

Sodium Dodecyl Sulphate (NaLS) Inhibition of the Nucleophilic Substitution Reaction Between Phenacyl Bromide and Aliphatic Carboxylates**

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The effect of varying concentration of sodium dodecyl sulphate (NaLS) as an anionic surfactant micelle has been studied on the reaction of phenacyl bromide and aliphatic carboxylates in 72 : 28 acetone-water mixture. The second order rate constant (k_s) decreases with increasing concentration of NaLS. The surfactant concentration has been maintained above the critical micelle concentration (cmc) value in the aqueous organic medium. The rate constants in two different solvent compositions have been compared. The activation parameters have been computed in the cases of two different carboxylates and discussed.

A good number of reactions have been studied during the past decade, which are specifically concerned with the characteristics of reactions occurring at the micellar surface. The results of these investigations have been computed by many authors¹⁻⁴. A survey of literature revealed that very little work on the effect of surfactants on nucleophilic substitution reactions has been done. We thought that aliphatic monocarboxylates as nucleophile⁵ would be interesting for the present work since they contain hydrophobic alkyl chain of variable carbon atoms. The effects of cationic and non-ionic surfactants on this reaction have been investigated⁶. The present study has been confined to the effect of anionic surfactant (NaLS) on the titled substitution reaction.

Experimental

Materials: Sodium lauryl sulphate (BDH, England) was purified by the method of Duynstee and Grunwald⁷. Phenacyl bromide was prepared and purified by the method of Rather and Ried⁸. The sodium salts of carboxylic acids were prepared from sodium ethoxide and the respective acid. They were washed with ethanol and dried *in vacuo* to a constant weight. Acetone was of AR grade and was used without further purification. Triply distilled water was used to prepare aqueous acetone of the required composition.

Method of rate measurement: Kinetic experiments were carried out in a thermostat at a desired temperature by mixing phenacyl bromide (0.02M, 20 ml) and sodium salt of aliphatic carboxylic acids (0.04M, 20 ml) in aqueous acetone in presence of 10 ml of aqueous NaLS of appropriate concentration. The estimations were done by chilling 5 ml aliquots of the reaction mixture in 10 ml of 6N HNO₃ and 5 ml of 0.02M AgNO₃ solution and titrating the bromide ion by Volhard's method⁹. The

second order rate α -efficients were calculated graphically from the plot of $\log \frac{b-x}{a-x}$ against time and also by least square method using the expression for $k_s = \frac{2.303}{t(b-a)} \frac{a(b-x)}{b(a-x)}$.

Results and Discussion

The effect of varying concentration of NaLS above its critical micelle concentration on the second order rate constant (k_s) for reaction between various aliphatic carboxylates and phenacyl bromide in two different acetone-water (v/v) mixtures have been studied at 35° (Tables 1 and 2). In general the rate of reaction decreases in presence of NaLS but the decrease does not follow a regular trend. This system has been studied upto a NaLS concentration of 0.06M in 72% acetone-water mixture (Table 1). On changing the solvent composition to 60% acetone-water (v/v) (Table 2) the minima were obtained at a higher detergent concentration (compare Table 1) i.e., at 0.04M and then increased a little upto 0.06M. In both the solvent composition, the values of second order rate constants were less than that in absence of micelle in a particular system.

In general the rate retardation has always been marked when nucleophilic substitution reaction has been carried out with an anionic nucleophile in presence of NaLS¹⁰. Recently Romsted¹¹ has put forward a theory which can very satisfactorily explain the observed inhibition of second order reactions in the micellar phase. The extent of inhibition increases with increasing concentrations of unreactive counter ions for the Stern layer. Since there is a possibility of competition between reactive and unreactive ions for sites in the Stern layer the rate of reaction decreases. However, the slight increase after the minimum is attained could not be explained by the Romsted theory.

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TABLE 1—RATE CONSTANTS AT DIFFERENT CONCENTRATIONS OF NaLS FOR THE REACTION OF PHENACYL BROMIDE(a) AND ALIPHATIC CARBOXYLATES(b) IN 72% ACETONE-WATER (v/v) AT 35°
(a=0.008M; b=0.016M)

Carboxylates	10 ³ [NaLS] in <i>M</i>	10 ³ <i>k_s</i> in litre mol ⁻¹ sec ⁻¹ at									$\frac{k_w}{k_m}$
		0.0	5	10	15	20	30	40	50	60	
Acetate		1.27	1.03	0.87	—	0.48	1.11	1.15	1.04	0.84	2.64
Propionate		3.97	3.40	2.83	2.31	2.10	2.29	2.35	2.24	1.82	1.89
Butyrate		4.57	3.82	3.45	3.20	3.04	3.46	3.80	2.96	2.55	1.50
Valerate		4.99	4.43	3.92	3.62	3.36	3.77	4.04	3.34	2.94	1.48
Caproate		5.40	5.02	4.66	4.16	3.57	3.88	4.25	3.47	3.29	1.50
Heptanoate		5.78	5.53	5.17	4.88	3.86	4.21	4.47	3.57	3.31	1.49
Caprylate		6.36	6.16	5.65	—	4.07	4.39	4.59	3.66	3.54	1.56

TABLE 2—RATE CONSTANTS AT DIFFERENT CONCENTRATIONS OF NaLS FOR THE REACTION OF PHENACYL BROMIDE(a) AND ALIPHATIC CARBOXYLATES(b) IN 60% ACETONE-WATER (v/v) AT 35°
(a=0.008M; b=0.016M)

Carboxylates	10 ³ k _s in litre mol ⁻¹ sec ⁻¹ at							
	10 ³ [NaLS] in M	0.0	10	20	30	40	50	60
Butyrate		2.99	2.76	—	2.14	2.06	2.20	2.33
Valerate		3.19	—	2.84	2.60	2.19	2.45	2.63
Heptanoate		3.55	3.14	2.91	2.84	2.28	2.73	2.58

The micelle affects the reaction rate by incorporating the substrate rather than by affecting the solvent properties. The cmc of the surfactant decreases by addition of organic solvents to water and the micelles will be smaller in aqueous organic solvent¹². When the water content in aqueous-acetone increases from 28 to 40% the rate constant decreases very slowly, the minima is shifted to a higher surfactant concentration and the same trend has been marked so far the rate profile is concerned. As rate could not be followed beyond 0.06M NaLS in reaction mixture (due to solubility problem) the further trend in rate profile in case of reaction in 60% acetone-water (v/v) (Table 2) could not be known. Rout *et al* observed that, in the absence of NaLS, with this type of solvent composition the rate decreases as water content increases. It is also found true here because with increasing ionising power of the solvent the difference in solvation of reactant and transition state would increase. This will result in an increase in activation energy and will reduce the rate¹³.

The order of reactivity of sodium salts for various aliphatic carboxylic acids is caprylate > heptanoate > caproate > valerate > butyrate > propionate > acetate. The same order of reactivity has been observed in the case of this reaction using cationic surfactant, CTAB⁶. Combination of Swain-Scott¹⁴ and Edwards¹⁵ equation clearly indicates the dependence of nucleophilicity on pK_a values. The pK_a values of the series under study increases, as a result the nucleophilicity would also increase. Hence the k_s values increase on increasing the chain length of the carboxylates. It has been further observed that as chain length increases the ratio of $\frac{k_w}{k_m}$ remains almost constant from C₄ to higher carboxylates (where k_w is the rate constant in absence of micelle and k_m the rate constant at micellar concentration of 0.02M) (Table 1). This indicates that the inhibition due to NaLS micelles is independent of the chain length of the carboxylate under this condition.

To examine the dependence of the reaction on electronic and other factors, the values of k_s of the carboxylates have been fitted to various parameters and the significant regression equation is given by equation(1).

$$k_s = b_1 pK_a + b_2 \log p + I \quad \dots (1)$$

This regression equation has been tested at each detergent concentration and the values of b_1 , b_2 are given in Table 3 along with other statistical data.

TABLE 3—SUMMARY OF STATISTICAL DATA FOR REGRESSION ANALYSIS WITH EQUATION (1)

Conc. of NaLS in M	b ₁	b ₂	R	S _{est}	F	I	S _{b₁}	t ₁	S _{b₂}	t ₂
0.005	3.58	0.859	0.9926	0.1594	103.73	—	13.983	4.399	0.8137	3.922
0.01	1.788	0.9856	0.9967	0.1116	228.44	—	6.013	3.082	0.5802	6.4219
0.015	3.432	0.944	0.9905	0.1881	52.115	—	14.28	6.761	0.5076	2.3914
0.02	12.359	0.08769	0.9874	0.1438	58.74	—	56.79	3.969	3.113	0.1976
0.03	16.272	—0.0804	0.9764	0.20889	30.7648	—	75.175	5.766	2.822	0.287
0.04	22.057	—0.326	0.9716	0.2498	25.352	—	102.647	6.8969	3.199	0.3434
0.05	13.743	—0.1658	0.996	0.0614	185.42	—	63.22	1.695	8.105	0.0844
0.06	12.886	—0.00427	0.996	0.07024	203.306	—	59.382	1.939	6.62	0.0965

where R= Multiple correlation coefficient; F=Value of F-test;
S_{est}, S_{b₁}, S_{b₂}=errors of estimate, b₁ and b₂ respectively,
t₁=Value of t-test for pK_a and t₂=Value of t-test for log P.

The values of b_1 and b_2 reflect the sensitivity of the rate constants to changes in pK_a^{16} (electronic factor) and $\log P^{17}$ (hydrophobic parameter) respectively. It can be noted from Table 3 that the values of b_1 increase and those of b_2 fall rapidly beyond 0.015M NaLS. Since the concentration of NaLS is very high compared to cmc in this aqueous organic medium, this point may indicate a change in structure of micelle. It is perhaps due to this change, that the electronic factor becomes more predominant compared to the hydrophobic factor.

Effect of salts on the reaction rate under investigation could not be studied due to solubility problem.

The reaction with sodium heptanoate and caprylate has been studied in 72% acetone-water at different temperatures in presence of varying concentration of NaLS and the activation parameters have been calculated (Table 4). Bunton *et al*^{10b}

in micellar phase indicates a highly polar transition state¹⁸. As change of micellar behaviour depends on large number of parameters, it is difficult to draw a clear cut conclusion from thermodynamic parameters.

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References

1. J. H. FENDLER and E. J. FENDLER, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, 1975.
2. O. A. BUNTON, *Solid State Chem.*, 1973, 8, 239.
3. E. H. CORDES and C. GITLER, *Prog. Bioorg. Chem.*, 1973, 2, 1.
4. E. H. CORDES, Ed., "Reaction Kinetics and Micelles", Plenum, New York, 1973.
5. T. R. MOHANTY, (Mrs.) P. MISHRA and P. L. NAYAK, *J. Indian Chem. Soc.*, 1974, 51, 799.
6. (Miss) S. MISHRA, B. N. DAS and B. K. SINHA, *Indian J. Chem.*, 1981, 20B, 728.
7. E. F. DUYNSTER and E. GRUNWALD, *J. Amer. Chem. Soc.*, 1959, 81, 4540, 4542.
8. A. RATHER and P. RIED, *J. Amer. Chem. Soc.*, 1919, 41, 75.
9. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis", ELBS and Longman, London, 1954, p. 267.
10. (a) J. L. WINTERS and E. GRUNWALD, *J. Amer. Chem. Soc.*, 1965, 87, 4608.
(b) O. A. BUNTON and L. ROBINSON, *J. Amer. Chem. Soc.*, 1968, 90, 5972.
11. L. S. ROMSTED, Ph.D. Thesis, Indiana University, 1975.
12. K. SHINODA, "Colloidal Surfactants", Chapter-I, (Eds.) K. SHINODA, T. NAGAGAWA, B. I. TAMAMUSHI, T. ISEMURA, Academic Press, New York, 1963.
13. M. J. KAMLET and D. J. GLOVER, *J. Amer. Chem. Soc.*, 1956, 78, 4556.
14. C. G. SWAIN and C. B. SCOTT, *J. Amer. Chem. Soc.*, 1953, 75, 141.
15. J. O. EDWARDS, *J. Amer. Chem. Soc.*, 1956, 78, 1819; J. O. EDWARDS, *J. Amer. Chem. Soc.*, 1954, 76, 1540.
16. I. L. FINAR, "Organic Chemistry", ELBS and Longman, 1970, vol 1, p. 203.
17. C. HANSCH, A. LEO and D. ELKINS, *Chem. Reviews*, 1971, 71, 525.
18. A. FROST and R. G. PEARSON, "Kinetics and Mechanism", Wiley, New York, 1961, p. 123.

TABLE 4—RATE CONSTANTS AT DIFFERENT TEMPERATURE AND AT VARIABLE [NaLS], AND THERMODYNAMIC PARAMETERS FOR THE REACTION BETWEEN PHENACYL BROMIDE (a) AND ALIPHATIC CARBOXYLATE (b) IN 72% ACETONE-WATER (v/v) (a=0.008M; b=0.016M sodium heptanoate)

$10^3[\text{NaLS}]$ in M	$10^3 k_a$ in litre $\text{mol}^{-1} \text{sec}^{-1}$ at				E_a k cal/mol	$-\Delta S^\ddagger$ e.u.
	25°	30°	35°	40°		
0	2.28	3.83	5.78	—	16.92	14.34
10	2.11	3.27	5.17	—	16.25	16.76
20	1.80	2.61	3.86	—	13.84	25.14
30	1.94	2.94	4.21	—	14.05	24.30
40	2.14	3.08	4.47	—	13.43	26.20
50	1.56	2.21	3.31	—	13.71	25.89
(a=0.008M; b=0.016M sodium caprylate)						
0	2.57	—	6.36	11.94	18.26	9.82
10	2.37	—	5.65	10.13	16.12	17.01
20	2.12	—	4.07	7.82	14.27	23.66
30	2.25	—	4.39	8.20	16.12	17.51
40	2.36	—	4.59	8.56	16.12	17.42

observed that the effect of micelles upon the activation parameters are smaller in aqueous alcohol than in water. In case of NaLS, they reported very little increase in activation enthalpy with increasing concentration of NaLS in aqueous ethanol. They calculated the parameters basing on two temperatures only. But in our case these parameters have been calculated properly and the enthalpy of activation values do not show any remarkable change. But it is higher in absence of NaLS. A large activation entropy in case of this bimolecular reaction