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Volume Changes of Ionization of Ethylenemalonic acid

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Abstract

Densities of aqueous solutions of 1,1-cyclopropanedicarboxylic acid (ethylenemalonic acid) have been determined at 25 ^{o}C for various degrees of neutralization of the acid. From the densimetric titration curve the apparent molar volume of undissociated acid, as well as the volume changes for ionization of the first and the second carboxylic group, ΔV_1 and ΔV_2, respectively, have been calculated. The resulting values at infinite dilutions, $\Delta V_1^{\infty} = -7.0$ ml/mol $COOH_{(1)}$ and $\Delta V_2^{\infty} = -28.9$ ml/mol $COOH_{(2)}$ are comparable to those found for other weak diprotic acids.

INTRODUCTION

During our recent physicochemical studies with aqueous solutions of fullerenehexamalonic acid it became evident that parallel studies with solutions of ethylenemalonic acid (EMA; 1,1-cyclopropanedicarboxylic acid) could be helpful in interpreting the experimental results. Therefore, some measurements with water solutions of this diprotic organic acid have been undertaken. In this contribution we present densimetric studies. On the basis of these experiments the apparent molar volume of unionized EMA,  $>\langle{}^{COOH}_{COOH}$, have been calculated, as well as the volume change for ionization of the first and of the second carboxylic groups.

EXPERIMENTAL SECTION

Materials. Ethylenemalonic acid (EMA, 1,1-cyclopropanedicarboxylic acid, ≥98%) was supplied by Fluka. In all experiments three times quartz distilled water was used.

The concentration of the stock solution of EMA was determined by potentiometric and conductometric titrations with NaOH.

Potentiometric titration curves were recorded at 25°C by Metrohm automatic titrator 736 GP Titrino using glass and calomel electrodes.

Densities of the solutions were measured with a Paar digital density meter DMA 60 with external measuring cell DMA 602. An ultrathermostat attached to the instrument controlled the temperature at 25.00 ± 0.002°C. The accuracy of density measurements was within $\pm 4.5 \cdot 10^{-6}$ g cm^{-3}.

RESULTS AND DISCUSION

The densimetric titration curve of aqueous solutions of ethylenemalonic acid is presented in Figure 1. As expected, the slope of the curve changes at the degree of neutralization $\alpha_n = 0.5$. From these values the apparent molar volume, ϕ_V, has been calculated from

$$\phi_V = \frac{1}{\rho_o}\left(\overline{M} - \frac{\rho - \rho_o}{c}\right) \tag{1}$$

where ρ and ρ_o are densities of a solution and water, respectively, and $\overline{M}$ is the molar mass of partially neutralized EMA. From eq 1 calculated values of ϕ_V are plotted as function of the degree of neutralization, α_n, in Figure 2. The value $\alpha_n = 1$ corresponds to complete neutralization of both carboxylic groups. Since the measurement were performed with solutions in which the solute concentration was small, the distinction between the degree of ionization, α, and neutralization, α_n

$$\alpha = \alpha_n + \left(\left[H^+\right] - \left[OH^-\right]\right) / c \tag{2}$$

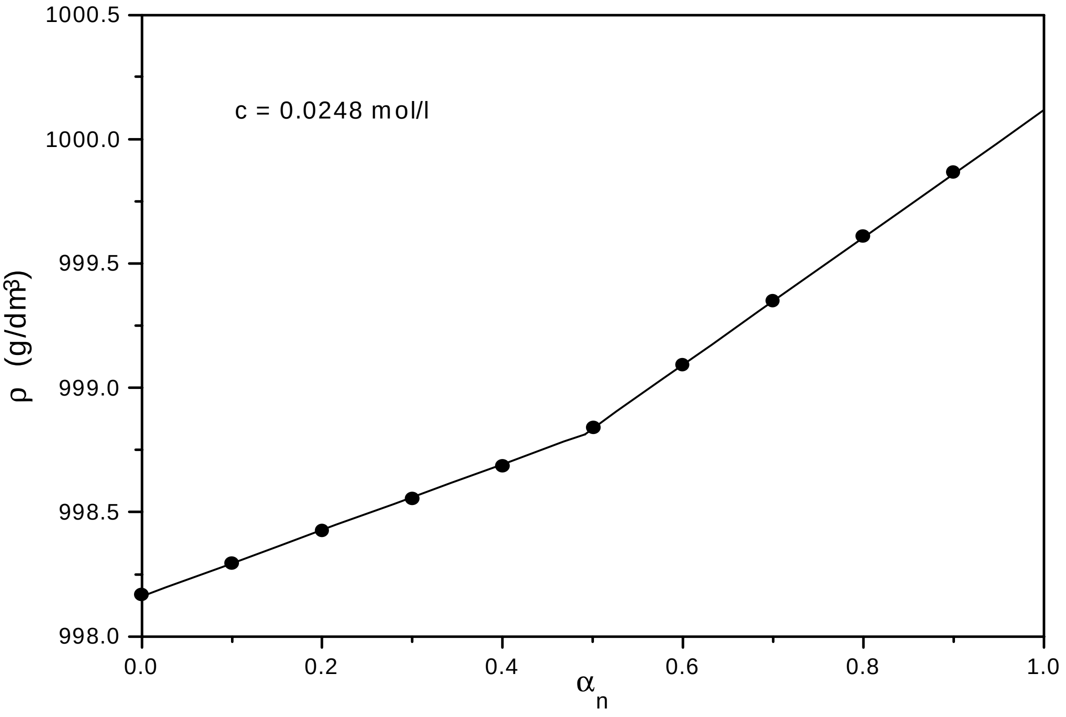
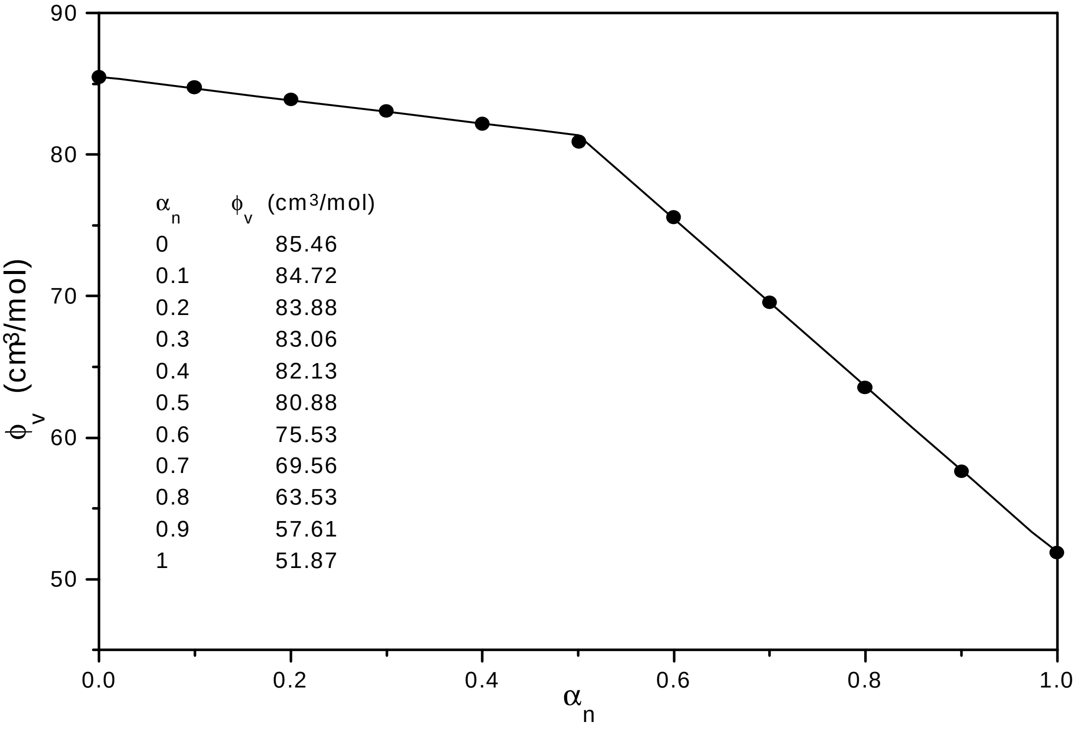


Figure 1. Densimetric titration of aqueous solutions of ethylenemalonic acid at 25 $^{\circ}$C and at concentration $c = 0.0248$ mol/L.

needed to be taken into account. In eq 2, which follows from the electroneutrality condition, the concentration of H^+ ions, $[H^+]$, was calculated from the measured pH by taking into account the activity coefficient of H^+ ion calculated from the Debye-Hückel limiting law. In most cases the concentration of OH^- ions, $[OH^-]$, can be neglected. Obviously, the degree of ionization of the first carboxylic group, α_1, is $\alpha_1 = 2\alpha$ for $0 \leq \alpha_n \leq 0.5$, and of the second group, α_2, is $\alpha_2 = 2\alpha - 1$ for $0.5 \leq \alpha_n \leq 1$. Figure 2 shows that the apparent molar volume first decreases with the increasing degree of neutralization until $\alpha_n = 0.5$, and after that a sharper decrease of the curve is observed. The added NaOH first reacts with the strong $COOH_{(1)}$ groups producing a break in the curve at the first equivalent point, followed by much steeper decrease of the curve when the weaker $COOH_{(2)}$ group starts to ionize.

From the experimental values for the acid and its monosodium and disodium salts we can



α_n	ϕ_v (cm^3/mol)
0	85.46
0.1	84.72
0.2	83.88
0.3	83.06
0.4	82.13
0.5	80.88
0.6	75.53
0.7	69.56
0.8	63.53
0.9	57.61
1	51.87

Figure 2. Apparent molar volume of partly neutralized EMA in water at 25 ^{o}C as a function of the degree of neutralization. Concentration c = 0.0248 mol/L.

estimate the apparent molal volume, ϕ_u, of undissociated acid, as well as the volume changes for ionization of the first and the second carboxylic groups, ΔV_1 and ΔV_2, respectively. The conductivity measurements have disclosed [1] that the ionization reaction

$$>\!\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right. \rightarrow\, >\!\left\langle\begin{matrix}COO^{-}\\COOH\end{matrix}\right. + H^{+} \qquad (3)$$

proceeds far at experimental concentrations. Therefore, the molecules and ions must contribute to the measured apparent molar volume, ϕ_V. It is well known that the additivity principle [2]

$$c\phi_V = \sum c_i\phi_i \qquad (4)$$

may be expected to be fulfilled very closely at high dilutions, and to be a reasonable approximation at moderate concentrations. By applying eq 4 to the process 3 we obtain

$$c\phi_V = c(1-\alpha_1)\phi_u + c\alpha_1\phi_{d1} + c\alpha_1\phi_{H+} \tag{5}$$

where ϕ_{d1} stands for the apparent molar volume of the $>\langle^{COO^-}_{COOH}$ constituent. Upon rearranging eq 5 we get

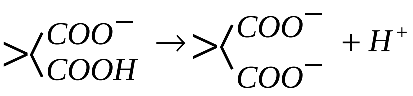
$$\phi_u = \frac{\phi_V}{1-\alpha_1} - \frac{\alpha_1}{1-\alpha_1}(\phi_{H^+} + \phi_{d1}) \tag{6}$$

The value of ϕ_{d1} was obtained from the extrapolated value of ϕ_V at $\alpha_1 = 1$ ($\alpha_n = 0.5$), which is ϕ_V of the $>\langle^{COONa}_{COOH}$ species, taking into account the value of the apparent molar volume [3] of Na^+ ion at the experimental concentration. The degree of ionization, α_1, of the first carboxylic group at $\alpha_n = 0.5$ has been calculated from eq 2. From eq 6 calculated value of ϕ_u is $\phi_u = 89.7$ ml /mol EMA.

We can calculate also the volume change of ionization for the process 3, ΔV_1, from

$$\Delta V_1 = \phi_{H^+} + \phi_{d1} - \phi_u \tag{7}$$

The resulting value is –6.7 ml/mol EMA, which is the ionization volume for the first carboxylic group. Similarly, we can obtain the ionization volume, ΔV_2, for the second ionization step



$$>\langle^{COO^-}_{COOH} \rightarrow >\langle^{COO^-}_{COO^-} + H^+ \tag{8}$$

$$\Delta V_2 = \phi_{H^+} + \phi_{d2} - \phi_{d1} \tag{9}$$

The apparent molar volume of the $>\langle^{COO^-}_{COO^-}$ species, $\phi_{d2} = 54.7$ ml/mol EMA, has been obtained from the experimental value of ϕ_V at $\alpha_n = 1$ ($\alpha_2 = 1$), taking into account $\phi_{V(Na+)}$

at the experimental concentration, which has been calculated from its conventional value at infinite dilution, $\phi_{Na^+}^{\infty}$, and the limiting expression of Debye and Hückel [4]

$$\phi_i = \phi_i^{\infty} + 0.660\, z_i^2 \left(\sum \nu_i z_i^2\right)^{1/2} \sqrt{c} \tag{10}$$

The resulting value is $\Delta V_2 = -27.9$ ml/mol COOH$_{(2)}$. We see that both ionization volumes are negative, a situation that is normal because of the electrostriction of water produced by the ions resulting in a ionization process.

For solutions in which EMA is partly neutralized with NaOH combination of eqs 3-7 gives

$$\phi_V = \phi_u + \alpha_1 \Delta V_1 + 2\alpha_n (\phi_{Na^+} - \phi_{H^+}) \tag{11}$$

for the range $0 \le \alpha_n \le 0.5$. From this expression we can obtain the intermediate volumes of ionization between the individual experimental points

$$\Delta V_1 = \frac{\Delta \phi_V}{\Delta \alpha_1} - 2(\phi_{Na^+} - \phi_{H^+}) \frac{\Delta \alpha_n}{\Delta \alpha_1} \tag{12}$$

Similarly, for the range $0.5 \le \alpha_n \le 1$ we get

$$\phi_V = (\phi_{Na^+} + \phi_{d1}) + \alpha_2 \Delta V_2 + 2\alpha_n (\phi_{Na^+} - \phi_{H^+}) \tag{13}$$

and

$$\Delta V_2 = \frac{\Delta \phi_V}{\Delta \alpha_2} - 2(\phi_{Na^+} - \phi_{H^+}) \frac{\Delta \alpha_n}{\Delta \alpha_2} \tag{14}$$

It has to be mentioned that for the range $0.5 \le \alpha_n \le 1$ the quotient $2\Delta\alpha_n/\Delta\alpha_2 \approx 1$. From eqs 12 and 14 calculated values of the intermediate volumes of ionization are presented in Figure 3. The sharp decrease of the curve at $\alpha_n = 0.5$ can be ascribed to the releasing of the proton from both carboxylate groups to which it is bound by the intramolecular

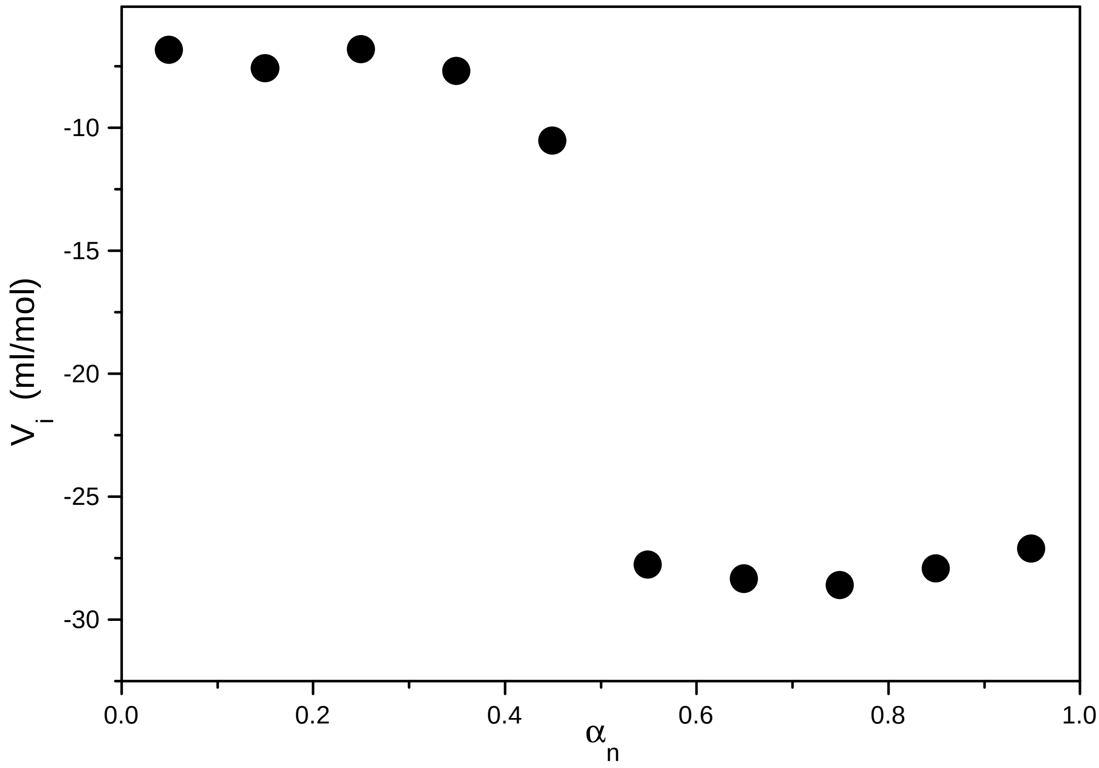


Figure3. Volume change on ionization of partly neutralized EMA at 25 °C as a function of the degree of neutralization. Concentration c = 0.0248 mol/L.

hydrogen bounds above α_n = 0.5. It is interesting that a similar ΔV_i curve has been observed with the high molecular weight copolymer of maleic acid with ethylene obtained by direct dilatometry [5].

Usually the ionization volumes at infinite dilution are reported. The apparent molar volumes of the H^+, Na^+, and the ethylenemalonate anions, $>\!\langle^{COOH}_{COO^-}$ and $>\!\langle^{COO^-}_{COO^-}$, have been expressed from eq 10, and for the apparent molar volume of undissociated acid ϕ_u it was assumed that $\phi_u = \phi_u^\infty$. The resulting values of the ionization volumes are $\Delta V_1^\infty = -7.0$ ml/mol $COOH_{(1)}$ and $\Delta V_2^\infty = -28.9$ ml/mol $COOH_{(2)}$. These values are comparable to those found for other weak acids.

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POVZETEK

Vodnim raztopinam 1,1-ciklopropandikarboksilne kisline (etilenmalonske kisline) smo za različne stopnje nevtralizacije kisline pri 25 °C izmerili gostote. Iz tako dobljene denzimetrične titracijske krivulje smo izračunali navidezni molski volumen neionizirane kisline in volumske spremembe za ionizacijo prve in druge karboksilne skupine ΔV_1 in ΔV_2. Dobljeni vrednosti pri neskončnem razredčenju, $\Delta V_1^{\infty} = -7.0$ ml/mol $COOH_{(1)}$ in $\Delta V_2^{\infty} = -28.9$ ml/mol $COOH_{(2)}$, sta primerljivi z rezultati, ki so jih dobili z drugimi šibkimi dvobaznimi kislinami.