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INTERACTION STUDIES OF TWEEN-40 WITH SOME ACIDIC SPECIES AT 20 ^{0}C

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Abstract: Interactions of tween-40 (polyoxyethylene-20-sorbitain monopalmitate) with acetic acid, chloroacetic acid, *o*-, *m*-, *p*-nitrophenols and picric acid have been described at 20°C using conductivity method. The studies are performed at cmc with an emphasis on pre- and post micellar regions. Data thus obtained is used to manipulate the interactions. Binding constants of the species have been computed using Satake equation, standard free energy changes are also obtained to further justify the results.

Keywords : *Association constants, Surfactants, Acidic species, Satake equation, Conductometry*

INTRODUCTION

Inclusion and exclusion complexation between surfactants and other non-ionic species involving hydrophobic interactions is known[1-4]. The role of interactions between macromolecules and other non-ionic substances in homogeneous and micellar catalysis has also been reported[5-7]. To further elaborate these interactions, various systems such as ionic surfactants with fatty acids[8] and with species of varying hydrophobicity[9-12] have been studied to get an insight into their associative tendencies. We have previously conducted preliminary work on the subject and have reported the interactions of tween-20 with organic molecules[13]. In the present communication associative interactions of tween-40 with organic acids and substituted phenols are reported.

Non-ionic surfactants induce changes in absorption and fluorescence spectra, surface and other physiochemical properties of many substances such as micellisations, solubilisation, active transport across the cell membrane, liquid crystalline phase studies etc[2, 14-17]. These changes are observed over a wide range of composition, below and above the critical micelle concentration (cmc), and are mainly attributed to hydrophobic interactions[11, 12].

EXPERIMENTAL

The chemicals used in the work were of analytical grade (Merck) with purity exceeding 99% according to the data of the suppliers. However, some of the compounds were distilled/recrystallised using the accepted procedures[8, 9, 13]. Deionized water (obtained from Pakarab Fertilizers Multan) with specific conductance lower than 8 μ S cm^{-1} and pH 6.8 ± 0.1 at 20°C was used. The solutions were prepared freshly and necessary precautions were taken to avoid the air/CO_2 contaminations.

The method used in present work has already been described[13, 17]. Conductivity was measured with an accuracy of ± 0.1 μ S using a conductivity meter, model 31 of YSI electronics. The cell constant was estimated[13, 17-19] as 1.001 ± 0.001 cm^{-1} at 20°C. Changes in conductivity of tween-40 solutions by adding the solution of second component i.e. organic acidic species (1×10^{-3} M) were recorded at 20°C. Measured values of specific conductance of tween-40 solution were converted to respective molar conductance after applying the volume fraction correction[16, 18, 19]. Plots of molar conductance of tween-40 solutions vs volume of organic acidic substances are drawn and are shown in figures 1-6. Molar conductance data were used to compute the values of binding constants, K, by applying least square regression to Satake[1-7, 16] equation (equation 1).

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$$\Delta\Lambda = \Delta\lambda / 2K\,C_S[K(C_S + C_C) + 1 - ([K(C_S + C_C) + 1]^2 - 4K^2\,C_S C_S)^{1/2}] \quad (1)$$

where

$\Delta\Lambda$ = Decrease in molar conductivity of tween-40 solution (S cm^2 mol^{-1})

$\Delta\lambda$ = Difference in molar conductivities of organic species (S cm^2 mol^{-1})

C_S =Concentration of tween-40 solution(mol cm^{-3})

C_C = Concentration of organic species solution (mol cm^{-3})

K = Binding constant (cm^3 mol^{-1})

Subsequently ΔG values were also computed using equation 2.

$$\Delta G = -RT \text{ In } K \quad (2)$$

where R is gas constant, T is temperature and K is binding constant. Corresponding data for blank samples were also obtained to accommodate the dilution and hydration effects. Each data point is an average of three independent measurements to ensure the reproducibility.

RESULTS AND DISCUSSION

For dilute solution, used in this work, the activity co-efficient ratio of various species can safely be set equal to unity[1-3, 13]. On the basis of this assumption, association constants, K,(Table 1) of tween-40 with acetic acid (AcOH), chloroacetic acid (Cl-AcOH), *o-, m-, p*-nitrophenols and picric acid are computed by using a computer programme in basic language and applying least square regression to the equation of Satake *et al*[1-7, 16].

Acetic acid and Chloroacetic acid Tween-40 Systems

Figure 1 shows the effects of addition of acetic acid (1 x 10^{-3}M) on molar conductance of various concentrations of tween-40 solution at cmc and in pre- and post micellar regions: cmc values (4 x 10^{-5}M ± 1 x 10^{-5} M) are measured conductometrically[11] and confirmed by surface studies method[17]. Initially, a sharp decrease in values of molar conductance can be seen which tends to become constant latter on. Subsequent additions of acetic acid show a little or no further change. Initial sharp decrease in molar conductance values in pre-micellar regions attributed to the interactions developing between the hydrophilic moiety of tween-40 molecules and acetic acid molecules mainly through hydrogen bonding and dipole-dipole interactions. Further additions of acetic acid cause a slight change in conductance value and it refers to the presence of excess acetic acid in the system.

In post-micellar region, as demonstrated in Fig.1, molar conductance decreases regularly by addition of acetic acid. It is because of the interactions between free surfactant molecules (not aggregated in micelles) and acetic acid are through hydrogen bonding and dipole-dipole interactions. However, further additions of the acid tend to shift the cmc values as well and cause disruption in the micellar structures[19].

Similar trends are observed for tween-40 and chloroacetic acid (1 x 10^{-3} M) system which are shown in Fig. 2. However, initial sharp decrease in molar conductance values show a gradual downward trend on further addition of the acid. Furthermore, overall molar conductance magnitude for chloroacetic acid is ~270 – 520 S cm^2 mol^{-1} which is lower than that of acetic acid system ~100 – 800 S cm^2 mol^{-1}. The variation in magnitude of K and ΔG values (Table 1) of these systems also reflect the intensity of the hetro-interactions, which develop between acids and tween-40 molecules after the break down of inter-molecular hydrogen bonding in acids.

o-, *m*-, *p*-Nitrophenols Tween-40 Systems

Figure 3 displays the effect of addition of *o*-nitrophenol (1 x 10^{-3} M) in tween-40 solutions. Shapes of the curves, of molar conductance vs volume of *o*-nitrophenol added, at cmc and in pre- and post-micellar regions resemble to that of acetic acid system. However, the hetro-interactions are somewhat weaker because the intramolecular hydrogen bonding between hydroxyl- and nitro- groups of *o*-nitrophenol prevent the possibilities of hydrogen bonding and dipole-dipole interactions among the phenol and tween-40 molecules. This observation is also supported by ΔG values (Table 1) which are the lowest among substituted phenol systems.

In case of m- and *p*-nitrophenols (Figs. 4 and 5 respectively) trends of, the molar conductance vs volume of substituted phenols added, curves are similar to those of *o*-nitrophenol, and therefore, similar reasoning can be given. However, in these systems hydroxyl- and nitro- groups are not likely to be involved in intramolecular hydrogen bonding and hence the chances for the development of hetero-interactions between phenolic molecules and tween-40 are more pronounced as compared to *o*-nitrophenol + tween-40 system. The overall magnitude of molar conductance of *o*-nitrophenol ~5-45 S cm^2 mol^{-1} is half than that of *m*- and *p*-nitrophenols ~ 20 – 120 S cm^2 mol^{-1} ΔG data (Table 1) also support these observations. Therefore, the ΔG values follow the following order:

o-nitrophenol < *m*-nitrophenol < *p*-nitrophenol

Picric acid Tween-40 System

Behaviour of picric acid in tween-40 solution (Fig.6) is similar to substituted phenols described above. It is a highly polarised molecule, due to the presence of three nitro- groups on a phenol, and can develop stronger associative hetro-interactions with the polar heads of the surfactant molecules leading to complex formation. Thus the molar conductance values(~200 – 275 S cm^2 mol^{-1}) are larger than those of nitro-phenols. K and ΔG data also support these findings.

CONCLUSIONS

Associations of surfactants with ionic and non-ionic substances are very important in practice.Their applications vary from very mundane (washing clothes) to highly sophisticated (microelectronics and micellar catalysis). Study of these interactions is important in understanding the phenomenon and stability of microemulsions, which are in general used as fuels and solvent for coatings and cleansing agents. Such studies also offer chances to discover new and interesting dimensions in chemistry.Property of the amphipathic molecules to form aggregates in the form of micelles in solutions reflects the degree of binding which is another interesting interfacial phenomenon. Efficiency of detergents, emulsification and solubilisation etc. depends on the existence of micelles in the solutions. These applications, in main, address to the studies of the phenomena of micellisation and interactions among homo- and hetero-substances. Further work to highlight these and some other aspects of interactions and micellisation is in progress and will be submitted for publication in due course.

ACKNOWLEDGEMENTS.

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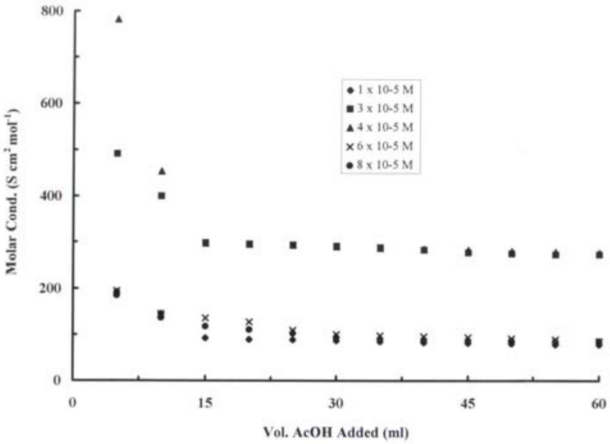

Fig. 1: Plot of Molar Conductance vs Volume of Acetic Acid (1 x 10^{-3}M) Added in Tween-40

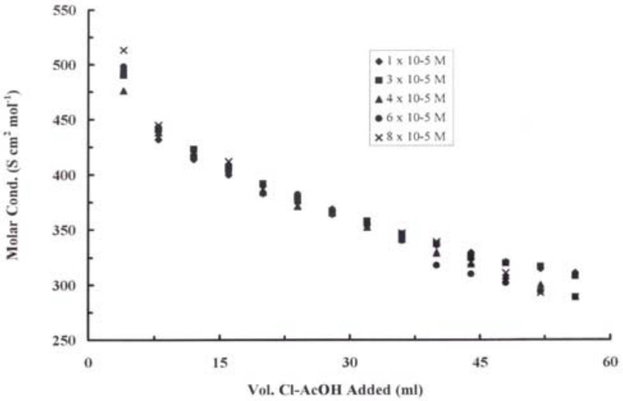

Fig. 2: Plot of Molar Conductance vs Volume of Chloroacetic Acid (1 x 10^{-3} M) Added in Tween-40

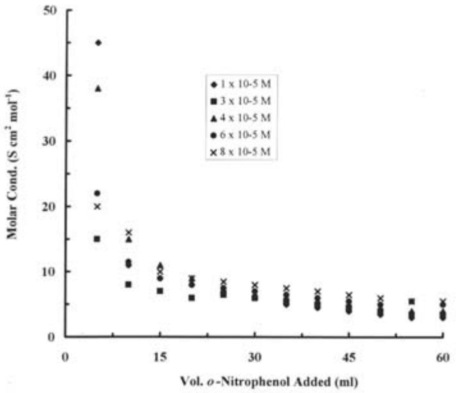

Fig.3: Plot of Molar Conductance vs Volume of *o*-Nitrophenol (1 x 10^{-3} M) Added in Tween-40

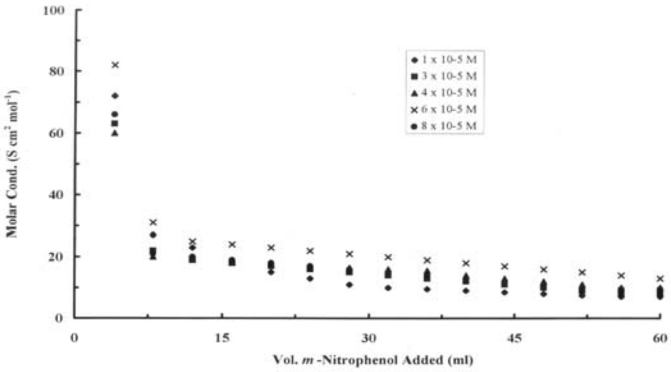

Fig. 4: Plot of Molar Conductance vs Volume of *m*-Nitrophenol (1 x 10^{-3} M) Added in Tween-40

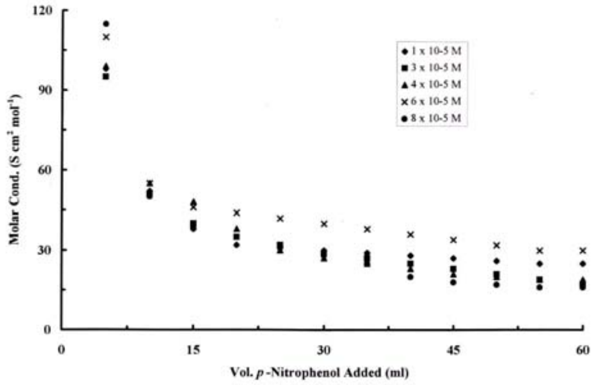

Fig.5: Plot of Molar Conductance vs Volume of *p*-Nitrophenol (1 x 10^{-3} M) added in Tween-40

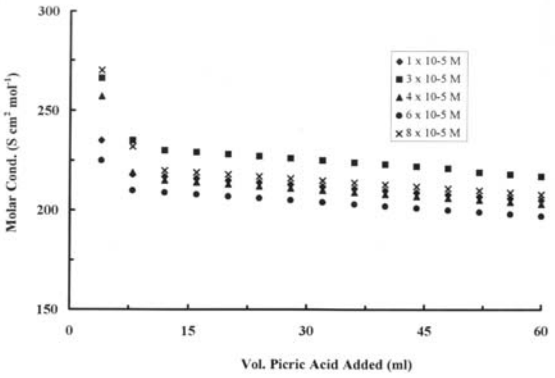

Fig. 6: Plot of Molar Conductance vs Volume of Picric Acid (1 x 10^{-3} M) Added in Tween-40

Table I: Thermodynamic and Conductance Data for Complexation Studies of Tween-40 with organic Substances (1 x 10^{-3} M)

Organic Substance	C 10^{-5} (mol cm^{-3})	Λ_m (S cm^2 mol^{-1})	$\Lambda_m - \Lambda_0$ (S cm^2 mol^{-1})	K (cm^3 mol^{-1})	$-\Delta G$ (kJ mol^{-1})
Acetic acid	1.0	300.00	20.00	1.80	1.43
	3.0	1413.40	733.39	6.01	4.37
	4.0	2051.27	991.28	4.21	3.50
	6.0	84.75	151.25	2.22	1.94
	8.0	86.60	47.39	2.45	2.17
Chloroacetic acid	1.0	1000.00	385.98	1.33	0.70
	3.0	172.42	442.59	1.38	0.78
	4.0	102.55	482.44	1.60	1.14
	6.0	84.75	515.26	1.46	0.92
	8.0	113.93	531.07	1.22	0.48
o-nitrophenol	1.0	2200.00	2145.00	8.83	5.31
	3.0	293.11	263.16	6.18	4.44
	4.0	589.73	538.73	7.89	5.03
	6.0	186.44	158.94	9.54	5.50
	8.0	126.58	101.08	7.31	4.85
m-nitrophenol	1.0	340.00	258.90	8.80	5.30
	3.0	124.14	32.14	8.35	5.17
	4.0	84.61	28.61	9.84	5.57
	6.0	61.02	20.98	8.85	5.31
	8.0	55.70	39.30	8.55	5.23
p-notrophenol	1.0	950.00	810.08	9.88	5.60
	3.0	317.23	179.24	9.84	5.61
	4.0	248.72	108.77	10.28	5.70
	6.0	179.66	33.43	9.85	5.57
	8.0	149.47	41.32	9.65	5.51
Picric acid	1.0	400.00	146.00	7.48	4.90
	3.0	120.70	152.31	7.87	5.02
	4.0	179.49	81.51	8.10.	5.10
	6.0	84.75	137.25	7.03	4.75
	8.0	101.26	169.74	7.66	4.96

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