Available online at www.sciencedirect.com
SCIENCE DIRECT
Colloids and Surfaces B: Biointerfaces 46 (2005) 45–51
COLLOIDS AND SURFACES B
www.elsevier.com/locate/colsurfb

Effect of surfactants on the dissociation constants of ascorbic and maleic acids

P.V. Jaiswal, V.S. Ijeri [1], A.K. Srivastava *

Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz(E), Mumbai 400098, Maharashtra, India

Received 3 April 2005; received in revised form 29 August 2005; accepted 1 September 2005
Available online 7 October 2005

Abstract

The dissociation equilibria of ascorbic and maleic acids have been studied in certain cationic, anionic and non-ionic micellar media and their pK_a values have been evaluated by the potentiometric, conductometric and spectrophotometric techniques. These pK_a values have been found to shift in micellar media as compared to those in pure water. The differences in the values have been attributed to the solvent properties of the interfacial and bulk phases involving contribution from the micellar surface potential in the case of charged micelles. The values of the limiting molar conductance of the acids have been determined in the various surfactants and were found to be different in different surfactants. In case of the cationic surfactants the limiting molar conductance was found to increase with increase in surfactant concentration.

Keywords: Dissociation equilibria; Ascorbic acid; Maleic acid; Micelles; pHmetry; Spectrophotometry; Conductometry

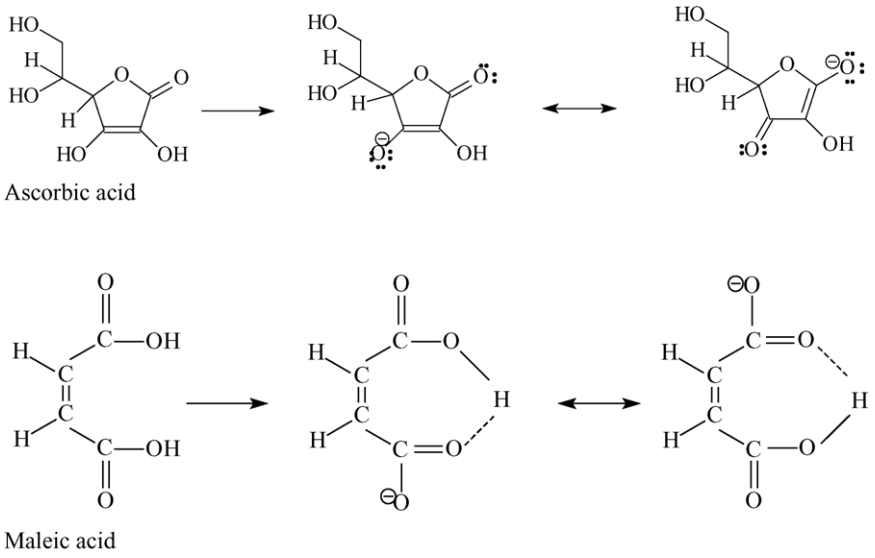
1. Introduction

The use of aqueous micellar media is wide and varied such as in analytical chemistry, pharmaceutics, organic synthesis and several industrial applications. Amphiphilic molecules, containing both hydrophobic and hydrophilic moieties, associate in water above a certain concentration to form colloidal particles called micelles [1,2]. Micellar systems can shift acid–base equilibria. This shift can be explained in terms of differences between the properties of the bulk solvent and of the interfacial region and perturbation of the acid–base equilibria by the electrostatic field effect of the charged interface. The dissociation equilibria of substituted benzoic acids in cationic and anionic micelles have been investigated potentiometrically [3]. It was shown that their pK_a values shift to about less than 1.0 in cationic micelles and by about 0.5–3.0 in anionic micelles. The acid–base equilibria of a number of phenols, amines and carboxylic acids in aqueous micellar solutions have been examined [4]. The spectral and acid–base properties of some solvatochromic acid–base indicators were studied in self-assembled surfactant aggregates [5,6]. Similar studies have been done for complexing agents [7], dyes [8] amino acids and peptides [9] and medicinal compounds [10,11]. Surfactant media also effect the complexation [12,13] and other electrochemical phenomena [14,15], which in turn have been exploited for electroanalysis of ascorbic acid and other vitamins [16,17]. The study of acid–base behaviour in surfactant media is important to the understanding of mechanisms of reactions in both in vitro and in vivo environments; and such a study is also useful in analytical and pharmaceutical applications.

The present work is an attempt to study the effects of cationic, anionic and non-ionic micellar solutions on the dissociation equilibria of the two biologically/industrially useful acids [18], viz., ascorbic and maleic acids in the surfactants cetyl pyridinium chloride (CPC), cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulphate (SDS) and Triton X 100 (TX 100). Ascorbic acid (or Vitamin C) is a well-known antioxidant, free radical scavenger, antiscorbutic factor and active in many biological processes. The ascorbic acid molecule (see Scheme 1) contains four hydroxyl groups in positions 2, 3, 5 and 6; the –OH group in position 3 is acidic (pK_{a_1} = 4.2), the hydroxyl in position 2 has pK_{a_2} = 11.6, while those in positions 5 and 6 behave as a secondary and primary alcoholic residue, respectively. It is very sensitive to heat, light, and to the action of

* Corresponding author.
E-mail address: akschbu@yahoo.com (A.K. Srivastava).
[1] Present address: Ecole Centrale de Lyon, H-9 CEGELY, 36 Avenue Guy de Collongue, F 69134 Ecully Cedex, France.

0927-7765/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfb.2005.09.001



Scheme 1. Dissociation of ascorbic and maleic acids.

oxidizing agents and metal ions. It is readily oxidized, especially in aqueous solutions, by reacting with atmospheric oxygen, and behaves as a two-electron donor. It is very unstable beyond pH 7. Maleic acid, a diprotic acid, is used in the manufacture of artificial resins, surface coatings, lubricant additives, plasticizers for retarding the rancidity of fats and in the dye industry.

For the determination of pK_a of the acids in micellar media, the technique of pHmetry and spectrophotometry was employed in both cases for comparison. The conductance behaviour of ascorbic acid was studied in the various surfactants above their critical micellization concentrations and an attempt was made to evaluate the pK_a values using the conductometric data too.

2. Materials and methods

Demineralized water, distilled from an all glass (corning) quick fit setup, over alkaline potassium permanganate was redistilled and used fresh. The average specific conductivity was less than 0.5 $\mu S/cm^2$. As ascorbic acid solutions are easily oxidized by exposure to air/dissolved oxygen, the use of distilled water eliminates all dissolved gases.

2.1. Reagents

The surfactants, cetyl pyridinium chloride (Loba Chemie), cetyl trimethyl ammonium bromide (Loba Chemie), sodium dodecyl sulphate (SD Fine), and Triton X 100 (SD Fine), were of analytical reagent grade (purity $\geq$99.8%) and were used as such without further purification.

Ascorbic acid (SD Fine) was recrystalized twice with absolute ethanol. Maleic acid (SD Fine) was recrystallized from acetone. Both were dried in a vacuum oven at about 40 °C before use. Fresh solutions were prepared for each set of experiments.

2.2. Apparatus

A Mettler Toledo DL53 autotitrator with automatic temperature compensation (ATC) was used for all potentiometric and conductometric measurements. The probes used were, glass electrode with an inbuilt calomel reference electrode (DG 111-SC) and conductometric sensor (Inlab 710). This assembly of titrator and the cell was air tight to prevent any atmospheric contamination.

Spectrophotometric measurements were carried out on a Shimadzu-2100 UV–visible spectrophotometer.

2.3. pH measurements

Titrations involving pH measurements were carried out using the glass electrode, which was calibrated regularly using standard buffer solutions. Surfactants were added to the buffer solutions to check for any deviations and the change observed was not more than $\pm$0.01 units as noted by other workers too [6,19].

All measurements were done at 25 ± 0.1 °C. A fixed volume of the acid solution ($\sim 2 \times 10^{-3}$ M), in the surfactant solution (0.01 M) was placed in the cell and its pH measured. To this, a previously standardized, concentrated NaOH solution ($\sim$0.1 M, freshly prepared everyday) was added in discrete amounts with continuous stirring. The pH was recorded continuously till a stable value was obtained before the next addition. The titration was continued till just after the equivalence point.

2.4. Spectrophotometric measurements

All spectrophotometric measurements were made in Britton & Robinson (BR) buffer (0.04 M w.r.t. acetic acid, boric acid and phosphoric acid), the required pH being adjusted with 0.02 M NaOH. The spectrum of the acid solution ($\sim 1 \times 10^{-4}$ M) was first obtained at a pH at which the compound to be measured was present wholly as a molecular species. This spectrum was then compared with that of the purely ionized species similarly isolated at another suitable pH. The isobestic wavelength was then chosen. At this wavelength and at various intermediate pH values, the absorbance values of the acid solutions were recorded. The ratio of ionized to molecular species was then calculated.

All absorbance measurements were corrected with the help of blank solutions containing the same concentration of surfactant in the buffer of required pH.

2.5. Conductometric measurements

All measurements were done at $25 \pm 0.1\,^{\circ}C$, using the conductometric sensor, which was calibrated regularly with standard potassium chloride solutions. A fixed volume of the surfactant solution at a particular concentration was placed in the cell and the conductance measured. A step by step increase in the acid concentration was effected by means of the autotitrator. The stock acid solutions were prepared in the same concentration of the surfactant to account for error arising due to dilution. The conductivity was measured after each addition, followed by mixing and the most stable reading over a span of 20 min was recorded. All molar conductivities were calculated after correcting for the surfactant conductivity.

3. Results and discussions

In a solution of a weak acid (HX), the equilibrium between the ions and the undissociated molecules may be given as

$$HX \Leftrightarrow H^+ + X^- \quad (1)$$

The dissociation constant may be expressed as

$$K_a = \frac{a_{H^+} a_{X^-}}{a_{HX}} \quad (2)$$

It has been recognized that the magnitude of the apparent pK_a, pK_a^{obsd}, of a prototropic moiety residing at or close to a charged interface depends on the electrostatic potential of the charged interface. This is quantified as follows [20–22]:

$$pK_a^{obsd} = pK_a^0 - \frac{F\Psi}{2.303RT} \quad (3)$$

where pK_a^0 is the intrinsic interfacial pK_a of the prototropic moiety, Ψ the mean field potential at the average site of residence, F the Faraday constant, R the universal gas constant and T is the absolute temperature.

The apparent acid–base equilibrium for a weak acid located within an aqueous micellar interfacial phase can be represented as

$$HX_i^{(z)} \Leftrightarrow H_w^{(+)} + X_i^{(z-1)} \quad (4)$$

where subscripts 'i' and 'w' denote the interfacial and bulk phases, respectively.

pH measurements were evaluated for the determination of pK_a of both acids by the Henderson's equation.

$$pH = pK + \log\left(\frac{C_{salt}}{C_{acid}}\right) + \log\left(\frac{\gamma_{salt}}{\gamma_{acid}}\right) \quad (5)$$

where C denotes concentration and γ denotes activity coefficient.

In the present work, we are primarily concerned with the effect of surfactants on pK_a at fixed concentration well above the cmc (0.01 M) so that the changes in cmc due to solute can be neglected [23]. So, in the present data treatment, the activity of water was assumed to be unity and self dissociation of water was considered to be negligible, though such small factors may contribute heavily to the observed properties at microscopic scales, including the replacement of 'activity' terms by 'concentration' at higher concentrations of the solute under study [24,25].

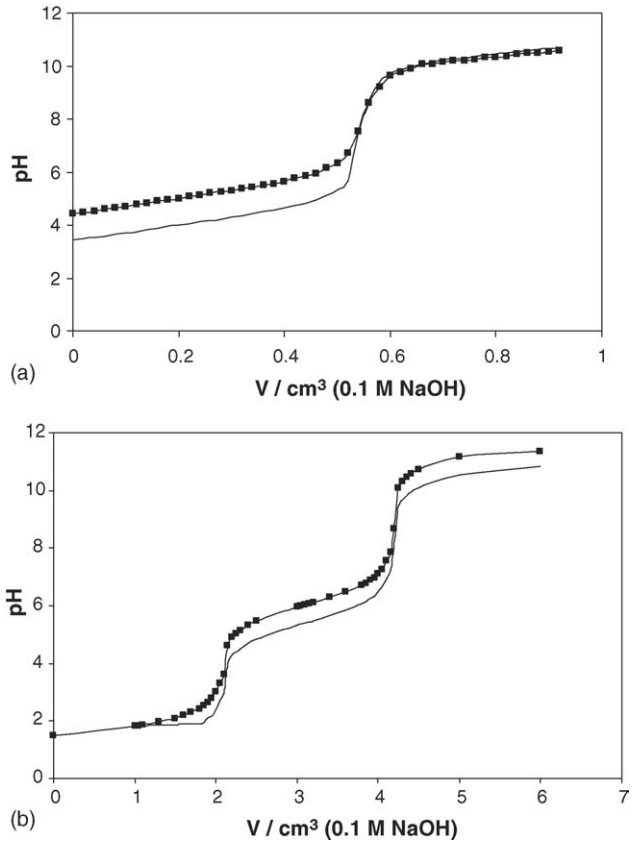


Fig. 1. (a) pH metric curves for ascorbic acid (■) in pure water (–) in 0.01 M CPC. (b) pH metric curves for maleic acid (■) in pure water (–) in 0.01 M CPC.

The pHmetric curves obtained for ascorbic acid and maleic acid in pure water and 0.01 M CPC, are representative of the other systems and are shown in Fig. 1. Table 1 contains the pK_a values obtained by this technique for both the acids.

The UV absorbance spectra, as shown in Fig. 2, of 1×10^{-4} M ascorbic acid in 0.01 M CPC at pH 7.5 (completely

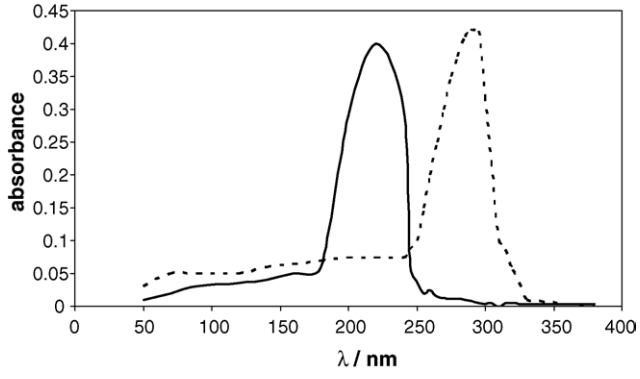


Fig. 2. A typical UV–absorbance spectra of ascorbic acid in 0.01 M CPC. (—) pH 1.5 and (- - -) pH 7.5.

Table 1
pK_a values obtained by pHmetric titrations and spectrophotometry

Medium	By pHmetry		By spectrophotometry	
	Ascorbic acid (pK_a)	Maleic acid (pK_{a_1}, pK_{a_2})	Ascorbic acid (pK_a)	Maleic acid (pK_{a_1},pK_{a_2})
Water[a]	4.13 (0.06)	1.83 (0.05), 6.07 (0.04)	4.13 (0.01)	1.82 (0.02), 6.06 (0.02)
0.01 M CPC	3.42 (0.08)	1.83 (0.05), 5.44 (0.05)	3.41 (0.02)	1.83 (0.02), 5.43 (0.01)
0.01 M CTAB	3.64 (0.05)	1.82 (0.05), 5.56 (0.04)	3.65 (0.01)	1.83 (0.02), 5.54 (0.04)
0.01 M SDS	4.09 (0.06)	1.80 (0.06), 5.99 (0.07)	4.09 (0.04)	1.83 (0.01), 5.98 (0.05)
0.01 M TX 100	4.40 (0.04)	1.86 (0.07), 6.24 (0.07)	4.41 (0.01)	1.85 (0.01), 6.22 (0.06)

Figures in parenthesis represent standard deviation.
[a] Literature values for ascorbic acid and maleic acids are 4.10, 1.83 and 6.07, respectively [CRC Handbook of Chemistry and Physics, 85th edition, 2004–2005].

ionized form) gave a maxima at wavelength 282.7 nm. The species in 0.01 M CPC at pH 1.5 (completely molecular form) gave a maxima at 243.6 nm and practically no absorbance at 282.7 nm (Fig. 2). Hence, this was chosen as the analytical wavelength at which the absorbance values of seven other solutions having different pH values were recorded. The pK_a values were then calculated as a function of pH using the formula:

$$pK = pH + \log\left[\frac{A_i - A}{A - A_m}\right] \quad (6)$$

where A_i is the absorbance of the completely ionized species, A_m the absorbance of the completely molecular species, and A is the absorbance observed at different pH values. In case of ascorbic acid in 0.01 M CTAB the maxima of the molecular species was obtained at 244.8 nm and that of the ionized species was obtained at 265.7 nm. It was observed that at 244.8 nm the ionized species gave very less absorbance hence this was chosen as the analytical wavelength. In case of both SDS and TX 100 the neutral form of the acid gave a maximum at 243.1 nm and the ionized form at 265.8 nm at which the neutral form absorbed very less hence 265.8 nm was chosen as the analytical wavelength.

The completely molecular form of dibasic maleic acid at pH 0.1 gave a maximum at 262.3 nm in both 0.01 M CPC and 0.01 M CTAB while the monoprotonated species at pH 4.08 gave a maximum at 230.2 nm. The maximum difference in absorbance was obtained at 230.2 nm and this was therefore taken as the isosbestic point. For determination of the second pK_a value, the deprotonated species obtained at pH 8.5 gave a maximum absorbance at 225.1 nm. The isosbestic wavelength was again taken at 230.2 nm where the maximum difference in absorbance was observed. In case of 0.01 M SDS and 0.01 M TX 100 at pH 0.1 the maximum was obtained at 242.0 nm, while at pH 4.08 it was obtained at 214.7 nm. The deprotonated species in both the media absorbed at 213.6 nm. For determination of the second pK_a value in both the cases the analytical wavelength thus chosen was 213.6 nm. Table 2 shows the spectroscopic data and the pK_a values thus evaluated for both the acids in different media, and the pK_a values are tabulated in Table 1.

For the evaluation of conductivity data, by recent conductance equations the most essential parameters that are required are the viscosity and the dielectric constants of the solvent media. These parameters were however unavailable for the acids in the surfactant media. Therefore, it was possible only, to evaluate the conductivity measurements, by the Kraus and Bray [26] conductance equation, which does not take into account the above mentioned parameters. This could be one of the main reasons as to why the pK_a values obtained by this method are lower as compared to those obtained by the other techniques.

The Kraus and Bray conductance equation is as follows:

$$\frac{1}{\lambda_c} = \frac{1}{\Lambda_0} + \frac{C\lambda_c}{\Lambda_0^2 K} \quad (7)$$

where λ_c is the molar conductance of the acid at concentration C, Λ_0 the molar conductance of the acid at infinite dilution, and K is the dissociation constant. Plots of $1/\lambda_c$ versus $C\lambda_c$ for the acids in the various media gave almost straight lines from whose slopes and intercepts were obtained the limiting molar conductance and dissociation constants, respectively. Fig. 3 shows one such Kraus and Bray plot.

The values of the molar conductance Λ as a function of concentration C in the various surfactant media are given in Table 3. The values of the limiting molar conductance for ascorbic acid in the various media, was found to increase in the order CPC > CTAB > SDS > TX 100. These values are given in Table 4 along with the pK_a values for the acid in the various media obtained by conductometric measurements.

The values obtained by the pHmetric and spectrophotometric techniques show excellent agreement with each other. However, the pK_a values obtained as a result of conductance measurements are slightly lower. This, as mentioned before is primarily

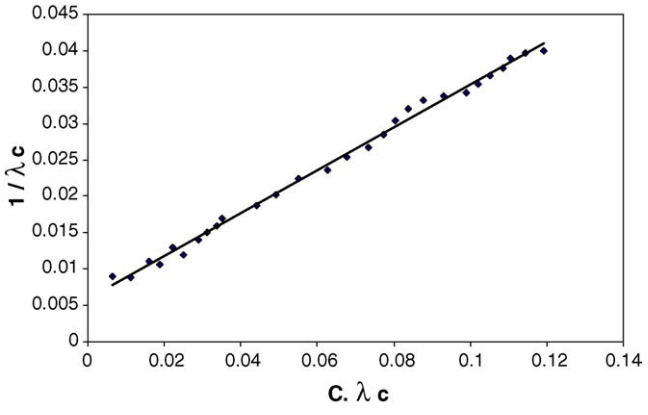


Fig. 3. A typical Kraus and Bray plot for ascorbic acid in 0.01 M TX 100.

Table 2
UV spectroscopic data for ascorbic acid in the different surfactant media

pH	Absorbance	pK_a
(a) Ascorbic acid		
(i) In water: λ = 265.8 nm, A_m = 0.259, A_i = 1.054		
4.7	0.894	4.13
4.5	0.827	4.13
4.3	0.746	4.11
4.1	0.656	4.14
3.9	0.566	4.12
3.7	0.485	4.12
3.5	0.418	4.13
Mean		4.13 (0.01)
(ii) In 0.01 M CPC: λ = 282.7 nm, A_m = 0, A_i = 0.424		
4.7	0.403	3.40
4.5	0.392	3.40
4.3	0.372	3.44
4.1	0.348	3.40
3.9	0.319	3.42
3.7	0.282	3.40
3.5	0.236	3.40
Mean		3.41 (0.02)
(iii) In 0.01 M CTAB: λ = 244.8 nm, A_m = 0.916, A_i = 0.169		
4.7	0.230	3.65
4.5	0.258	3.63
4.3	0.303	3.64
4.1	0.365	3.65
3.9	0.438	3.65
3.7	0.521	3.65
3.5	0.623	3.65
Mean		3.65 (0.01)
(iv) In 0.01 M SDS: λ = 265.8 nm, A_m = 0.300, A_i = 0.934		
4.7	0.807	4.10
4.5	0.753	4.10
4.3	0.753	3.99
4.1	0.545	4.13
3.9	0.545	4.10
3.7	0.481	4.10
3.5	0.427	4.11
Mean		4.09 (0.04)
(v) In 0.01 M TX 100: λ = 265.8 nm, A_m = 0.555, A_i = 0.925		
4.7	0.800	4.40
4.5	0.759	4.41
4.3	0.715	4.42
4.1	0.678	4.40
3.9	0.644	4.40
3.7	0.615	4.41
3.5	0.596	4.40
Mean		4.41 (0.01)
(b) Maleic acid		
(i) In water: λ = 214.7 nm (for pK_{a_1}), A_m = 0.100, A_i = 1.224		
1.23	0.334	1.81
1.43	0.425	1.82
1.63	0.529	1.84
1.83	0.660	1.83
2.03	0.788	1.83
2.23	0.903	1.83
2.43	0.994	1.84
Mean		1.82 (0.01)
λ = 213.7 nm (for pK_{a_2}), A_m = 0.333, A_i = 0.849		
5.47	0.440	6.05
5.67	0.484	6.05
5.87	0.538	6.05
6.07	0.594	6.07
6.27	0.652	6.06
6.47	0.707	6.05
6.67	0.749	6.05
Mean		6.06 (0.01)
(ii) In 0.01 M CPC: λ = 230.2 nm (for pK_{a_1}), A_m = 0.201, A_i = 0.986		
1.23	0.364	1.81
1.43	0.428	1.82
1.63	0.500	1.84
1.83	0.592	1.83
2.03	0.681	1.83
2.23	0.762	1.83
2.43	0.825	1.84
Mean		1.83 (0.01)
λ = 230.2 (for pK_{a_2}), A_m = 0.212, A_i = 0.745		
4.84	0.321	5.43
5.04	0.369	5.42
5.24	0.421	5.43
5.44	0.482	5.44
5.64	0.541	5.43
5.84	0.595	5.43
6.04	0.640	5.43
Mean		5.43 (0.01)
(iii) In 0.01 M SDS: λ = 214.7 nm (for pK_{a_1}), A_m = 0.109, A_i = 1.104		
1.23	0.310	1.83
1.43	0.397	1.82
1.63	0.488	1.84
1.83	0.605	1.83
2.03	0.718	1.83
2.23	0.820	1.83
2.43	0.901	1.84
Mean		1.83 (0.01)
λ = 213.6 (for pK_{a_2}), A_m = 0.210, A_i = 0.810		
5.47	0.372	5.90
5.67	0.401	6.00
5.87	0.461	6.01
6.07	0.536	6.07
6.27	0.600	6.00
6.47	0.684	5.89
6.67	0.704	6.00
Mean		5.98 (0.06)
(iv) In 0.01 M TX 100: λ = 214.7 nm (for pK_{a_1}), A_m = 0.104, A_i = 0.992		
1.23	0.275	1.85
1.43	0.344	1.86
1.63	0.433	1.86

Table 2 (*Continued*)

pH	Absorbance	pK_a
1.83	0.532	1.83
2.03	0.638	1.85
2.23	0.726	1.86
2.43	0.803	1.86
Mean		1.85 (0.01)
$\lambda = 213.6$ (for pK_{a_2}), $A_m = 0.210$, $A_i = 0.810$		
5.47	0.297	6.24
5.67	0.337	6.24
5.87	0.392	6.23
6.07	0.448	6.07
6.27	0.520	6.24
6.47	0.587	6.24
6.67	0.647	6.24
Mean		6.22 (0.06)

because, physical parameters such as viscosity and dielectric constants have not been considered in the conductance equation. Nevertheless, the basic trend in the values obtained by all the three techniques is very similar.

Conductance measurements were also carried out for ascorbic acid in different concentrations of the surfactants. In case of cationic surfactants CPC and CTAB, it has been found that the Λ_0 values for both the acids increased as the concentration of the surfactants increased. These values have been shown as tabulation in Table 5.

This can be explained on the basis of the high field strengths arising in the solutions due to high surfactant concentrations. At higher field strengths the ions are accelerated appreciably, ionic atmosphere interactions are reduced and the equivalent conductance is increased. This fractional increase in conductance is much larger for weak electrolytes as compared to strong electrolytes. These effects are collectively known as Wien effects [27].

The above results show that the shifts in pK_a values (second pK_a value in case of maleic acid) are more in case of cationic surfactants CPC and CTAB as compared to the anionic surfactant SDS or the non-ionic surfactant TX 100. Both acids behave more strongly in case of CPC and CTAB whose interfacial layer is positively charged. This is mainly because the anion, $X^{(z-1)}$,

Table 4
Limiting molar conductance and pK_a of ascorbic acid in different surfactant media

Medium	Λ_0 (S cm^2 mol^{-1})	pK_a
0.01 M CPC	308.45	3.15 (0.07)
0.01 M CTAB	267.99	3.26 (0.05)
0.01 M SDS	142.40	3.71 (0.06)
0.01 M TX 100	137.02	3.88 (0.07)

Table 5
Limiting molar conductance of ascorbic acid in cationic surfactants at different concentrations

Medium	Λ_o (S cm^2 mol^{-1})
0.002 M CPC	196.01
0.005 M CPC	267.22
0.010 M CPC	308.45
0.002 M CTAB	182.22
0.005 M CTAB	215.12
0.010 M CTAB	267.99

is strongly attracted to the interfacial layer of the cationic surfactants due to attraction between opposite charges, coupled with its strong hydrophobic character. This creates a strain on the acid molecule causing it to dissociate more strongly. In case of CTAB the hydrocarbon chain contains a large number of methyl substituents that restrict the rotational degree of freedom around the C–C bond causing the chains to tilt, thus preventing them from packing in a close manner [28]. This decreases the interfacial charge on the CTAB micelles as compared to the CPC micelles. Hence, there is a lesser degree of attraction between the anion from the acid molecule and the CTAB micellar interface as compared to the CPC micellar interface. This leads to lesser strain caused on the acid molecule followed by lower dissociation and higher pK_a values in CTAB micelles as compared to that in CPC micelles. In case of maleic acid, the first deprotonation is easy (strongly acidic) with a pK_a value of about 1.83 in all the media. After the first ionization, intramolecular hydrogen bonding stabilizes the monoanion (Scheme 1). As a result the first ionization is easier and the second is difficult. So, the effect of surfactants is visible for the second dissociation. Ascorbic acid is a weaker

Table 3
Molar conductance Λ at concentration C of ascorbic acid in pure water and the various surfactant media

C ($\times 10^4$ mol dm^{-3})	Λ (S cm^2 mol^{-1})				
	Water	0.01 M CPC	0.01 M CTAB	0.01 M SDS	0.01 M TX 100
1.4977	120.18	220.99	208.31	130.86	106.83
2.9910	106.32	189.57	174.19	109.32	83.58
4.4798	93.53	169.65	166.36	100.45	75.00
9.9009	71.10	126.65	121.40	72.518	49.59
17.1990	58.08	101.87	104.19	55.20	39.36
24.3920	50.35	93.56	87.21	45.84	32.92
29.1262	46.73	89.91	82.77	42.50	30.11
36.1445	42.71	85.82	81.59	38.12	28.22
43.0622	39.64	80.46	75.68	35.25	25.68

acid. In ascorbate ion (the conjugate base of ascorbic acid), the negative charge is shared between the two oxygens (Scheme 1), by way of the intervening carbon atoms. This stabilization of the anion is similar to that in carboxylic acids and is enough to make ascorbic acid about as acidic as acetic acid.

In case of anionic surfactant SDS, the interface is negatively charged and the anion is repelled, thus leading to a decrease in acidity. Also, there is a possibility of electrostatic attraction of H^+ to the SDS micelles, which would cause an increase in the acidity. However, in present case, the sum total of these factors cause little or no strain on the acid molecule leading to almost similar pK_a values as compared to those in water.

In case of non-ionic surfactant TX 100 the acid dissociates even lesser as compared to that in pure water. The TX 100 molecule is made up of a large number of electron releasing polyoxyethylene headgroups. Due to negative inductive effect, the electron density on the carbon atom in the acid molecule increases which in turn increases the electron density on the adjoining C–OH bond. The overall effect is that of an increase in electron density in the O–H bond. This leads to difficulty in the release of proton by the acid molecule causing lower dissociation of the acid and higher pK_a values. In the absence of any strong electrostatic effect in case of non-ionic surfactants, the polarity effect is expected to play a larger role. The dielectric constant of the micellar phase is smaller than that of water, and so when the acid is solubilised at this phase the dissociation equilibrium is shifted to the left, thereby increasing the pK_a value. It is also possible that the presence of several ethoxylated oxygen atoms should increase the number of hydrogen bonds, and therefore promote dissociation. But according to the results observed, it seems that the inductive and dielectric factors outweigh the possibility of hydrogen bonding causing an over all decrease in dissociation. Similar increase in the value of pK_a was observed for dissociation of phenyl salicylate in Brij 35, a non-ionic surfactant [29].

It should be remembered that values reported in the present work are all with reference to a fixed concentration of surfactant which is well above the cmc of the surfactants. At several other intermediate concentrations or added salts/counterions the effects are pronouncedly different [6,24].

To the best of our knowledge, conductance studies of this type have not been reported earlier. We have been only partially successful in determining the pK_a values by conductance measurements. However, the values obtained by the potentiometric and spectrophotometric methods in pure water are very close to the literature values and those in the various surfactant systems are in excellent agreement with each other thus making it very clear that the acid–base equilibria do shift under the influence of micelles. Further scope of this work lies in the better evaluation of pK values by using recent conductance equations, thus making it possible to analyze various other systems without the limitations encountered in this work.

References

[1] M.J. Rosen, Surfactants and Interfacial Phenomena, Wiley, New York, 1978.
[2] Mc Intire, L. Gregory, Crit. Rev. Anal. Chem. 21 (1990) 257.
[3] P. Ezzio, P. Edmondo, Anal. Chim. Acta 117 (1980) 403.
[4] C.J. Drummond, F. Grieser, T.W. Healy, J. Chem. Soc., Faraday Trans. I 85 (1989) 521.
[5] C.J. Drummond, F. Grieser, T.W. Healy, J. Phys. Chem. 92 (1988) 2604.
[6] Z. Yuanqin, L. Fan, L. Xiaoyan, L. Jing, Talanta 56 (2002) 705–710.
[7] N. Pourreza, S. Rastegarzadeh, J. Chem. Eng. Data 50 (2005) 206–210.
[8] M. Khamis, B. Bulos, F. Jumean, A. Manassra, M. Dakiky, Dyes Pigments 66 (2005) 179–183.
[9] M.G. Khaledi, A.H. Rodgers, Anal. Chim. Acta 239 (1990) 121–128.
[10] A. Rodríguez, E. Junquera, P. del Burgo, E. Aicart, J. Colloid Interf. Sci. 269 (2004) 476–483.
[11] B. Castro, P. Gameiro, José L.F.C. Lima, C. Matos, S. Reis, Mater. Sci. Eng. C 18 (2001) 71–78.
[12] M. Szymula, S. Radzki, Colloid Surf. B 35 (2004) 249–257.
[13] P.V. Jaiswal, V.S. Ijeri, A.K. Srivastava, J. Incl. Phenom. Macro Chem. 49 (2004) 219–224.
[14] M. Szymula, J.N. Michalek, Colloid Polym. Sci. 281 (2003) 1142–1148.
[15] X.L. Wen, Y.H. Jia, Z.L. Liu, Talanta 50 (1999) 1027–1033.
[16] P.V. Jaiswal, V.S. Ijeri, A.K. Srivastava, Anal. Chim. Acta 441 (2001) 201–206.
[17] P.V. Jaiswal, V.S. Ijeri, A.K. Srivastava, Bull. Chem. Soc. Jpn. 74 (2001) 2053–2057.
[18] Merck Index, 13th ed., 2001.
[19] B. Castro, V. Domingues, P. Gameiro, Joseĭ L.F.C. Lima, A. Oliveira, S. Reis, Int. J. Pharm. 187 (1999) 67–75.
[20] P. Mukerjee, K.A. Banerjee, J. Phys. Chem. 68 (1964) 3567.
[21] B. Lovelock, F. Grieser, T.W. Healy, J. Phys. Chem. 89 (1985) 501.
[22] C.J. Drummond, F. Grieser, Langmuir 3 (1987) 855.
[23] C.A. Bunton, L. Sepuiveda, J. Phys. Chem. 83 (1979) 680–683.
[24] Z.M. He, P.J. O'Connor, L.S. Romsted, D. Zanette, J. Phys. Chem. 93 (1989) 4219–4226.
[25] M.S. Fernandez, P. Fromherz, J. Phys. Chem. 81 (1977) 1755–1761.
[26] C.A. Kraus, W.C. Bray, J. Am. Chem. Soc. 35 (1913) 1315.
[27] E. Yeager, A.J. Salkind, Techniques of Electrochemistry, vol. 2, Wiley, New York, 1973, p. 4.
[28] A.K. Chattopadhayay, K.C. Mittal, Surfactants in Solutions, Marcel Dekker Inc., 1996.
[29] M.N. Khan, Z. Arifin, M.R. Yusoff, E. Ismail, J. Colloid Interf. Sci. 220 (1999) 474–476.