

Apparent Dissociation Constant of Cellulose Gum Acid

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Gums are widely used in the paper, textile and petroleum industries. Gums, such as carboxymethyl cellulose (CMC) is synthetically derived from cellulose are used for microencapsulation of medicinal and food products. The aim of the study was to determine its ionization properties and acidic property. The dissociation behaviour of cellulose gum has been investigated by potentiometric titration. The apparent acidity constant, pK_a and the intrinsic acidity constant, pK_0 , have been determined from potentiometric titrations of carboxymethyl cellulose [degree of substitution (DS) = 0.70-0.85] in salt-free aqueous solutions of various concentrations at 20 °C. Furthermore effect of different neutralizing agents were tested on the titration curves. It was found that the extended Henderson-Hasselbalch equation reproduced measured data well and the dissociation suppressed progressively either by decreasing CMC concentration or with increasing counterion size. The concentration dependence of pH for different values of degree of dissociation (α), was found in the following form for CMC (degree of substitution = 0.70-0.85), $[pH]_0^\alpha = 5.04 + 2.72 \log [\alpha/(1-\alpha)]$.

Keywords: Potentiometric titration, Carboxymethyl cellulose, Apparent acidity constant.

INTRODUCTION

Carboxymethyl cellulose (CMC) is a natural polyelectrolyte used as a stabilizer, thickener and protective agent in food and drug industries. For example in frozen products, gums help prevent the formation of ice crystals [1]. Sodium carboxymethyl cellulose is a bulk chemical with wide applications in the cellulose and food industries. Its trade name is CMC or cellulose gum [2]. Carboxymethyl cellulose has been used as a model substance in studied of the acid–base properties of polyelectrolytes by the potentiometric titration technique [3]. Acid–base properties of many polyelectrolyte solutions have been reported for polyvinylsulfonic acid [4], polysaccharide acids [5], arabic acid [6,7] and carboxymethyl cellulose acid [8,9]. The potentiometric titration of weak polyacids in aqueous solutions has been extensively studied to understand the behaviour of polyelectrolyte systems both from experimental and theoretical points of view [10-12].

The purpose of this study was a further understanding of the polymer concentration and the size of counterion on the CMC (degree of substitution: 0.70-0.85) acid dissociation parameters in aqueous salt-free solutions at 20 °C.

EXPERIMENTAL

A cation exchange (Amberlite IR 120) resin column was used for getting CMC acid. Also the low viscosity of NaCMC

(0.70-0.85 degree of substitution) (Sigma-Aldrich Chemie GmbH CH-9471 Buchs Switzerland), LiOH, NaOH, KOH and HCl (E.Merck AG, Darmstadt, Germany) were used.

Preparation of CMC acid: 30 g Amberlit IR 120 (sodium-activated resin) was set up in a column (50 × 1 cm). The resin was changed to a hydrogen activated resin by running a 10 % solution of hydrochloric acid through the column and then rinsing with distilled water. Regeneration of the column was carried out in the same manner. 40 g (Amberlite IR 120) resin was used also for the getting CMC acid, (HCMC), prepared from the low density of 1 % NaCMC solution and then the more concentrated solution of HCMC was prepared by evaporating it under vacuum at 40 °C. The concentration of this stock solution was determined by electrometric pH titration and was found to be 2.7×10^{-2} eq g/L referred to COOH, from which the rest of the desired concentrations were prepared [5]. The equivalent weight of dried CMC acid was found to be 281.6 g/eq by potentiometric titration. Concentrated stock solutions of dry polymer were made up weight [6]. The standard lithium hydroxide, sodium hydroxide and potassium hydroxide solutions were prepared in conductivity water.

Methods and measurements: Potentiometric titrations and pH measurements were performed at 20 °C with Metrohm Model 632 Digital pH-meter (Metrohm AG, CH-9100 Herisau, Switzerland) with a combined glass electrode and the drifts in measurements were eliminated by using a magnetic stirrer

during the course of the titration. For adjusting pH, buffer solutions (pH: 4.00 and 7.00) were used.

The potentiometric titrations of (i) CMC acid (DS: 0.70-0.85) solution of different concentrations with NaOH and of (ii) solution with different neutralizing agents, was carried out in salt-free system at 20 °C.

Treatment of data: The fraction of carboxyls ionized (α) is given by

$$\alpha = [(H^+) + (NaOH) - (OH^-)]/(\text{polymer})$$

where (H^+) refers to molarity of free H^+ ; ($NaOH$), the molarity of added titrant; (OH^-), the molarity of free OH^- ; and (polymer), the total molarity of CMC acid and residues. In practice, the value of (OH^-) is negligible. The value of (H^+) was obtained from titration of solvent, using the assumption that the activity coefficient of hydrogen ion is not significantly affected by polymer in concentrations used.

The pH of the polyelectrolyte solution is given by a modified form of Henderson equation [13]:

$$pH = pK_a + n \log [\alpha/(1-\alpha)] \quad (1)$$

where pK_a is the value of pH at half neutralization, α the degree of dissociation and n , an empirical index of the intramolecular electrostatic interactions. A related problem is that of obtaining the intrinsic acid dissociation constant, pK_0 , from experimental data [12]. The apparent dissociation constant is given by following equation [8].

$$pK_a = pK_0 + m.\alpha^{1/3} \quad (2)$$

K_0 is the intrinsic dissociation constant of a single acid group in the uncharged molecule in the polymer (*i.e.* to the limiting value for zero degree of ionization). m and n are constants for a given titration.

The concentration dependence of pH for different values of α could be represented by Katchalsky and Spitnik [13] as follows:

$$[pH]_c^\alpha = [pH]_0^\alpha - Ac^{1/2} \quad (3)$$

where c is the concentration of carboxyl groups, in moles per liter, $[pH]_c^\alpha$ is the pH at a concentration c and degree of dissociation (α), $[pH]_0^\alpha$ is the pH extrapolated to infinite dilution [14] at degree of dissociation (α).

Statistical analysis: All experiments were performed in triplicate and results expressed as mean $\pm$ standard deviation. Descriptive statistical analyses were performed using MICROCAL ORIGIN 8.0 (Origin Lab Corp., Northampton, MA, USA) for calculating the mean and the standard error of the mean. (SPSS Inc., Chicago, IL, USA) for Windows version 13, the data were evaluated by ANalysis Of VAriance (ANOVA) [15].

RESULTS AND DISCUSSION

Effect of concentration: It is generally recognized that the acid behaviour of the carboxyl groups in polyelectrolytes may be described by a modified form of Henderson equation, eqn. 1. The empirical equations [13], eqn. 1 and eqn. 2, relating pK_a , pK_0 and α had been applied to potentiometric titration data of arabic acid and carboxymethyl cellulose [8,9]. α is the degree of dissociation and K_a and K_0 are the apparent and intrinsic dissociation constants respectively. m and n are constants for a given titrations.

In this study, the neutralization curves of CMC acid with various concentrations were shown in Fig. 1. It may be seen from the curves that the arabic acid behaves like a strong monobasic acid [7,19]. The Henderson-Hasselbalch plots, according to eqn. 1, shows the titration behaviour of CMC acid at four different concentrations (Fig. 2).

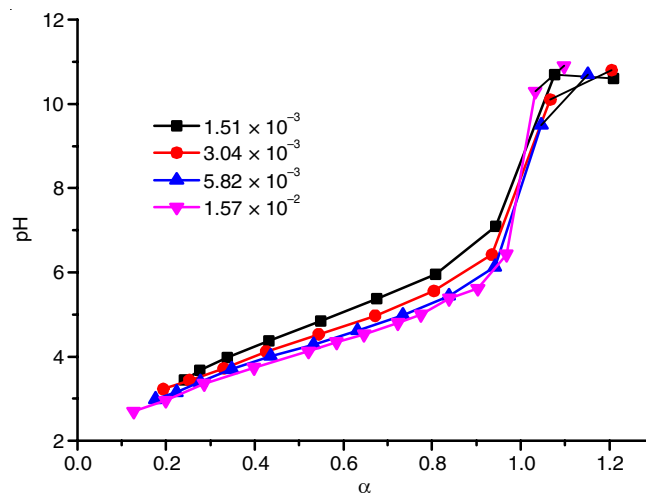


Fig. 1. Potentiometric titrations of carboxymethyl cellulose (degree of substitution = 0.70-0.85) solution at different concentrations: (eq.g/L referred to COOH)

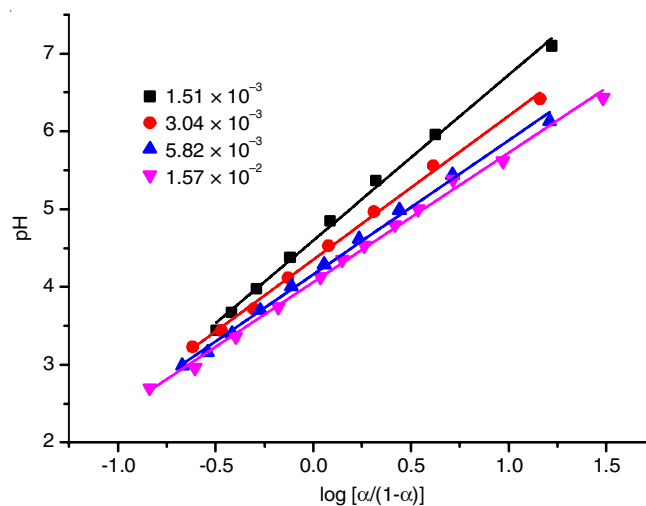


Fig. 2. Henderson-Hasselbalch plots for different concentrations of carboxymethyl cellulose (DS = 0.7-0.85) acid; (eq.g/L referred to COOH)

The values of pK_a obtained from Henderson-Hasselbalch parameters decrease smoothly with increasing concentration (Table-1) whereas pK_0 is intensive to changes in concentrations as is evident from Fig. 3 for CMC acid titrated with NaOH. The concentration dependence of pH for different values of degree of dissociation (α) was found in the following form for CMC acid (as shown in Figs. 4 and 5 for CMC):

$$[pH]_0^\alpha = 5.04 + 2.72 \log [\alpha/(1-\alpha)] \text{ for CMC acid}$$

Effect of different neutralizing agents: pH values of CMC (6.57×10^{-3} eq.g/L referred to COOH) solution was measured during the process of neutralization with LiOH, NaOH and KOH. The results obtained were shown in Fig. 6 and the values of pK_a and pK_0 obtained from eqns. 1 and 2, respectively, were

TABLE-1
VALUES OF pK_a , n , m AND pK_0 FOR CARBOXYMETHYL CELLULOSE [DEGREE OF SUBSTITUTION (DS) = 0.70-0.85] ACID AS A FUNCTION OF THE POLYMER CONCENTRATION IN SALT-FREE SYSTEMS

	Concentration ($N \times 10^3$)	pK_a	n	pK_0	m
CMC acid	1.51	4.60 ± 0.03	2.13 ± 0.05	0.80 ± 0.27	4.96 ± 0.33
	3.04	4.35 ± 0.02	1.85 ± 0.04	1.70 ± 0.22	3.48 ± 0.28
	5.82	4.16 ± 0.02	1.72 ± 0.04	1.91 ± 0.12	2.96 ± 0.15
	15.72	4.06 ± 0.02	1.66 ± 0.03	1.97 ± 0.19	2.76 ± 0.23

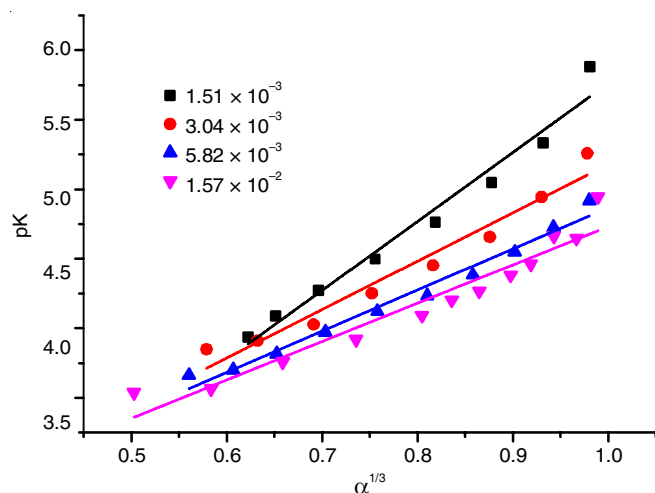


Fig. 3. Plots of pK against $\alpha^{1/3}$ for various concentrations of carboxymethyl cellulose (DS = 0.70-0.85) acid, (eq.g/L referred to COOH) titrated with NaOH in absence of neutral salt

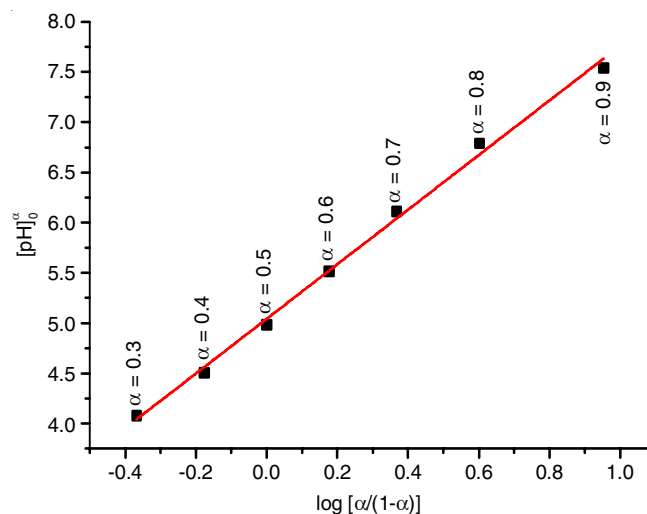


Fig. 5. Plots of $[pH]_0^\alpha$ versus $\log[\alpha/(1-\alpha)]$ for carboxymethyl cellulose (DS = 0.70-0.85); α = degree of dissociation

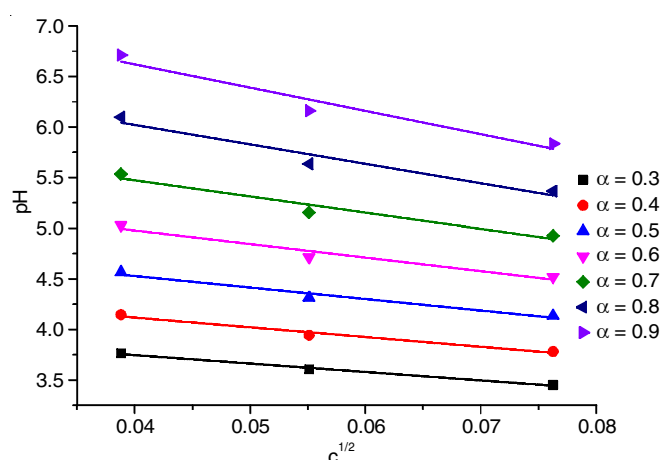


Fig. 4. Plots of pH vs. square root concentration of carboxyl groups for different values of α for carboxymethyl cellulose (DS = 0.70-0.85), (1.51×10^{-3} , 3.04×10^{-3} and 5.82×10^{-3} eq.g/L referred to COOH) acid; α = degree of dissociation

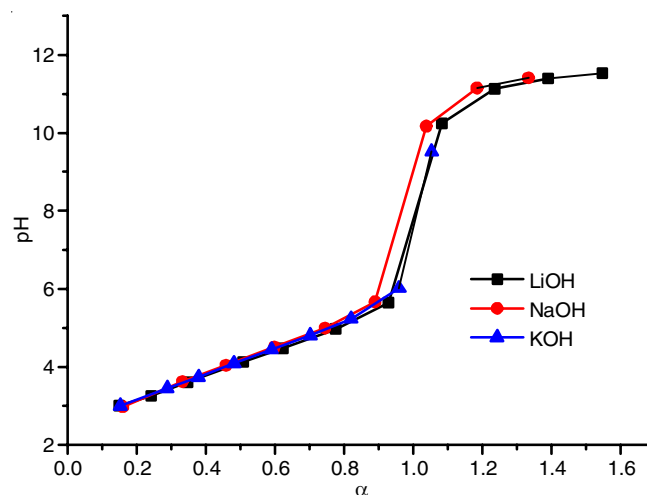


Fig. 6. Titrations of CMC acid (6.57×10^{-3} mol/L referred to COOH) with LiOH, NaOH and KOH; α : degree of dissociation

tabulated in Table-2. The Henderson-Hasselbalch parameters for CMC titrated with different neutralizing agents were also shown in Table-2. The values of n and K_a , apparent dissociation constant, increased with increasing size of the dehydrated counterions. Since the potential on the polyion increases with

the size of the counter ions, site binding becomes less significant as the size of the dehydrated counter ion increases [9,17]. The structures of the hydrated metal ions in aqueous solution display a variety of configurations depending on the size and electronic properties of the metal ion. The hydrated alkali metal ions display the expected coordination numbers and configurations based

TABLE-2
HENDERSON-HASSELBALCH PARAMETERS FOR TITRATION OF CARBOXYMETHYL CELLULOSE [DEGREE OF SUBSTITUTION (DS) = 0.70-0.85] ACID WITH DIFFERENT NEUTRALIZING REAGENTS IN SALT-FREE SYSTEMS, ION RADII FOR 6-COORDINATED

	Cation	Cation radius ($\text{\AA}$)	pK_a	n	pK_0	m
CMC acid (6.57×10^{-3} N)	Li^+	0.79	4.08 ± 0.03	1.48 ± 0.06	2.63 ± 0.17	1.91 ± 0.21
	Na^+	1.07	4.18 ± 0.02	1.68 ± 0.03	2.25 ± 0.20	2.52 ± 0.25
	K^+	1.38	4.13 ± 0.04	1.49 ± 0.06	2.45 ± 0.15	2.21 ± 0.19

on their ionic radii. The coordination numbers and figures of the alkali metal ions are still not characterized in aqueous solution in such a way that certain values can be given even though the lithium and sodium ions seem to be octahedral and the potassium ions square antiprismatic [18]. New proposed ionic radii [19] are for six-coordinate lithium, 0.79 Å as well as for sodium, 1.07 Å and potassium, 1.38 Å.

Conclusion

Food gums have hydrophilic molecules, which can combine with water to form viscous solutions and gels. The high hydration has a thickening and stabilizing effect and also the ability to form gels. The properties of food gums depend on their ionization properties and acidic property. The dissociation behaviour of cellulose gum has been investigated by potentiometric titration. It was found that the extended Henderson-Hasselbalch equation reproduced measured data well and the dissociation suppressed progressively either by decreasing CMC acid concentration.

The values of pK_a and n have been found to depend (i) on the nature of the polymer, (ii) on the concentration of neutral salts in the system, (iii) on the concentration of the polyion itself and (iv) on the distance between the carboxyl groups along the polymer backbone [8,9]. An important problem in polyelectrolyte theory is the prediction of the titration curve of weak polyacids, in particular predicting the salt dependence of pK_a , apparent dissociation constant of the polyacid, as a function of the degree of acid ionization in the solution.

REFERENCES

1. A. Asghar, F.M. Anjum, M.W. Tariq and S. Hussain, *Turk. J. Biol.*, **29**, 237 (2005).
2. M. Glicksman, *Gum Technology in the Food Industry*, Academic Press, New York, p. 412 (1969).
3. I. Aggeryd and A. Olin, *Talanta*, **32**, 645 (1985); [https://doi.org/10.1016/0039-9140\(85\)80160-0](https://doi.org/10.1016/0039-9140(85)80160-0).
4. H. Eisenberg and G.R. Mohan, *J. Phys. Chem.*, **63**, 671 (1959); <https://doi.org/10.1021/j150575a008>.
5. J.V. Swintosky, L. Kennon and J. Tingstad, *J. Am. Pharm. Assoc.*, **44**, 109 (1955); <https://doi.org/10.1002/jps.3030440216>.
6. D.R. Briggs, *J. Phys. Chem.*, **38**, 867 (1933); <https://doi.org/10.1021/j150358a002>.
7. R.H. Schleif, T. Higuchi and L.W. Busse, *J. Am. Pharm. Assoc.*, **40**, 98 (1951); <https://doi.org/10.1002/jps.3030400213>.
8. H.C. Trivedi, C.K. Patel and R.D. Patel, *Makromol. Chem.*, **182**, 3561 (1981); <https://doi.org/10.1002/macp.1981.021821218>.
9. H.C. Trivedi, C.K. Patel and R.D. Patel, *Makromol. Chem.*, **182**, 3569 (1981); <https://doi.org/10.1002/macp.1981.021821219>.
10. M. Nagasawa, T. Murase and K. Kondo, *J. Phys. Chem.*, **69**, 4005 (1965); <https://doi.org/10.1021/j100895a060>.
11. R.L. Cleland, J.L. Wang and D.M. Detweiler, *Macromolecules*, **15**, 386 (1982); <https://doi.org/10.1021/ma00230a037>.
12. C.P. Woodbury, *J. Phys. Chem.*, **97**, 3623 (1993); <https://doi.org/10.1021/j100116a030>.
13. A. Katchalsky and P. Spitnik, *J. Polym. Sci., Polym. Phys. Ed.*, **2**, 487 (1947); <https://doi.org/10.1002/pol.1947.120020504>.
14. F.H. Chowdhury and S.M. Neale, *J. Polym. Sci. Part A*, **1**, 2881 (1963); <https://doi.org/10.1002/pol.1963.100010911>.
15. J.C. Miller and J.N. Miller, *Statistics for Analytical Chemistry*, Ellis Horwood, Prentice Hall, London, U.K., edn 3 (1993).
16. J.Th.G. Overbeek, *Pure Appl. Chem.*, **46**, 91 (1976); <https://doi.org/10.1351/pac197646020091>.
17. H.P. Gregor and M. Frederick, *J. Polym. Sci., Polym. Phys. Ed.*, **23**, 451 (1957); <https://doi.org/10.1002/pol.1957.1202310338>.
18. I. Persson, *Pure Appl. Chem.*, **82**, 1901 (2010); <https://doi.org/10.1351/PAC-CON-09-10-22>.
19. J. Mähler and I. Persson, *Inorg. Chem.*, **51**, 425 (2012); <https://doi.org/10.1021/ic2018693>.