Adsorption of Organic Acids on Weakly Basic Ion Exchanger: Equilibria for Binary Systems

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The separation of organic acids is very important, because they are starting materials for chemicals, especially biodegradable plastics. Their purities affect the cost and quality of products. Takatsuji and Yoshida (1994) reported that organic acids (citric acid and malic acid) were removed well from wine by adsorption on weakly, basic ion exchangers. The adsorption isotherms were expressed by the Langmuir equation. However, it was suggested that the equilibria should be analyzed by considering more complex adsorption reactions. In a previous article (Takatsuji and Yoshida, 1997), we presented the theoretical equations for adsorption isotherms of organic acids (acetic acid, malic acid, and citric acid) on a weakly basic resin, DIAION WA30, in the single component systems.

In the present work, we have investigated the equilibrium isotherms for adsorption of organic acids on DIAION WA30 in the three sets of the binary systems prepared using the acetic, malic and citric acids. It was assumed that these organic acids were adsorbed by the neutralization reaction with the fixed amino group of the weakly basic resin. By applying the mass action law and considering the material balance, theoretical equations for adsorption isotherms were derived. The experimental titration curves were compared with those theoretical equations.

Experimental Studies

The ion exchanger used in this experimental study was a commercial weakly basic resin DIAION WA30 (Mitsubishi Chemical Co.). The experimental physical properties are listed in Table 1. The resin particles were prepared as described in the previous article (Takatsuji and Yoshida, 1997). Since the equilibria for the binary systems were fully reached in 7 days, the resin particles and the organic acid solutions were contacted for 7 days. All experiments were carried out at 293 K.

Results and Discussion

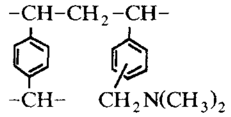
Adsorption of acetic acid and malic acid

Figure 1 shows the titration curves for the single and binary component systems which consist of acetic and malic acids. The one point dashed and dotted lines show the theoretical ones for the single component systems of acetic acid (Eq. 1) and malic acids (Eq. 2), respectively. The theoretical equations were derived in the previous article (Takatsuji and Yoshida, 1997)

$$q_A = \frac{K_A Q[\mathrm{AH}]}{1 + K_A[\mathrm{AH}]} \tag{1}$$

$$q_M = \frac{Q}{2} + \frac{(1 - K_{M1}[\mathrm{MH_2}])\left\{(1 + K_{M1}[\mathrm{MH_2}]) - \sqrt{(1 + K_{M1}[\mathrm{MH_2}])^2 + 8K_{M2}[\mathrm{MH_2}]Q}\right\}}{8K_{M2}[\mathrm{MH_2}]} \tag{2}$$

Table 1. Experimental Physical Properties of DIAION WA30

Unit molecular structure	
Particle diameter (m)	6.505×10^{-4}
Apparent density (kg of wet resin/m^3 of wet resin)	1,131
Porosity	0.486
Water content (kg of water/kg of wet resin)	0.429
Saturation capacity of HCl, Q (kmol/m^3)	2.80

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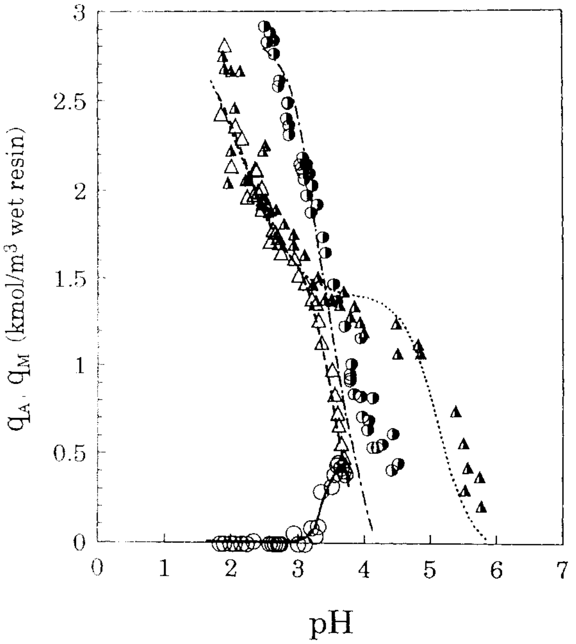

Figure 1. Titration curve for adsorption of acetic acid and malic acid on WA30 in the single and binary systems.

(◑) Acetic acid and (▲) malic acid in the single system; (○) acetic acid and (△) malic acid in the binary system; (- - -) Eq. 1; (-----) Eq. 2; (——) Eq. 3; (— — —) Eq. 4.

where [AH] and $[MH_2]$ represent the equilibrium concentrations of undissociated acetic acid ($C_2H_4O_2$) and malic acid ($C_4H_6O_5$) in the liquid phase (kmol/m^3), respectively. q_A and q_M denote the adsorbent-phase concentrations of acetic acid and malic acid (kmol/m^3 of wet resin), respectively. Q is the saturation capacity determined by measuring the equilibrium isotherm of HCl (kmol/m^3). K_A (m^3/Kmol). K_{M1} (m^3/kmol) and K_{M2} (m^3/kmol)^2, are the equilibrium constants and they are shown in Table 2.

The solid and dashed lines show the theoretical ones for the binary component system of acetic acid and malic acid. The theoretical equations (Eqs. 3 and 4) were derived by applying the mass action law to Eqs. A1–A10 given in Appendix 1

$$q_A = \frac{K_A[AH]\left\{\sqrt{(1+K_A[AH]+K_{M1}[MH_2])^2+8K_{M2}[MH_2]Q}-(1+K_A[AH]+K_{M1}[MH_2])\right\}}{4K_{M2}[MH_2]} \qquad (3)$$

$$q_M = \frac{Q}{2} + \frac{(1+K_A[AH]-K_{M1}[MH_2])\left\{(1+K_A[AH]+K_{M1}[MH_2])-\sqrt{(1+K_A[AH]+K_{M1}[MH_2])^2+8K_{M2}[MH_2]Q}\right\}}{8K_{M2}[MH_2]} \qquad (4)$$

Considering the material balance for the organic acids in the batch system, Eqs. 5 and 6 are obtained

$$\rho V(C_{A0}-C_A) = Wq_A \qquad (5)$$

$$\rho V(C_{M0}-C_M) = Wq_M \qquad (6)$$

where ρ, V and W are the apparent density of the resin (kg of wet resin/m^3 of wet resin), the volume of the solution (m^3) and the weight of the wet resin particles (kg), respectively. C_{A0} and C_{M0} are the initial concentrations of acetic acid and malic acid in the liquid phase (kmol/m^3), respectively. C_A and C_M are the equilibrium concentrations of acetic acid and malic acid in the liquid phase (kmol/m^3), respectively, and they can be related with [AH] and $[MH_2]$ as follows

$$C_A = [AH]+[A^-] = \left(1+\frac{K_a}{[H^+]}\right)[AH] \qquad (7)$$

$$C_M = [MH_2]+[MH^-]+[M^2] = \left(1+\frac{K_{ma1}}{[H^+]}+\frac{K_{ma1}K_{ma2}}{[H^+]^2}\right)[MH_2] \qquad (8)$$

where pK_a, pK_{ma1} and pK_{ma2} are 4.56, 3.24 and 4.71 at 293 K, respectively (Martell and Smith, 1977). The condition of the electroneutrality gives

$$[H^+] = [A^-]+[MH^-]+2[M^{2-}]+[OH^-] = \frac{K_a[AH]}{[H^+]}+\frac{K_{ma1}[MH_2]}{[H^+]}+\frac{2K_{ma1}K_{ma2}[MH_2]}{[H^+]^2}+\frac{K_W}{[H^+]} \qquad (9)$$

where K_W is 0.682×10^{-14} at 273 K. Using Eqs. 3–9, Eqs. 10 and 11 are obtained

$$(2K_Af_2f_3-K_Af_1f_4-K_{M1}f_1f_3)[AH]^2 + \left\{C_{A0}(K_Af_4+K_{M1}f_3)+\left(2C_{M0}-\frac{WQ}{\rho V}\right)+K_Af_4+2K_Af_2f_5 - f_1f_4-K_{M1}f_1f_5\right\}[AH]+C_{A0}(f_4+K_{M1}f_5)=0 \qquad (10)$$

$$[MH_2] = -\frac{f_3[AH]+f_5}{f_4} \qquad (11)$$

where

$$f_1 = 1+\frac{k_a}{[H^+]} \qquad (12)$$

$$f_2 = 1+\frac{K_{ma1}}{[H^+]}+\frac{K_{ma1}K_{ma2}}{[H^+]^2} \qquad (13)$$

Table 2. Equilibrium Constants of Adsorption of Acetic Acid, Malic Acid and Citric Acid

Adsorption of Acetic Acid (AH)				
AH:				
CH_3COOH	Equilibrium constant of Eq. A1	K_a	$(kmol/m^3)$	2.75×10^{-5}
	Equilibrium constant of Eq. A4	K_A	$(m^3/kmol)$	1.5×10^2
Adsorption of Malic Acid (MH_2)				
MH_2:				
CH(OH)COOH | CH_2COOH	Equilibrium constant of Eq. A5	K_{ma1}	$(kmol/m^3)$	5.75×10^{-4}
	Equilibrium constant of Eq. A6	K_{ma2}	$(kmol/m^3)$	1.95×10^{-5}
	Equilibrium constant of Eq. A9	K_{M1}	$(m^3/kmol)$	3.5×10^4
	Equilibrium constant of Eq. A10	K_{M2}	$[(m^3/kmol)^2]$	2.1×10^7
Adsorption of Citric Acid (CH_3)				
CH_3:				
CH_2COOH | C(OH)COOH | CH_2COOH	Equilibrium constant of Eq. A11	K_{ca1}	$(kmol/m^3)$	1.35×10^{-3}
	Equilibrium constant of Eq. A12	K_{ca2}	$(kmol/m^3)$	4.47×10^{-5}
	Equilibrium constant of Eq. A13	K_{ca3}	$(kmol/m^3)$	2.04×10^{-6}
	Equilibrium constant of Eq. A17	K_{C1}	$(m^3/kmol)$	1.0×10^5
	Equilibrium constant of Eq. A18	K_{C2}	$[(m^3/kmol)^2]$	8.0×10^8
	Equilibrium constant of Eq. A19	K_{C3}	$[(m^3/kmol)^3]$	2.0×10^{10}

$$f_3 = K_a[H^+] \tag{14}$$

$$f_4 = K_{ma1}[H^+] + 2K_{ma1}K_{ma2} \tag{15}$$

$$f_5 = [H^+](K_W - [H^+]^2) \tag{16}$$

From Eqs. 10–16, [AH] and $[MH_2]$ can be calculated by measuring pH in the solution.

The solid line (q_A) and dashed line (q_M) in Figure 1 show the theoretical ones calculated from Eqs. 3 and 4, respectively. The values of K_A, K_{M1} and K_{M2} in the single component systems given in Table 2 were used. The theoretical lines correlate the data reasonably well. In pH < 3.5, the adsorbent phase concentration of acetic acid in the binary system (q_A) shown by (—O—) decreased with decreasing pH. In pH < 3, $q_A \risingdotseq 0$. On the other hand, the absorbent phase concentration of malic acid in the binary system (q_M) shown by (-- △ --) coincided with that in the single component system (--- ▲ ---) in pH < 3. It will be noted that the malic acid may be selectively adsorbed in the binary system of the acetic and malic acids.

Adsorption of acetic acid and citric acid

Figure 2 shows the titration curves for the single and binary systems of acetic and citric acids. The one point dashed and dotted lines show the theoretical ones of the single component systems of acetic acid and citric acid, respectively. Those theoretical equations (Eqs. 1 and 17) were derived in the previous article (Takatsuji and Yoshida, 1997)

$$q_C = \frac{Q}{3} + \frac{2K_{C2}}{27K_{C3}}\left(1 - 2K_{C1}[CH_3] + \frac{2K_{C2}^2[CH_3]}{9K_{C3}}\right) + \left(\frac{2}{3} - \frac{4K_{C2}}{27K_{C1}K_{C3}} - \frac{1}{3K_{C1}[CH_3]}\right)A + \frac{K_{C2}}{3K_{C1}^2[CH_3]}A^2 \tag{17}$$

where

$$A = \omega^r\sqrt[3]{-\frac{b}{2}+\sqrt{R}} + \omega^{-r}\sqrt[3]{-\frac{b}{2}-\sqrt{R}} \quad (R > 0) \quad (r = 0,1,2) \tag{18}$$

$$A = (-1)^r 2\sqrt{-a}\cos\frac{\theta + r\pi}{3} \quad (R < 0) \quad (r = 0,1,2) \tag{19}$$

$$\omega = \frac{-1+\sqrt{3}\,i}{2} \tag{20}$$

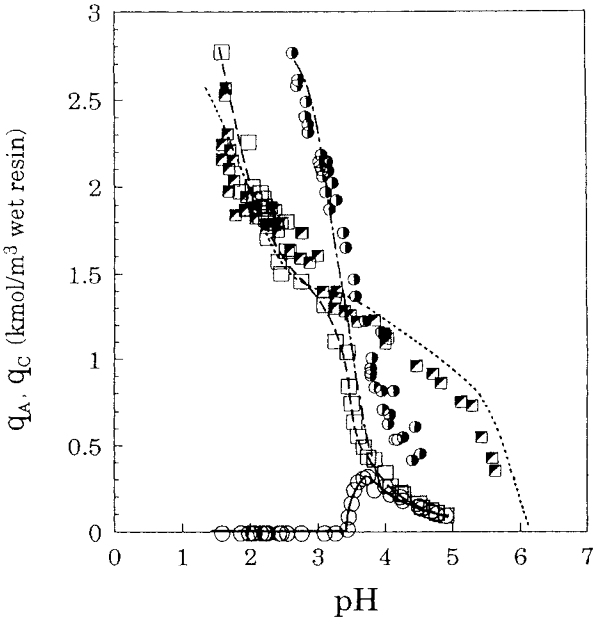

Figure 2. Titration curve for adsorption of acetic acid and citric acid on WA30 in the single and binary systems.

(◑) Acetic acid and (◪) citric acid in the single system; (○) acetic acid and (□) citric acid in the binary system; (–·–) Eq. 1; (-----) Eq. 17; (——) Eq. 25; (— — —) Eq. 26.

$$R = \frac{b^2}{4} + a^3 \tag{21}$$

$$\cos\theta = -\frac{b}{2\sqrt{-a^3}} \tag{22}$$

$$a = \frac{K_{C1}^2}{3^2 K_{C3}}\left(K_{C1} - \frac{2^2 K_{C2}^2}{3^2 K_{C3}}\right)[\mathrm{CH_3}]^2 + \frac{K_{C1}^2}{3^2 K_{C3}}[\mathrm{CH_3}] \tag{23}$$

$$b = \frac{2K_{C1}^3 K_{C2}}{3^3 K_{C3}^2}\left(\frac{2^3 K_{C2}^2}{3^3 K_{C3}} - K_{C1}\right)[\mathrm{CH_3}]^3 - \frac{K_{C1}^3}{3K_{C3}}\left(\frac{2K_{C2}}{3^2 K_{C3}} + Q_C\right)[\mathrm{CH_3}]^2 \tag{24}$$

where $[\mathrm{CH_3}]$ represents the equilibrium concentration of undissociated citric acid ($C_6H_8O_7$) in the liquid phase (kmol/m^3). q_C denotes the adsorbent-phase concentration of citric acid (kmol/m^3 of wet resin). K_{C1} (m^3/kmol), K_{C2} (m^3/kmol)^2, and K_{C3} (m^3/kmol)^3 are the equilibrium constants, and they are shown in Table 2.

The solid and dashed lines show the theoretical ones in the binary component system of acetic acid and citric acid, and those theoretical equations were derived as below. Applying the mass action law to Eqs. A1–A4 and Eqs. A11–A19 in Appendix 1, Eqs. 25–27 are derived

$$q_A = \frac{K_A[\mathrm{AH}]}{K_{C1}[\mathrm{CH_3}]} q_{C1} \tag{25}$$

$$q_C = q_{C1} + \frac{K_{C2}}{K_{C1}^2[\mathrm{CH_3}]} q_{C1}^2 + \frac{K_{C3}}{K_{C1}^3[\mathrm{CH_3}]^2} q_{C1}^3 \tag{26}$$

$$q_{C1}^3 + \frac{2K_{C1}K_{C2}[\mathrm{CH_3}]}{3K_{C3}} q_{C1}^2 + \frac{K_{C1}^2[\mathrm{CH_3}](1 + K_A[\mathrm{AH}] + K_{C1}[\mathrm{CH_3}])}{3K_{C3}} q_{C1} - \frac{K_{C1}^3[\mathrm{CH_3}]^2 Q}{3K_{C3}} = 0 \tag{27}$$

where q_{C1} denotes $[\mathrm{R\text{-}NH^+CH_2^-}]$. Considering the material balance for the organic acids in the batch system, Eqs. 5 and 28 are obtained

$$\rho V(C_{C0} - C_C) = Wq_C \tag{28}$$

where C_{C0} and C_C are the initial and the equilibrium concentrations of citric acid in the liquid phase (kmol/m^3), respectively. C_C can be correlated with $[\mathrm{CH_3}]$ by Eq. 29

$$C_C = [\mathrm{CH_3}] + [\mathrm{CH_2^-}] + [\mathrm{CH^{2-}}] + [\mathrm{C^{3-}}] = \left(1 + \frac{K_{ca1}}{[\mathrm{H^+}]} + \frac{K_{ca1}K_{ca2}}{[H^+]^2} + \frac{K_{ca1}K_{ca2}K_{ca3}}{[\mathrm{H^+}]^3}\right)[\mathrm{CH_3}] \tag{29}$$

where pK_{ca1}, pK_{ca2} and pK_{ca3} are 2.87, 4.35, and 5.69 at 293 K, respectively (Martell and Smith, 1977). The condition of the electroneutrality gives

$$[\mathrm{H^+}] = [\mathrm{A^-}] + [\mathrm{CH_2^-}] + 2[\mathrm{CH^{2-}}] + 3[\mathrm{C^{3-}}] + [\mathrm{OH^-}] = \frac{K_a[\mathrm{AH}]}{[\mathrm{H^+}]} + \frac{K_{ca1}[\mathrm{CH_3}]}{[\mathrm{H^+}]} + \frac{2K_{ca1}K_{ca2}[\mathrm{CH_3}]}{[\mathrm{H^+}]^2} + \frac{3K_{ca1}K_{ca2}K_{ca3}[\mathrm{CH_3}]}{[\mathrm{H^+}]^3} + \frac{K_W}{[\mathrm{H^+}]} \tag{30}$$

Using Eqs. 5, 7 and 25–30, Eqs. 31 and 32 are obtained

$$\begin{aligned}&\left(3K_A^2 f_6 f_7 - K_A^2 f_1 f_8 - 2K_A K_{C1} f_1 f_7 + \frac{\rho V}{W} K_{C2} f_1^2 f_7\right)[\mathrm{AH}]^3 \\ &+ \left\{\left(K_A^2 f_8 + 2K_A K_{C1} f_7 - \frac{2\rho V}{W} K_{C2} f_1 f_7\right) C_{A0} + 3K_A^2 f_8 C_{C0} \right. \\ &\quad + 3K_A^2 f_6 f_9 - K_A f_1 f_8 - 2K_A K_{C1} f_1 f_9 \\ &\quad \left. + \frac{\rho V}{W} K_{C2} f_1^2 f_9 - \frac{WQ}{\rho V} K_A^2 f_8 \right\}[\mathrm{AH}]^2 \\ &+ \left\{\left(K_A f_8 + 2K_A K_{C1} f_9 - \frac{2\rho V}{W} K_{C2} f_1 f_9\right) C_{A0} \right. \\ &\quad \left. + \frac{\rho V}{W} K_{C2} f_7 C_{A0}^2 \right\}[\mathrm{AH}] + \frac{\rho V}{W} K_{C2} f_9 C_{A0}^2 = 0\end{aligned} \tag{31}$$

$$[\mathrm{CH_3}] = \frac{f_7[\mathrm{AH}] + f_9}{f_8} \tag{32}$$

where

$$f_6 = 1 + \frac{K_{cal}}{[\mathrm{H^+}]} + \frac{K_{ca1}K_{ca2}}{[\mathrm{H^+}]^2} + \frac{K_{cal}K_{ca2}K_{ca3}}{[\mathrm{H^+}]^3} \tag{33}$$

$$f_7 = K_a[\mathrm{H^+}]^2 \tag{34}$$

$$f_8 = K_{cal}[\mathrm{H^+}]^2 + 2K_{ca1}K_{ca2}[\mathrm{H^+}] + 3K_{ca1}K_{ca2}K_{ca3} \tag{35}$$

$$f_9 = [\mathrm{H^+}]^2(K_W - [\mathrm{H^+}]^2) \tag{36}$$

From Eqs. 31–36, [AH] and $[\mathrm{CH_3}]$ can be calculated by measuring pH in the solution.

The solid line (q_A) and dashed line (q_C) in Figure 2 show the theoretical ones calculated from Eqs. 25 and 26, respectively, and they correlate the data reasonably well. The values of K_A, K_{C1}, K_{C2}, and K_{C3} in the single component systems listed in Table 2 were used. q_A (—O—) showed a peak around pH = 3.7. In pH < 3.5, $q_a \fallingdotseq 0$. q_C (--□--) increased with decreasing pH. In pH < 3, it was close to that in the single component system (----▨----). It can be assumed that the citric acid may be selectively adsorbed in the binary component system in pH < 3.5. In pH > 4, $q_A \fallingdotseq q_C$.

Adsorption of malic acid and citric acid

Figure 3 shows the titration curves for the single and binary systems of malic and citric acids. The one point and

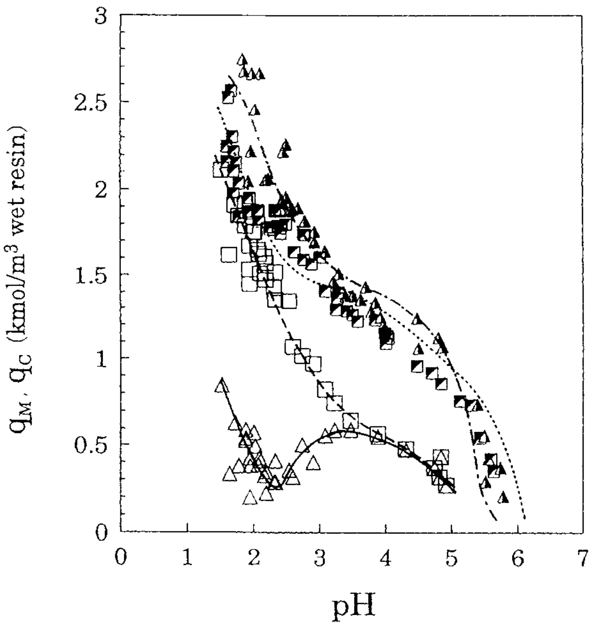

Figure 3. Titration curve for adsorption of malic acid and citric acid on WA30 in the single and binary systems.

(▲) Malic acid and (◩) citric acid in the single system; (△) malic acid and (□) citric acid in the binary system; (---) Eq. 2, (-----) Eq. 17, (——) Eq. 37; (— — —) Eq. 26.

dotted lines show the theoretical ones of the single component systems of malic acid and citric acid calculated from Eqs. 2 and 17, respectively. The solid and dashed lines show the theoretical ones for the binary component system of malic acid and citric acid, and those theoretical equations were derived as below. Applying the mass action law to Eqs. A5–A19, Eqs. 26, 37, and 38 are derived

$$q_M = \frac{K_{M1}[\mathrm{MH_2}]}{K_{C1}[\mathrm{CH_3}]} q_{C1} + \frac{K_{M2}[\mathrm{MH_2}]}{K_{C1}^2[\mathrm{CH_3}]^2} q_{C1}^2 \tag{37}$$

$$q_{C1}^3 + \left(\frac{2K_{M2}K_{C1}[\mathrm{MH_2}]}{3K_{C3}} + \frac{2K_{C1}K_{C2}[\mathrm{CH_3}]}{3K_{C3}} \right) q_{C1}^2 + \frac{K_{C1}^2[\mathrm{CH_3}](1 + K_{M1}[\mathrm{MH_2}] + K_{C1}[\mathrm{CH_3}])}{3K_{C3}} q_{C1} - \frac{K_{C1}^3[\mathrm{CH_3}]^2 Q}{3K_{C3}} = 0 \tag{38}$$

Considering the material balance for the malic and citric acids in the batch system, Eqs. 6 and 28 are obtained, respectively. The condition of the electroneutrality gives

$$[\mathrm{H^+}] = [\mathrm{MH^-}] + 2[\mathrm{M^{2-}}] + [\mathrm{CH_2^-}] + 2[\mathrm{CH^{2-}}] + 3[\mathrm{C^{3-}}] + [\mathrm{OH^-}] = \frac{K_{ma1}[\mathrm{MH_2}]}{[\mathrm{H^+}]} + \frac{2K_{ma1}K_{ma2}[\mathrm{MH_2}]}{[\mathrm{H^+}]^2} + \frac{K_{ca1}[\mathrm{CH_3}]}{[\mathrm{H^+}]} + \frac{2K_{ca1}K_{ca2}[\mathrm{CH_3}]}{[\mathrm{H^+}]^2} + \frac{3K_{ca1}K_{ca2}K_{ca3}[\mathrm{CH_3}]}{[\mathrm{H^+}]^3} + \frac{K_W}{[\mathrm{H^+}]} \tag{39}$$

Using Eqs. 6, 8, 26, 28, 29 and 37–39, Eqs. 40 and 41 are obtained

$$[\mathrm{MH_2}] = \frac{4\rho V C_{M0} K_{C2}}{4\rho V K_{M2} f_1 + W K_{M1}^2 (d^2 - 1)} \tag{40}$$

$$[\mathrm{CH_3}] = \frac{f_{10}[\mathrm{MH_2}] + f_9}{f_8} \tag{41}$$

where

$$f_{10} = K_{ma1}[\mathrm{H^+}]^2 + 2K_{ma1}K_{ma2}[\mathrm{H^+}] \tag{42}$$

The value of d in Eq. 40 can be obtained by solving the following equation (Eq. 43)

$$\begin{aligned}
&\frac{W}{4\rho V} K_{M1}^4 K_{C2} f_9 d^4 \\
&\quad + \frac{W}{2\rho V} (K_{M1}^4 K_{C2} f_9 - 2K_{M1}^3 K_{M2} K_{C1} f_9 - K_{M1}^3 K_{M2} f_8) d^3 \\
&+ \Bigg\{ (K_{M1}^2 K_{M2} K_{C2} f_{10} + 2K_{M1}^2 K_{M2}^2 f_8) C_{M0} + 3K_{M1}^2 K_{M2}^2 f_8 C_{C0} \\
&\quad - \left(K_{M1}^3 K_{M2} K_{C1} f_9 + \frac{3K_{M1}^3 K_{M2} f_8}{2} + K_{M1}^2 K_{M2}^2 f_8 Q \right) \frac{W}{\rho V} \\
&\quad + 3K_{M1}^2 K_{M2}^2 f_6 f_9 + K_{M1}^2 K_{M2} K_{C2} f_2 f_9 \Bigg\} d^2 \\
&+ \Bigg\{ (2K_{M1}^2 K_{M2} K_{C2} f_{10} - 4K_{M1} K_{M2}^2 K_{C1} f_{10} + 2K_{M1}^2 K_{M2}^2 f_8) C_{M0} \\
&+ \left(K_{M1}^3 K_{M2} K_{C1} f_9 - \frac{K_{M1}^4 K_{C2} f_9}{2} + \frac{K_{M1}^3 K_{M2} f_8}{2} \right) \frac{W}{\rho V} \\
&- 4K_{M1} K_{M2}^2 K_{C1} f_2 f_9 + 2K_{M1}^2 K_{M2} K_{C2} f_2 f_9 - 2K_{M1} K_{M2}^2 f_2 f_8 \Bigg\} d \\
&+ \left(K_{M1}^2 K_{M2} K_{C2} f_{10} - 4K_{M1} K_{M2}^2 K_{C1} f_{10} + \frac{12\rho V}{W} K_{M2}^3 f_6 f_{10} \right) C_{M0} \\
&+ \left(\frac{12\rho V}{W} K_{M2}^3 f_2 f_8 - 3K_{M1}^2 K_{M2}^2 f_8 \right) C_{C0} \\
&+ \frac{12\rho V}{W} K_{M2}^3 f_2 f_6 f_9 + \Bigg(K_{M1}^3 K_{M2} K_{C1} f_9 - \frac{K_{M1}^4 K_{C2} f_9}{4} \\
&+ \frac{K_{M1}^3 K_{M2} f_8}{2} + K_{M1}^2 K_{M2}^2 f_8 Q \Bigg) \frac{W}{\rho V} \\
&- 3K_{M1}^2 K_{M2}^2 f_6 f_9 - 4K_{M1} K_{M2}^2 K_{C1} f_2 f_9 + K_{M1}^2 K_{M2} K_{C2} f_2 f_9 \\
&\qquad - 2K_{M1} K_{M2}^2 f_2 f_8 - 4K_{M2}^3 f_2 f_8 Q = 0
\end{aligned} \tag{43}$$

From Eqs. 40–43, $[\mathrm{MH_2}]$ and $[\mathrm{CH_3}]$ can be calculated by measuring pH in the solution.

The solid line (q_M) and dashed line (q_C) in Figure 3 show the theoretical ones calculated from Eqs. 37 and 26, respectively, and they correlate the data reasonably well. The values of K_{M1}, K_{M2}, K_{C1}, K_{C2}, and K_{C3} in the single component systems listed in Table 2 were used for the theoretical calculations. Around pH = 3.3, q_M (—△—) showed a peak but in pH < 2.3, it increased with decreasing pH. q_C (--□--) increased with decreasing pH. The citric acid was selectively adsorbed in the binary system of the malic and citric acids in pH < 3.3. However, the malic acid was adsorbed even when low pH. This is totally different from the behavior of acetic acid in the binary systems of (acetic acid + malic acid) and (acetic acid + citric acid), that is, acetic acid was adsorbed little in low pH. In addition, in pH > 3.3, $q_M = q_C$.

Notation

K_a = equilibrium constant, kmol/m^3
K_A = equilibrium constant, m^3/kmol
K_{ma1} = equilibrium constant, kmol/m^3
K_{ma2} = equilibrium constant, kmol/m^3
K_{M1} = equilibrium constant, m^3/kmol
K_{M2} = equilibrium constant, (m^3/kmol)^2
K_{ca1} = equilibrium constant, kmol/m^3
K_{ca2} = equilibrium constant, kmol/m^3
K_{ca3} = equilibrium constant, kmol/m^3
Q = saturation capacity for adsorption of HCl, kmol/m^3

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Appendix 1: Neutralization Reactions Between Amino Groups Fixed in the Resin Phase and Organic Acids in the Liquid Phase

AH

$$\mathrm{AH} \xrightleftharpoons{K_a} \mathrm{H^+ + A^-} \tag{A1}$$

$$\mathrm{R{-}N + H^+} \xrightleftharpoons{K_1} \mathrm{R{-}NH^+} \tag{A2}$$

$$\mathrm{R{-}NH^+ + A^-} \xrightleftharpoons{K_2} \mathrm{R{-}NH^+A^-} \tag{A3}$$

Equation A4 is obtained by summing Eqs. A1–A3.

$$\mathrm{R{-}N + AH} \xrightleftharpoons{K_A} \mathrm{R{-}NH^+A^-} \tag{A4}$$

MH$_2$

$$\mathrm{MH_2} \xrightleftharpoons{K_{ma1}} \mathrm{H^+ + MH^-} \tag{A5}$$

$$\mathrm{MH^-} \xrightleftharpoons{K_{ma2}} \mathrm{H^+ + M^{2-}} \tag{A6}$$

$$\mathrm{R{-}NH^+ + MH^-} \xrightleftharpoons{K_3} \mathrm{R{-}NH^+\,MH^-} \tag{A7}$$

$$\mathrm{2R{-}NH^+ + M^{2-}} \xrightleftharpoons{K_4} \mathrm{(R{-}NH^+)_2M^{2-}} \tag{A8}$$

Equations A9 and A10 are obtained by summarizing Eqs. A5–A8 and A2.

$$\mathrm{R{-}N + MH_2} \xrightleftharpoons{K_{M1}} \mathrm{R{-}NH^+\,MH^-} \tag{A9}$$

$$\mathrm{2R{-}N + MH_2} \xrightleftharpoons{K_{M2}} \mathrm{(R{-}NH^+)_2M^{2-}} \tag{A10}$$

CH$_3$

$$\mathrm{CH_3} \xrightleftharpoons{K_{ca1}} \mathrm{H^+ + CH_2} \tag{A11}$$

$$\mathrm{CH_2^-} \xrightleftharpoons{K_{ca2}} \mathrm{H^+ + CH^{2-}} \tag{A12}$$

$$\mathrm{CH^{2-}} \xrightleftharpoons{K_{ca3}} \mathrm{H^+ + C^{3-}} \tag{A13}$$

$$\mathrm{R{-}NH^+ + CH_2^-} \xrightleftharpoons{K_5} \mathrm{R{-}NH^+\,CH_2^-} \tag{A14}$$

$$\mathrm{2R{-}NH^+ + CH^{2-}} \xrightleftharpoons{K_6} \mathrm{(R{-}NH^+)_2CH^{2-}} \tag{A15}$$

$$\mathrm{3R{-}NH^+ + C^{3-}} \xrightleftharpoons{K_7} \mathrm{(R{-}NH^+)_3C^{3-}} \tag{A16}$$

Equations A17–A19 are obtained by summing Eqs. A11–A16 and A2.

$$\mathrm{R{-}N + CH_3} \xrightleftharpoons{K_{C1}} \mathrm{R{-}NH^+\,CH_2^-} \tag{A17}$$

$$\mathrm{2R{-}N + CH_3} \xrightleftharpoons{K_{C2}} \mathrm{(R{-}NH^+)_2CH^{2-}} \tag{A18}$$

$$\mathrm{3R{-}N + CH_3} \xrightleftharpoons{K_{C3}} \mathrm{(R{-}NH^+)_3C^{3-}} \tag{A19}$$

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