hydrotrope concentration (c_{max}). The c_{max} values of citric acid, sodium benzoate, sodium salicylate, and urea with respect to butyl acetate are 2.00, 2.25, 2.25, and 2.00 mol/L, respectively. From the analysis of the experimental data, it is observed that further increase in hydrotrope concentration beyond c_{max} does not bring any appreciable increase in the solubility of butyl acetate even up to 3.00 mol/L of citric acid in the
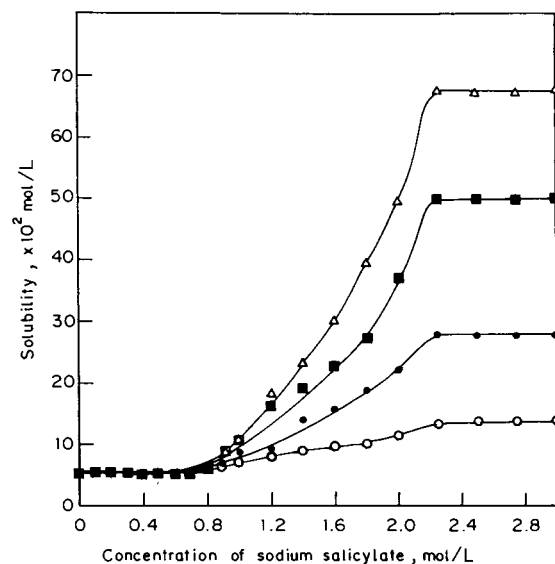
aqueous phase. Similar to the MHC values, the c_{max} values of hydrotropes also remained unaltered with increase in system temperature.

The knowledge of MHC and c_{max} values of each hydrotrope with respect to a particular solute assumes greater significance in this study, since it indicates the beginning and saturation of the solubilization effect of hydrotropes. However, the effect of hydrotrope was found to be predominant at concentrations close to the c_{max} value of a hydrotrope in most cases. The values of MHC and c_{max} of a hydrotrope with respect to butyl acetate may be useful in determining the recovery of the dissolved butyl acetate even to an extent of calculated amount from hydrotrope solutions at any concentration between MHC and c_{max} by simple dilution with distilled water. This is the unique advantage of the hydrotropic solubilization technique.

From the experimental data plotted in Figure 1, it can further be observed that in order to achieve the particular solubility of butyl acetate to a value of, say, 50×10^{-2} mol/L, it is required to maintain the citric acid concentration
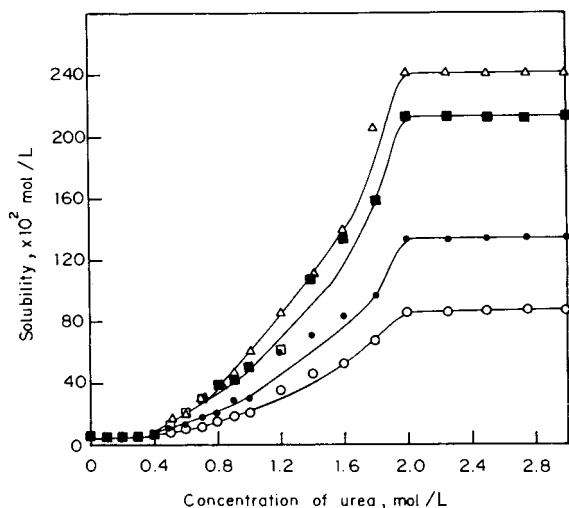
Figure 4. Effect of urea concentration on the solubility of butyl acetate in water (■, 333 K; ▲, 323 K; ●, 313 K; ○, 303 K).

Table 5. Effect of Hydrotrope Concentration [*C*] on the Mass-Transfer Coefficient of Butyl Acetate

hydrotrope	C, mol/L	mass-transfer coefficient, $10^5 k_L{}^a$ s^{-1}	enhancement factor for mass-transfer coefficient, ϕ_{mtc}
citric acid	0.00	1.06	
	0.30	1.16	1.09
	0.40	1.52	1.43
	1.00	2.98	2.81
	1.40	5.54	5.23
	2.00	9.51	8.97
	3.00	9.65	9.10
sodium benzoate	0.00	1.06	
	0.60	1.16	1.09
	1.00	1.73	1.63
	1.40	3.06	2.89
	2.00	7.47	7.05
	3.00	7.47	7.05
sodium salicylate	0.00	1.06	
	0.80	1.18	1.11
	0.90	1.69	1.59
	1.60	2.42	2.28
	2.25	3.36	3.17
	3.00	3.39	3.20
urea	0.00	1.06	
	0.30	1.06	1.00
	0.40	1.47	1.39
	1.00	5.11	4.82
	1.60	10.97	10.18
	2.00	18.09	17.07
	3.00	18.21	17.18

of 1.94 mol/L at 303 K, 1.38 mol/L at 313 K, 1.09 mol/L at 323 K, and 0.92 mol/L at 333 K in the aqueous phase. As the temperature increases, the concentration of citric acid required in the aqueous phase to achieve a particular solubility of butyl acetate is decreased. A similar trend has been observed for other systems also.

In the concentration range of citric acid between 0.00 and 3.00 mol/L, four different regions were observed. It was inactive below MHC of 0.20 mol/L, above which an appreciable increase in the solubility of butyl acetate was found up to c_{max} of 2.00 mol/L, beyond which there is no further solubilization effect of hydrotrope. Therefore citric acid was found to be an effective hydrotrope in the concentration range between 0.20 and 2.00 mol/L toward butyl acetate. It has also been observed that the solubilization effect of citric acid was not a linear function of the concentration of the citric acid solution. A similar trend in the solubilizing effect of citric acid was observed at

increased system temperatures, viz., 313, 323, 333 K with the values of MHC, and c_{max} remained unaltered even at higher temperatures. The solubilization effect of citric acid increases with increase in hydrotrope concentration and also with system temperature. The maximum enhancement factor values observed for the butyl acetate + water system at 303, 313, 323, and 333 K are 9.88, 18.29, 28.04, and 31.47, respectively.

A similar trend has been observed in the solubilization effect of other hydrotropes, namely, sodium benzoate, sodium salicylate, and urea. It has also been observed that the MHC values of hydrotrope used in the work range between 0.20 and 0.80 mol/L, which seem to depend on the hydrophilicity of a hydrotrope. The c_{max} values of hydrotropes range between 2.00 and 2.25 mol/L in most cases. The maximum solubilization enhancement factors (ϕ_s) effected by various hydrotopes for butyl acetate range between 2.42 and 39.11. The values of ϕ_s of butyl acetate increases with increase in system temperature in most cases. The highest ϕ_s value of 39.11 is reported in the case of urea at 333 K. The analysis of the ϕ_s values for this system shows that urea serves as the effective hydrotrope at all temperatures to bring about maximum solubilization of butyl acetate. For example, ϕ_s effected by urea at 323 K, i.e., 35.01, is more than that effected by citric acid at 333 K, i.e., 31.47.

(b) Mass-Transfer Coefficient. This section is concerned with a study on the effect of hydrotropes on the mass-transfer coefficient of butyl acetate in water in the presence of hydrotropes. For this purpose, an agitated vessel was used.

The mass-transfer coefficient of the butyl acetate + water system in the absence of any hydrotrope has been determined as 1.06×10^{-5} s^{-1} (Table 5). The effect of different hydrotropes on the mass-transfer coefficient of butyl acetate at different hydrotope concentrations is also given in the same table. It can be seen that a threshold value, i.e., 0.20 mol/L, which is nothing but MHC of citric acid for butyl acetate, is to be maintained to have significant enhancement in the mass-transfer coefficient of butyl acetate + water system as observed in the case of solubility determinations. The mass-transfer coefficient of the butyl acetate + water system increases with increase in citric acid concentration. Beyond c_{max} of 2.00 mol/L, there is no appreciable increase in the mass-transfer coefficient of butyl acetate, as observed in the case of solubility determinations. The maximum enhancement in the mass-transfer coefficient of the butyl acetate + water system in the presence of citric acid was found to be 9.10. These observations suggest the fact that increase in mass-transfer coefficient is found to occur upon increased solubilization. A similar trend in mass-transfer coefficient enhancement (ϕ_{mtc}) of butyl acetate has been observed for other hydrotropes, namely, sodium benzoate, sodium salicylate, and urea. The highest value of ϕ_{mtc} (17.18) has been observed in the presence of urea as the hydrotrope at the c_{max} of 2.00 mol/L.

Effectiveness of Hydrotropes

The effectiveness factor of each hydrotrope with respect to butyl acetate at different system temperatures has been determined by analyzing the experimental solubility data for each case, applying the model suggested by Pathak and Gaikar (1993) as given by the equation

$$\log[s/s_m] = K_s[c_s - c_m] \tag{1}$$

Table 6. Setschenow Constant [K_s] Values of Hydrotropes with Respect to Butyl Acetate

	K_s			
T, K	citric acid	sodium benzoate	sodium salicylate	urea
303	0.545	0.460	0.257	0.691
313	0.696	0.576	0.468	0.798
323	0.801	0.807	0.622	0.901
333	0.826	0.734	0.703	0.922

where s and s_m are the solubilities of butyl acetate at any hydrotrope concentration c_s and minimum hydrotrope concentration c_m, respectively. The Setschenow constant K_s 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, citric acid, sodium benzoate, sodium salicylate, and urea for the butyl acetate + water system at different system temperatures are listed in Table 6. The highest value has been observed as 0.922 in the case of urea as hydrotrope.

Conclusions

The solubility of butyl acetate, which is practically insoluble in water, has been increased to a maximum value of 39.11 in the presence of citric acid as hydrotrope with corresponding increase in mass-transfer coefficient. This would be very useful in increasing the rate of output of the desired product made from butyl acetate. The separation of butyl acetate from any liquid mixture which is found to be difficult can be carried out effectively using this technique. The MHC and c_{max} values of hydrotropes with respect to butyl acetate can be used for the recovery of the dissolved butyl acetate and hydrotrope solutions at any hydrotrope concentration between MHC 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 butyl acetate from its solution.

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