

## Effect of surfactants on protonation equilibria of oxalic and malonic acids

B. B. V. Sailaja, Tesfahun Kebede, G. Nageswara Rao and M. S. Prasada Rao\*

Bio-inorganic Chemistry Laboratories, School of Chemistry, Andhra University, Visakhapatnam-530 003, India

E-mail : Muvvala\_2000@yahoo.com Fax : 91-0891-555547

Manuscript received 13 November 2000, revised 27 April 2001, accepted 31 May 2001

Protonation equilibria of oxalic and malonic acids are investigated in aqua-micellar media of varying composition (0–2.5%, w/w) electrometrically at an ionic strength of 0.17 mol dm<sup>-3</sup> and at temperature 303 K. The best-fit chemical models are arrived at based on statistical grounds employing crystallographic *R* factor,  $\chi^2$ , skewness and kurtosis. The variation in the protonation constants with the dielectric constant of the medium is attributed to the electrostatic and non-electrostatic forces.

Amphiphilic molecules profoundly influence the bulk properties of physiological systems. They can solubilize, concentrate and compartmentalize ions and molecules<sup>1</sup>. The effect of surfactant on protonation equilibria was recognised long back<sup>2</sup>. Therefore, the influence of micellar media on the protonation equilibria of oxalic and malonic acids is investigated in the presence of sodium lauryl sulfate (SLS), cetyltrimethylammonium bromide (CTAB) and Triton X-100 (TX) under mimicked physiological conditions. An insight into the protonation equilibria is also

helpful in understanding the metal-ligand equilibria associated with these ligands.

### Results and Discussion

*Protonation equilibria* : The analysis of alkalimetric titration data of oxalic and malonic acids in micellar media shows that the acidobasic equilibria are active in the pH range 1.5–5.0 and 1.7–7.0, respectively. The protonation constants along with statistical parameters are tabulated in Tables 1 and 2. A very low standard deviation in log  $\beta$  values indicates the precision of these parameters. The

Table 1. Best-fit chemical models of acidobasic equilibria of oxalic acid in micellar media

$\mu = 0.17 \text{ mol dm}^{-3}$ , pH meter readability = 0.01, Temp. = 303 K

Composi- tion	log $\beta_1$ (SD)	log $\beta_2$ (SD)	NP	$U_{\text{corr}}$	Skew.	Kurt.	$\chi^2$	<i>R</i>
CTAB (% w/w) :								
0.0	3.83(1)	4.82(2)	50	1.54	-1.29	6.28	3.40	0.0065
0.5	3.82(2)	5.09(2)	109	5.46	-0.70	6.53	21.34	0.0099
1.0	3.88(2)	4.84(2)	108	6.49	-0.28	3.93	8.30	0.0108
1.5	3.98(1)	5.75(1)	109	1.60	-0.54	5.15	12.71	0.0040
2.0	3.74(1)	4.96(1)	108	1.12	0.20	4.26	10.61	0.0034
2.5	3.84(1)	5.68(1)	106	4.17	-0.03	3.15	7.85	0.0086
TX (% v/v) :								
0.5	3.96(1)	5.04(2)	84	1.85	-0.68	3.87	1.71	0.0072
1.0	3.85(1)	5.13(1)	88	0.38	-0.34	4.33	2.55	0.0032
1.5	3.93(1)	5.32(1)	88	0.72	-1.10	6.04	6.55	0.0043
2.0	3.67(1)	4.64(1)	87	1.40	0.17	2.45	4.85	0.0063
2.5	3.94(1)	5.48(1)	90	0.79	-0.47	3.48	3.11	0.0044
SLS (% w/w) :								
0.5	3.88(1)	5.32(1)	84	1.06	-0.22	3.63	4.15	0.0037
1.0	3.73(2)	4.92(2)	77	6.45	-0.18	3.21	6.10	0.0134
1.5	3.62(1)	4.48(1)	94	4.96	0.24	7.39	11.83	0.0092
2.0	4.04(3)	5.56(7)	112	50.09	-0.26	2.47	4.36	0.0236
2.5	3.95(4)	5.05(5)	98	46.2	-0.35	8.21	12.30	0.0352

Table 2. Best-fit chemical models of acidobasic equilibria of malonic acid in micellar media

 $\mu = 0.17 \text{ mol dm}^{-3}$ , pH meter readability = 0.01, Temp. = 303 K

Composi- tion	$\log \beta_1(\text{SD})$	$\log \beta_2(\text{SD})$	NP	$U_{\text{corr.}}$	Skew.	Kurt.	$\chi^2$	R
CTAB (% w/w) :								
0.0	5.26(1)	7.92(1)	70	1.0	-0.11	3.14	0.80	0.0050
5.0	5.25(1)	7.88(1)	104	0.13	0.69	6.96	18.62	0.0016
1.0	5.34(1)	7.97(1)	101	1.44	-1.31	5.26	16.69	0.0055
1.5	5.40(1)	8.14(1)	103	0.94	-0.28	3.71	11.40	0.0044
2.0	5.30(1)	7.95(1)	103	0.77	1.01	3.65	10.16	0.0039
2.5	5.37(1)	8.14(1)	102	2.01	0.85	3.49	4.00	0.0064
TX (% v/v) :								
0.5	5.47(1)	8.15(1)	99	2.54	-0.27	2.84	7.90	0.0069
1.0	5.46(1)	8.23(1)	101	1.11	0.04	4.12	8.06	0.0045
1.5	5.33(1)	8.06(1)	105	0.54	0.32	3.88	7.52	0.0033
2.0	5.12(1)	7.63(1)	101	0.66	-0.43	4.10	5.05	0.0037
2.5	5.31(1)	8.08(1)	104	1.05	0.60	3.21	6.15	0.0046
SLS (% w/w) :								
0.5	5.28(1)	7.84(1)	117	2.98	-0.20	2.24	9.93	0.0060
1.0	5.23(1)	7.96(1)	114	4.34	-0.18	3.20	5.75	0.0074
1.5	5.26(2)	8.00(3)	104	6.16	-0.26	3.35	3.40	0.0126
2.0	5.57(4)	8.19(5)	106	82.21	-0.79	3.79	10.34	0.0287
2.5	5.60(3)	8.22(4)	110	75.23	-0.66	2.88	9.71	0.0331

small values of  $U_{\text{corr}}$  (sum of squares of deviations in concentrations of ligand and hydrogen ion at all experimental points corrected for degrees of freedom) indicate that the model can present the experimental data. The kurtosis values of most of the systems indicate that the residuals form platykurtic pattern. The values of skewness between -1.29 and 0.24 for oxalic acid, and -0.79 and 1.01 for malonic acid evince that the residuals of many systems form a part of normal distribution; hence, least-squares method can be applied to the present data. The sufficiency of the model is further evident from the low crystallographic  $R$  value.

**Secondary formation functions :** Secondary formation functions like number of moles of alkali consumed per mole of ligand ( $a$ ) and average number of protons bound per mole of ligand ( $\bar{n}_H$ ) can detect the number of equilibria and polymeric species, respectively. A plot of  $a$  with pH (Fig. 1) has two plateaus along the  $a$ -axis indicating the existence of two equilibria. Plots of  $\bar{n}_H$  vs pH for different concentrations of the ligand should overlap if there are no polymeric species. The present study rules out the polymerization of oxalic and malonic acids. The pH values at the multiples of 0.5 values of  $\bar{n}_H$  correspond to the protonation constants of the ligands. The arrows in Fig. 1 indicate the pH values at  $\bar{n}_H = 0.5$  and 1.5 that correspond to  $\log K_1$  and  $\log K_2$  values. Two values are observed (Fig. 1B) in the case of malonic acid but only one for oxalic acid (Fig. 1A) because  $\log K_1$  is out of the pH range of the study for the latter.

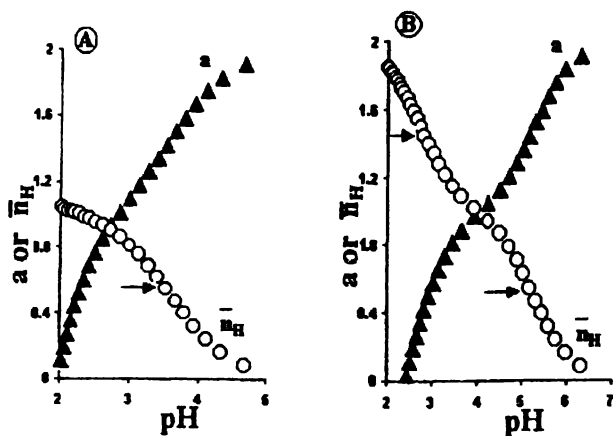


Fig. 1. Variation of  $\bar{n}_H$  and  $a$  with pH : (A) oxalic acid, (B) malonic acid.

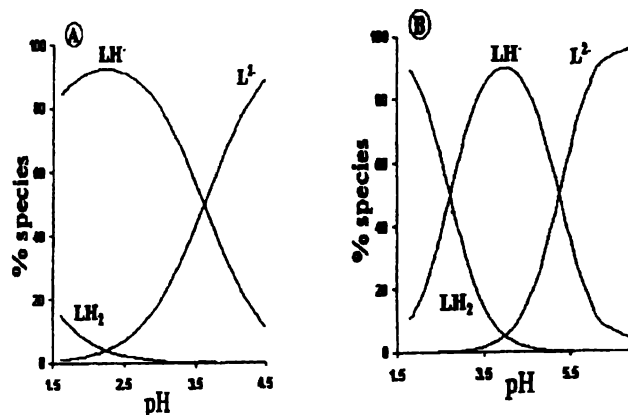
**Effect of systematic errors :** The results of a study on the effect of systematic errors in the concentrations of ingredients and electrode calibration on the magnitude of protonation constants are given in Table 3 for a typical system. The order of ingredients that influences the magnitudes of protonation constants due to incorporation of errors is alkali > ligand > acid > correction factor as was observed in our earlier studies<sup>3</sup>. Increase in the standard deviations of  $\log \beta$  upon incorporation of errors indicates that the experimental data have minimum errors.

**Table 3.** Effect of errors in dangerous parameters on the protonation constants of malonic acid in 1.5% (w/w) SLS-water mixture

Ingredient	Error %	log $\beta$ (SD)	
		0 1 1	0 1 2
log F	0	5.26(2)	8.00(3)
	-5	5.25(2)	7.97(3)
	-2	5.25(2)	7.98(3)
	+2	5.26(2)	8.00(3)
	+5	5.26(2)	8.00(3)
Alkali	-5	5.57(4)	8.45(6)
	-2	5.38(3)	8.16(4)
	+2	5.14(2)	7.82(3)
	+5	4.98(2)	7.59(3)
	-5	5.13(2)	7.73(3)
Acid	-2	5.21(2)	7.89(3)
	+2	5.31(2)	8.09(4)
	+5	5.38(3)	8.26(4)
	-5	5.09(2)	7.76(3)
	-2	5.19(2)	7.90(3)
Ligand	+2	5.32(3)	8.08(4)
	+5	5.42(3)	8.20(5)

**Distribution diagrams :** The distribution of  $LH_2$  and  $LH^-$  species of both oxalic and malonic acids at different pH values is shown in Fig. 2. The  $LH_2$  species is predominant at low pH. As the pH increases its concentration decreases exponentially and becomes almost zero at around pH 5 in case of oxalic acid and at pH 7 in case of malonic acid. The  $LH^-$  species of oxalic acid has the maximum concentration at  $\sim$ pH 2.0 (Fig. 2A) and that of malonic acid at  $\sim$ 5.0 (Fig. 2B). The free ligand ( $L^{2-}$ ) concentration progressively increases and attains the maximum at higher pH values. This conclusion is useful in predicting the possible metal-ligand complexes at a given pH.

**Effect of micelles :** The shift in the magnitude of protonation constants in micellar media compared to

**Fig. 2** Distribution diagrams of (A) oxalic acid and (B) malonic acid in 1.5% SLS-water mixture.

aqueous solution is attributed to the creation of a concentration gradient of protons between the interface and the bulk solution<sup>4</sup>. Further, micelles alter the medium dielectric constant which has a direct influence on the protonation equilibria<sup>5,6</sup>. The effective dielectric constant of the micellar surface differs from that of bulk water, but differs also from that expected for the paraffinic core of the micelle. An effective dielectric constant was estimated<sup>7</sup> as 32 for micelle surface of CTAB and SDS and 36 for TX. The surfactant concentration maintained in the present study are above critical micellar concentrations (0.0084 M for SLS, 0.0093 M for CTAB and 0.0089 M for TX) so that micelles are ensured in the solution. The ionic charge decreases during protonation of the carboxylate ions (eqns. 1 and 2),



This charge decrease is encouraged in the medium of decreasing dielectric constant. Hence the magnitudes of protonation constants must increase as the surfactant con-

**Table 4.** Total initial concentrations of ingredients (in mmol) in proton-ligand titrations

[NaOH] = 0.2 mol dm <sup>-3</sup> , V = 50 cm <sup>3</sup> , Temp. = 303 K, [Mineral acid] = 1.0 mmol, $\mu$ = 0.17 mol dm <sup>-3</sup>								
CTAB %(w/w)	TLO		TX-100 %(v/v)	TLO		SLS %(w/w)	TLO	
	Oxalic acid	Malonic acid		Oxalic acid	Malonic acid		Oxalic acid	Malonic acid
0.0	0.4478	0.6662	0.5	0.4478	0.4743	0.5	0.4478	0.4662
	0.7462	0.7770		0.7462	0.7905		0.7462	0.7770
1.0	0.4478	0.4527	1.0	0.4478	0.4743	1.0	0.4478	0.4662
	0.7462	0.7545		0.7462	0.7005		0.7462	0.7770
1.5	0.4478	0.4527	1.5	0.4478	0.4527	1.5	0.4478	0.4743
	0.7462	0.7545		0.7462	0.7545		0.7462	0.7905
2.0	0.4459	0.4527	2.0	0.4478	0.4527	2.0	0.4478	0.4743
	0.7462	0.7545		0.7462	0.7547		0.7462	0.7905
2.5	0.4459	0.4527	2.5	0.4478	0.4527	2.5	0.4478	0.4743
	0.7462	0.7545		0.7462	0.7545		0.7462	0.7905

centration increases. This is true in the case of TX as given in Figs. 3 and 4.

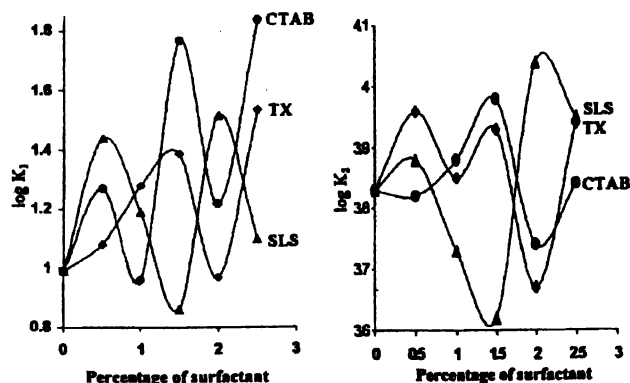


Fig. 3. Variation of stepwise protonation constants ( $\log K_1$  and  $\log K_2$ ) of oxalic acid with percentage of surfactant.

The SLS micellar surface has negative charge and so positively charged species or less negatively charged species are stabilized by SLS micelles. Hence the protonation constants of oxalic and malonic acids must be higher in SLS medium than that in TX medium. But the non-linear trend may be due to the dilution effect and competition between carboxylate in and negatively charged micelles for hydrogen ions<sup>8</sup>.

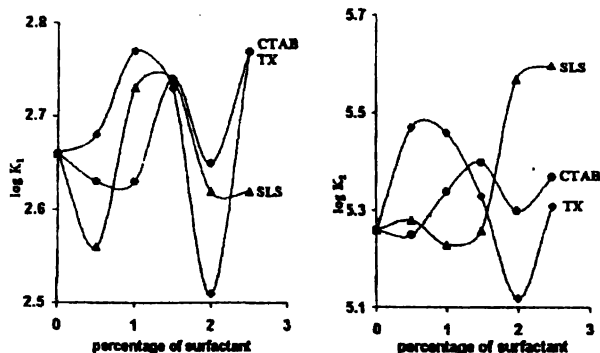


Fig. 4. Variation of stepwise protonation constants ( $\log K_1$  and  $\log K_2$ )

The CTAB micelles have positive surface charge and more negative ions, i.e. the deprotonated carboxylate ions are stabilized on the micellar surface. It means that the protonation constants are to be decreased, but dielectric constant of the medium enhances stability of the protonated species. Due to these opposing factors, a non-linear trend is observed in CTAB medium.

## Experimental

Oxalic acid and malonic acid (E. Merck, G.R.) solutions were prepared in triple-distilled water. Aqueous solutions of SLS (MW = 288.38; Qualigens A.R.), CTAB (MW = 364.45; B.D.H.), and TX (MW = 647,  $d = 1.07$ ; Merck) were also prepared in triple-distilled water.

The alkalimetric titrations were carried out in media containing varying compositions of SLS (0.5–2.5%, w/w), CTAB (0.5–2.5%, w/w) and TX (0.5–2.5%, v/v) maintaining an ionic strength of  $0.17 \text{ mol dm}^{-3}$  with sodium chloride at  $303 \pm 0.05 \text{ K}$ . A Systronics 335 pH meter was used. In each of the titrations, the titrand consisted of approximately 1 mmol of perchloric acid in SLS and TX media or hydrochloric acid in CTAB medium (because of the precipitation with perchloric acid). The concentrations of ingredients are given in Table 4. Potassium hydrogen phthalate ( $0.05 \text{ mol dm}^{-3}$ ) and borax ( $0.01 \text{ mol dm}^{-3}$ ) solutions were used to check the response of glass electrode in acidic and basic regions. The glass electrode was equilibrated for a week by immersing it in a well-stirred aquamicellar mixture containing inert electrolyte. Titration of strong acid with alkali was carried out at regular intervals to check whether complete equilibrium was achieved.

**Modelling strategy :** The approximate protonation constants of oxalic and malonic acids were calculated with the computer program SCPHD<sup>9</sup>. The best-fit chemical models were arrived at using the computer program MINIQUAD75<sup>10</sup>. The best set of protonation constants was selected based on chemical validation and residual analysis.

## References

1. E. Pelizzetti and E. Pramaro, *Anal. Chim. Acta*, 1983, **169**, 1.
2. G. S. Hartley, *Trans. Faraday Soc.*, 1934, **30**, 444.
3. M. S. Babu, G. N. Rao, K. V. Ramana and M. S. P. Rao, *J. Indian Chem. Soc.*, 2000, **77**, 380.
4. G. S. Hartley and J. W. Roe, *Trans. Faraday Soc.*, 1940, **36**, 101.
5. C. A. Bunton, *Catal. Rev. Sci. (Eng.)*, 1979, **20**, 1.
6. C. A. Bunton, L. S. Romsted and L. Supulveda, *J. Phys. Chem.*, 1980, **84**, 2611.
7. P. Mukherjee and A. Ray, *J. Phys. Chem.*, 1966, **70**, 2144.
8. J. S. Sukumar, G. N. Rao, K. V. Ramana and M. S. P. Rao, *Indian J. Chem., Sect. A*, 1996, **35**, 121.
9. R. S. Rao, A. Satyanarayana and G. N. Rao, Unpublished work.
10. P. Gans, A. Sabatini and A. Vacca, *Inorg. Chim. Acta*, 1976, **18**, 237.