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Removal of Organic Acids from Wine by Adsorption on Weakly Basic Ion Exchangers: Equilibria for Single and Binary Systems

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ABSTRACT

In order to remove or reduce the organic acids from wine and liqueur, we investigated their adsorption on weakly basic resins. CC-S, WA-10, and WA-30, which were made from chitosan, acryl, and styrene, respectively, appeared technically feasible. The concentration of the fixed amino group in CC-S, WA-10, and WA-30 is 3.31, 2.37, and 2.81 kmol/m^3, respectively. These resins adsorbed citric acid and malic acid from wine selectively. The equilibrium isotherms for single component systems of citric acid or malic acid were little affected by the initial concentration (C_0 = 0.01, 0.02, and 0.03 kmol/m^3) and by ethanol. The equilibrium data were correlated by the Langmuir equation. The equilibrium data were correlated by the Langmuir equation. The equilibrium isotherms for the binary system of citric and malic acids were affected by the initial concentration (C_{A0} = 0.02, C_{B0} = 0.03 kmol/m^3; C_{A0} = 0.014, C_{B0} = 0.004 kmol/m^3). The equilibrium data were correlated reasonably well by the Markham–Benton equation. The equilibrium constants for citric acid were much larger than those for malic acid. By using these constants, the equilibrium data for adsorption of citric and malic acids from wine could be adequately correlated by the Markham–Benton equation.

INTRODUCTION

In the production of juice or wine made from fruit, the removal of acids or the reduction of concentration of acids are important to improve the final quality, especially the taste. The removal of acids from fruit juice has been investigated by Voss (1), Adhikary et al. (2), Maeda (3), and Orita et al. (4). Voss (1) and Adhikary et al. (2) treated acids in fruit juice by electrodialysis, and Maeda (3) and Orita et al. (4) reported that acids were removed from fruit juice by an ion-exchange resin. Recently, acids in fruit juices have been treated by an ion-exchange method because it is more economical and convenient than the electrodialysis method. In wine production the acid taste is adjusted by microorganisms. The ion-exchange method has not yet been used for removing or reducing organic acids from wine and liqueur. If the ion-exchange method is used, the removal and/or reduction of acids from wine or liqueur may be easily controlled.

The adsorption of acid (H^+A^-) on a strongly basic resin may be expressed by

$$R\text{—}OH + H^+A^- \rightleftharpoons R\text{—}A + H_2O \quad (1)$$

where R—OH denotes a strongly basic resin (OH^- type), and the desorption is expressed by

$$R\text{—}A + Na^+OH^- \rightleftharpoons R\text{—}OH + Na^+A^- \quad (2)$$

The adsorption generally shows high selectivity because Eq. (1) is the ion-exchange reaction with a neutralization reaction, but desorption is not so easy.

The adsorption of acid on a weakly basic resin may be expressed by

$$R\text{—}NH_2 + H^+A^- \rightleftharpoons R\text{—}NH_3^+A^- \quad (3)$$

where R—NH_2 denotes the weakly basic resin. The acid is adsorbed selectively on the resin by the acid/base neutralization reaction. The desorption may be expressed by

$$R\text{—}NH_3^+A^- + Na^+OH^- \rightleftharpoons R\text{—}NH_2 + Na^+A^- + H_2O \quad (4)$$

The acid may be desorbed irreversibly from the resin by ion exchange in the neutralization reaction. From the above considerations, organic acids may be removed more efficiently from wine or liqueur by using a weakly basic resin than by using a strongly basic resin. Experimental work on the adsorption of strong acids (HCl, HNO_3, and H_2SO_4) on weakly basic resin have been reported by Bhandari et al. (5, 6), Rao and Gupta (7), and Helfferich and Hwang (8). Experimental works on the adsorption of weak acids (HCOOH and $ClCH_2COOH$) on the weakly basic resin have been reported by Bhandari et al. (9). The authors have considered the possibility of using a weakly basic resin and chitosan resins in order to recover organic acids from wine or liqueur. As chitosan is natural biopolymer, it may be easily applied in the food or medical industries. The removal of organic acids by using chitosan has not been reported.

EXPERIMENTAL

To clean the resin before measuring the equilibrium isotherm, we packed the resin particles (about 10 g) into a column which was of 1 cm inside diameter, and passed 5×10^{-3} m^3 of 500 mol/m^3 aqueous NaOH solution through the bed at a flow rate of 1.16 cm^3/min. Thereafter we washed the bed with distilled and deionized water thoroughly, and we kept the resin particles in pure water.

At first we made a sample screening test to find feasible ion exchangers for the adsorption of organic acids from plum wine. Next we determined the equilibrium isotherms for adsorption of the organic acids on the feasible ion exchangers in single component and binary systems. Further, we determined the equilibrium isotherms for the adsorption of the organic acids from plum wine.

We measured equilibrium isotherms by the batch method. Just before measuring the weight of the resin particles, the water on the surface of the resin particles was removed by using a centrifugal filter (Sanyou Rikagaku-kiki Seisakusho) at 5000 rpm for 3 minutes. The resin particles were contacted with the organic acid solutions and well mixed. Equilibrium was fully reached in 5 days. All experiments were carried out at 293 K. The adsorbed phase concentration was calculated according to

$$q = \frac{(C_0 - C)\rho V}{W} \tag{5}$$

where C_0 and C are the initial and the equilibrium concentrations (mol/m^3), respectively, q denotes the adsorbed phase concentration (mol/m^3 wet resin), V and W are the volume of the solution (m^3) and the weight of the wet resin particles (kg), respectively, and ρ is the apparent density (kg/m^3).

The composition of a plum wine is given in Table 1. The plum wine contains eight different organic acids and glucose. Acidity was the volume (cm^3) of 100 mol/m^3 aqueous NaOH solution which was needed to neutralize 10 cm^3 of the sample. The acidity means the total amount of acids in a plum wine. Glucose was analyzed by the Lane–Eynon method (10). The concentration of ethanol was analyzed by a Riken AL-2 alcohol analyzer. We analyzed the solutions for organic acids with a Shimadzu High Performance Liquid Chromatography Organic Acid Analysis System.

TABLE 1
Composition of Plum Wine

Ethanol (mol/m^3)	1920
($cm^3/100\ cm^3$)	11.1
Glucose (mol/m^3)	183
Acidity (cm^3 NaOH/10 cm^3 Sample)	7.2
Convert acidity into citric (mol/m^3)	21.9
pH	2.8
Organic acid (mol/m^3):	
Phosphate	1.33
Citric	13.8
Pyruvic	0.36
Malic	3.75
Succinic	1.85
Lactic	0.78
Formic	0.84
Acetic	6.95

Resin

The resins used in this experimental study and their experimental physical properties are listed in Table 2. BCW2510, CC-T, CC-S, and CC-I are chitosan derivatives whose fixed functional groups are shown in Table 2. Chitosan is made from chitin by deacetylation. Chitin is a natural biopolymer which is extracted from the shells of such arthropods as lobsters, shrimps, and crabs. Since chitosan is abundantly available, these chitosan derivatives are cheaper than commercial ion exchangers. DIAION WA-10, DIAION WA-30, and Amberlite IRA-94 are commercial weakly basic ion exchangers. Maeda (3) reported that they are excellent adsorbents for the removal of acids from juice.

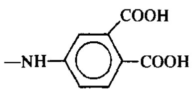
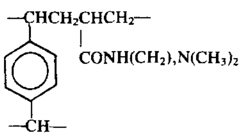
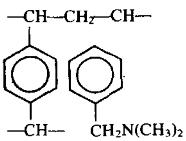
The concentration of the amino group in the adsorbent phase was obtained by measuring the equilibrium isotherm for adsorption of HCl. The reaction may be expressed by the following acid/base neutralization reaction:

$$R{-}NH_n + HCl \rightleftharpoons R{-}NH_{n+1}^{+}Cl^{-}, \qquad n = 0, 1, 2 \tag{6}$$

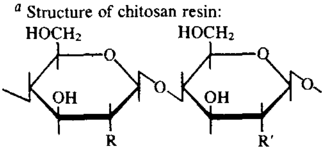
where $R{-}NH_n$ denotes a weakly basic resin. Figure 1 shows the experimental equilibrium isotherms for adsorption of HCl on CC-S, WA-10, and WA-30. The solid lines represent the theoretical line calculated according to the Langmuir equation, Eq. (7), which is derived by applying the mass action law to Reaction (6):

$$q = \frac{QKC}{1 + KC} \tag{7}$$

TABLE 2
Physical Properties of Ion Exchangers

Resin[a]	Functional group	Diameter (cm)	Apparent density (kg/m^3)	Porosity (—)	Saturation capacity of HCl, Q ($kmol/m^3$)
Chitosan derivative (spherical particles):					
BCW 2510[b]		0.1265	1122	0.896	0.70
R, R':	CH_3 CH_3 $—NHCH_2CHCH_2N(CH_2)_6NCH_2CHCH_2OH$ OH CH_3 CH_3 OH				
CC-T[b]		0.0504	1280	0.694	2.36
R, R';					
CC-S[b]		0.0475	1276	0.921	3.31
R:	—NHR				
R':	$—NHCH_2CHCH_2$—PEI[c] OH				
CC-I[b]		0.0539	1168	0.774	1.34
R, R':	$—N(CH_2COOH)_2$				
Acryl:					
WA-10[d]		0.0536	1140	0.692	2.37
Styrene:					
WA-30[d]		0.067	1125	0.496	2.81
IRA-94[e]	$—N(H_3)_2$	0.0477	1085	0.639	2.20

[a] Structure of chitosan resin:



[b] Fuji Spinning Co., Ltd.

[c] PEI: Poly(ethylene imine), molecular weight is 10,000.

[d] Mitsubishi Kasei Co., Ltd.

[e] Organo Co., Ltd.

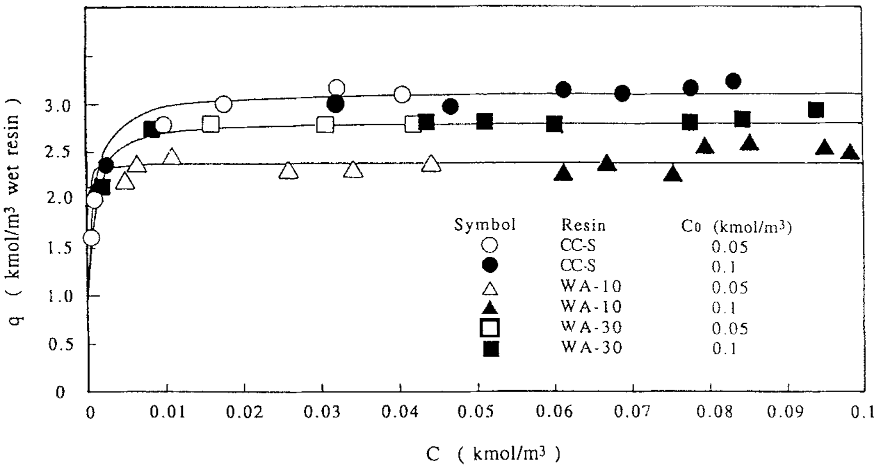


FIG. 1 Equilibrium isotherms for adsorption of HCl on CC-S, WA-10, and WA-30. T = 293 K.

where K and Q are the equilibrium constant (m^3/kmol) and the saturation capacity (kmol/m^3), respectively. They are given in Table 2. The saturation capacity for adsorption of HCl gives the concentration of fixed amino group in the resin phase. The saturation capacities of WA-10, WA-30, and CC-S are larger than those of the others.

RESULTS AND DISCUSSION

Screening Test of Ion Exchangers

Since the object of this study is the removal or reduction of organic acids from plum wine, we made a sample screening test to find feasible ion exchangers for adsorption of the organic acids from plum wine. The resin particles (1 g wet resin) were in contact with plum wine (50 cm^3) for 6 days at 293 K, and the equilibrium concentration of each component was analyzed by the methods mentioned earlier.

Table 3 shows the amounts of ethanol, glucose, and total acid in plum wine on the ion exchangers. Total acid can be represented as citric acid by reference to the fermentation analytical technique (11). C/C_0 is the ratio of the equilibrium concentration (C) and initial concentration (C_0) in the liquid phase, and q is the equilibrium concentration in the resin phase. The ion exchangers listed in Table 3 did not adsorb ethanol. Glucose was adsorbed on the resins, but the C/C_0 was 0.97 to 0.98. Therefore, the sweetness of the plum wine was not influenced by the adsorption of glucose. The amount of acids adsorbed was larger than that of glucose,

TABLE 3
Adsorption Characteristics of Ethanol, Glucose, and Acid in Plum Wine[a]

Resin	Ethanol		Glucose		Total acid (convert acidity into citric)	
	C/C_0 (—)	q (mol/m^3)	C/C_0 (—)	q (mol/m^3)	C/C_0 (—)	q (mol/m^3)
BCW2510	1.0	0	0.98	246	0.77	305
CC-T	1.0	0	0.98	273	0.62	561
CC-S	1.0	0	0.97	416	0.37	948
CC-I	1.0	0	0.97	317	0.68	433
WA-10	1.0	0	0.97	363	0.38	814
WA-30	1.0	0	0.97	285	0.22	970
IRA-94	1.0	0	0.97	356	0.38	795

[a] Resin particles: 1 g wet resin. Plum wine: 50 cm^3. Temperature: 293 K.

although the value of C_0 of acid is about 12% that of glucose. This means that the selectivity for the adsorption of acid is much higher than for glucose. The order of the selectivity for adsorption of acids is WA-30 $\doteqdot$ CC-S > WA-10 > IRA-94 > CC-T > CC-I > BCW2510. The amounts of the acid adsorbed on WA-30, CC-S, WA-10, and IRA-94 are relatively larger than the others. The values of C/C_0 for WA-30, CC-S, WA-10, and IRA-94 are 0.22 to 0.38 and are smaller than the others. The acid taste in the plum wine decreased with the adsorption of acid. However, WA-30 and IRA-94 added a strong smell of amine contaminants to the plum wine.

Table 4 shows the amounts of the organic acids adsorbed on the resins from the plum wine. The experimental conditions were the same as those of Table 3. The resin phase concentration of each acid was calculated from Eq. (5). Table 4 shows that CC-S adsorbs the acids well, except for lactic acid. The amounts of acids adsorbed on CC-S are larger than for

TABLE 4
Amounts of Organic Acids Adsorbed from Plum Wine on Resin (mol/m^3)[a]

Resin	Phosphate	Citric	Pyruvic	Malic	Succinic	Lactic	Formic	Acetic	Total
BCW2510	6.63	192	2.75	11.1	7.18	0	0	19.3	239
CC-T	0	147	0.61	8.58	3.67	0	1.84	17.2	179
CC-S	17.5	732	1.25	94.8	13.8	0	8.74	4.99	873
CC-I	10.3	251	0	25.1	7.98	4.56	0	10.3	309
WA-10	0	516	0	79.5	17.4	0	42.4	12.5	668
WA-30	12.3	583	0	91.0	31.7	0.51	3.58	16.9	739
IRA-94	0	518	4.27	58.2	20.3	0.53	0.53	5.23	607

[a] Resin particles: 1 g wet resin. Plum wine: 50 cm^3. Temperature: 293 K.

almost all the other resins. The total amount of acids adsorbed on CC-S is the largest. The total amounts of acids on WA-30 and WA-10 are also large. From the results obtained above, we conclude that CC-S, WA-10, and WA-30 may be feasible for the removal of acids or the reduction of the concentration of acids from plum wine, and that these resins adsorb citric acid and malic acid from plum wine selectively.

Equilibria in Single Component System

CC-S, WA-10, and WA-30 could improve the taste of the wine, and these resins adsorbed citric acid and malic acid from plum wine very well. The equilibrium isotherms for the adsorption of citric acid and malic acid on these resins were investigated. We first measured their equilibrium isotherms for a single component system. We used their aqueous solutions and solutions in which ethanol existed.

Figure 2 shows the equilibrium isotherms for the adsorption of malic

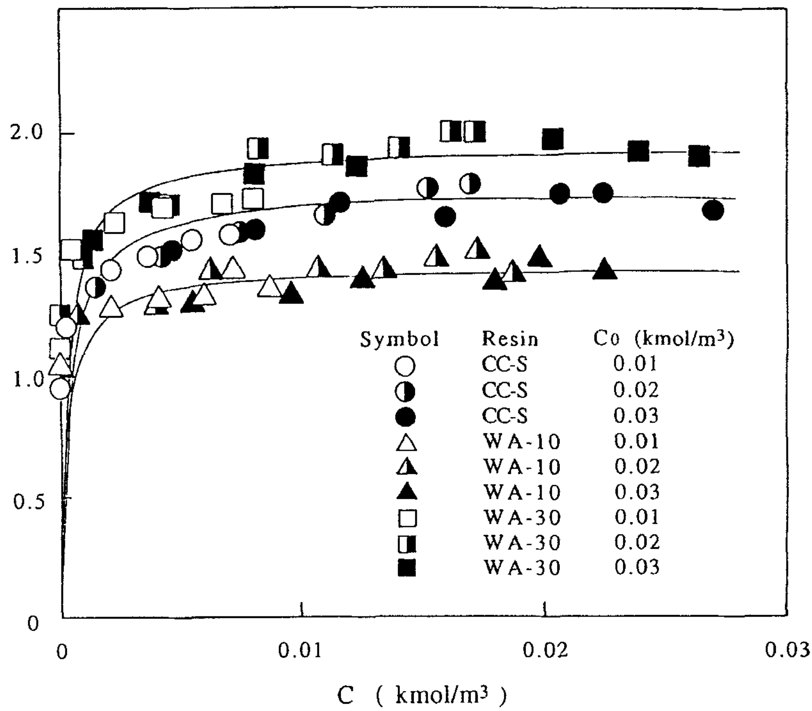


FIG. 2 Equilibrium isotherms for adsorption of malic acid on CC-S, WA-10, and WA-30. T = 293 K. Malic acid was dissolved in pure water.

TABLE 5
Experimental Langmuir Equilibrium·Constants and Saturation Capacities in Single Component Systems

Solution	Resin	K (m^3/kmol)	q_0 (kmol/m^3)	q_0/Q (—)
Malic–water	CC-S	2500	1.75	0.56
	WA-10	3000	1.45	0.61
	WA-30	3000	1.94	0.69
Citric–water	CC-S	2500	1.64	0.52
	WA-10	3000	1.41	0.59
	WA-30	3000	1.83	0.65
Malic–(ethanol[a] + water)	CC-S	2500	1.75	0.56
	WA-10	3000	1.50	0.63
	WA-30	2500	2.01	0.72
Citric–(ethanol[a] + water)	CC-S	2500	1.70	0.54
	WA-10	3000	1.50	0.63
	WA-30	3000	1.95	0.69

[a] The concentration of ethanol was 1920 mol/m^3, which was the same as the plum wine.

acid dissolved in water. The solid lines show the Langmuir isotherm (Eq. 8):

$$q = \frac{q_0 KC}{1 + KC} \tag{8}$$

where q_0 denotes the saturation capacity. The data correlate well by the Langmuir equation. We measured the isotherms for three different initial concentrations (C_0 = 0.01, 0.02, and 0.03 kmol/m^3). The equilibrium isotherms are not affected by C_0. The experimental equilibrium constants and the saturation capacities are listed in Table 5. It is understood that CC-S, WA-10, and WA-30 have high abilities for the adsorption of malic acid because their equilibrium constants are large. The order of the saturation capacity is WA-30 > CC-S > WA-10. The saturation quantities are 60–70% of the concentration of the fixed amino group of the resin (Q) (see Table 2). This is because malic acid has two carboxyl groups on one molecule. The reaction between adsorbent and malic acid may be expressed by

$$\mathrm{R{-}NH}_n + \underset{\displaystyle \mathrm{CH_2COOH}}{\mathrm{CH(OH)COOH}} \rightleftharpoons \mathrm{R{-}NH^+}_{n+1}\underset{\displaystyle \mathrm{CH_2COOH}}{\mathrm{CH(OH)COO^-}} \tag{9}$$

$$2\mathrm{R{-}NH}_n + \underset{\displaystyle \mathrm{CH_2COOH}}{\mathrm{CH(OH)COOH}} \rightleftharpoons (\mathrm{R{-}NH^+}_{n+1})_2\underset{\displaystyle \mathrm{CH_2COO^-}}{\mathrm{CH(OH)COO^-}} \tag{10}$$

where n = 0, 1, 2.

Actually, a detailed expression for the equilibrium isotherm based on Reactions (9) and (10) needs to be derived. However, from an engineering point of view, Eq. (8) may be an useful expression, because it correlates with the data in Fig. 2 fairly well, and we must investigate the more complex adsorption in binary systems for equilibria and dynamics.

Figure 3 shows the equilibrium isotherms for the adsorption of citric acid dissolved in water. The data also correlated well with the Langmuir equation (Eq. 8). The equilibrium isotherms are not affected by the initial concentration of citric acid. The experimental equilibrium constants and saturation capacities are listed in Table 5. The equilibrium constants agree with those for the adsorption of malic acid. The saturation capacities are 50–60% of the concentration of the fixed amino group of the resin (Q). Since citric acid has three carboxyl groups on one molecule, citric acid

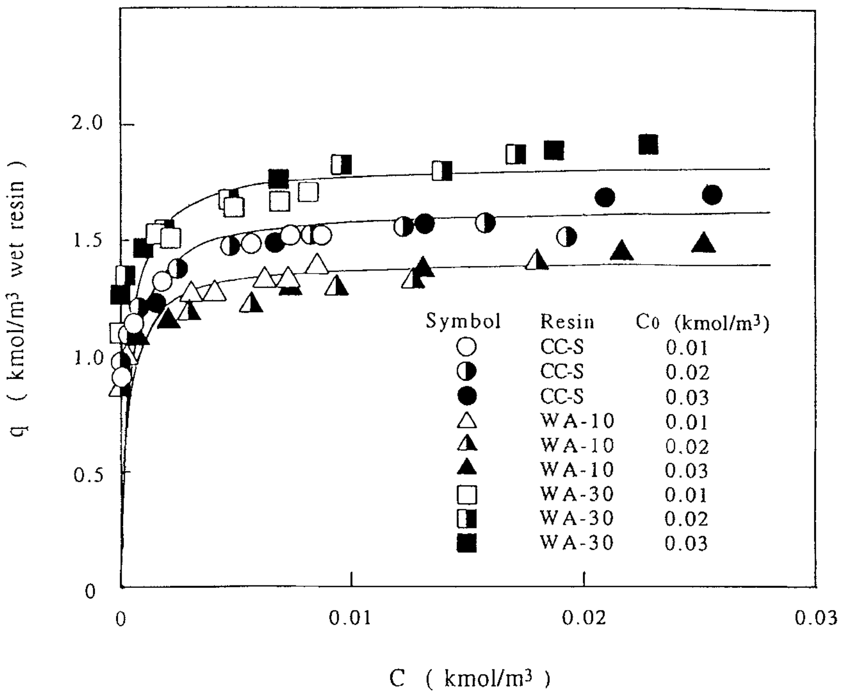


FIG. 3 Equilibrium isotherms for adsorption of citric acid on CC-S, WA-10, and WA-30. $T = 293$ K. Citric acid was dissolved in pure water.

may be adsorbed on the resin not only by Reaction (11) but also by Reactions (12) and (13):

$$R\text{—}NH_n + \begin{array}{c} CH_2COOH \\ | \\ C(OH)COOH \\ | \\ CH_2COOH \end{array} \rightleftharpoons R\text{—}NH^+{}_{n+1}\begin{array}{c} CH_2COOH \\ | \\ C(OH)COO^- \\ | \\ CH_2COOH \end{array} \qquad (11)$$

$$2R\text{—}NH_n + \begin{array}{c} CH_2COOH \\ | \\ C(OH)COOH \\ | \\ CH_2COOH \end{array} \rightleftharpoons (R\text{—}NH^+{}_{n+1})_2\begin{array}{c} CH_2COO^- \\ | \\ C(OH)COO^- \\ | \\ CH_2COOH \end{array} \qquad (12)$$

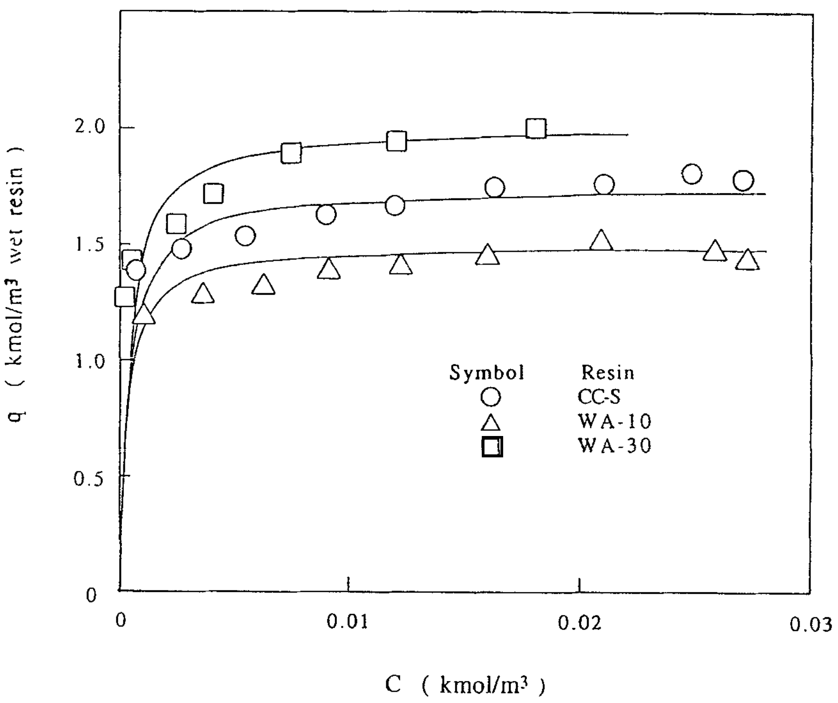


FIG. 4 Equilibrium isotherms for adsorption of malic acid on CC-S, WA-10, and WA-30. T = 293 K, C_0 = 0.03 kmol/m^3. Malic acid was dissolved in ethanol–water solution. Concentration of ethanol was 1.92 kmol/m^3.

$$3R{-}NH_n + \begin{array}{c} CH_2COOH \\ | \\ C(OH)COOH \\ | \\ CH_2COOH \end{array} \rightleftharpoons (R{-}NH^+{}_{n+1})_3\begin{array}{c} CH_2COO^- \\ | \\ C(OH)COO^- \\ | \\ CH_2COO^- \end{array} \qquad (13)$$

where $n = 0, 1, 2$.

Figures 4 and 5 show the equilibrium isotherms for the adsorption of malic acid in ethanol aqueous solution and for the adsorption of citric acid in ethanol aqueous solution, respectively. The concentration of ethanol was 1920 mol/m^3, which is the same as that of the plum wine. The theoretical lines in Figs. 4 and 5 were calculated according to the Langmuir equation (Eq. 8). They correlate well with the data. The experimental equilibrium constants and the saturation capacities are listed in Table 5. Since the Langmuir coefficients in ethanol aqueous solution are close to those without ethanol in water, ethanol has little effect on the equilibria.

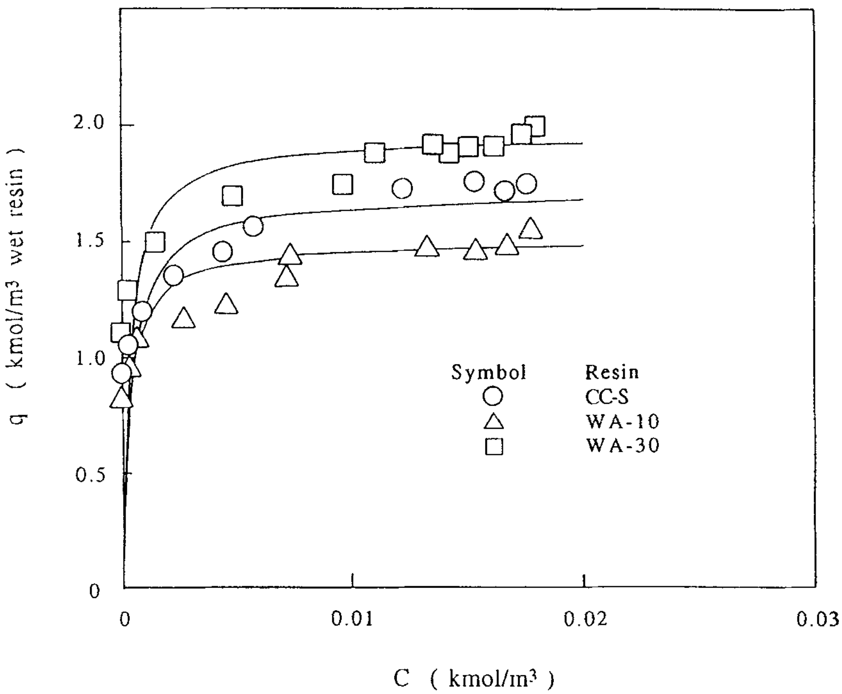


FIG. 5 Equilibrium isotherms for adsorption of citric acid on CC-S, WA-10, and WA-30. T = 293 K, C_0 = 0.02 kmol/m^3. Citric acid was dissolved in ethanol–water solution. Concentration of ethanol was 1.92 kmol/m^3.

Equilibria in Binary Systems

Figure 6 shows the equilibrium isotherms for the adsorption of citric and malic acids on CC-S, WA-10, and WA-30 when there was no ethanol in the solution. The data were obtained for two different initial concentrations of citric acid and malic acid: 0.02 and 0.03 kmol/m^3, and 0.014 and 0.004 kmol/m^3, respectively. The solid and dotted lines are theoretical

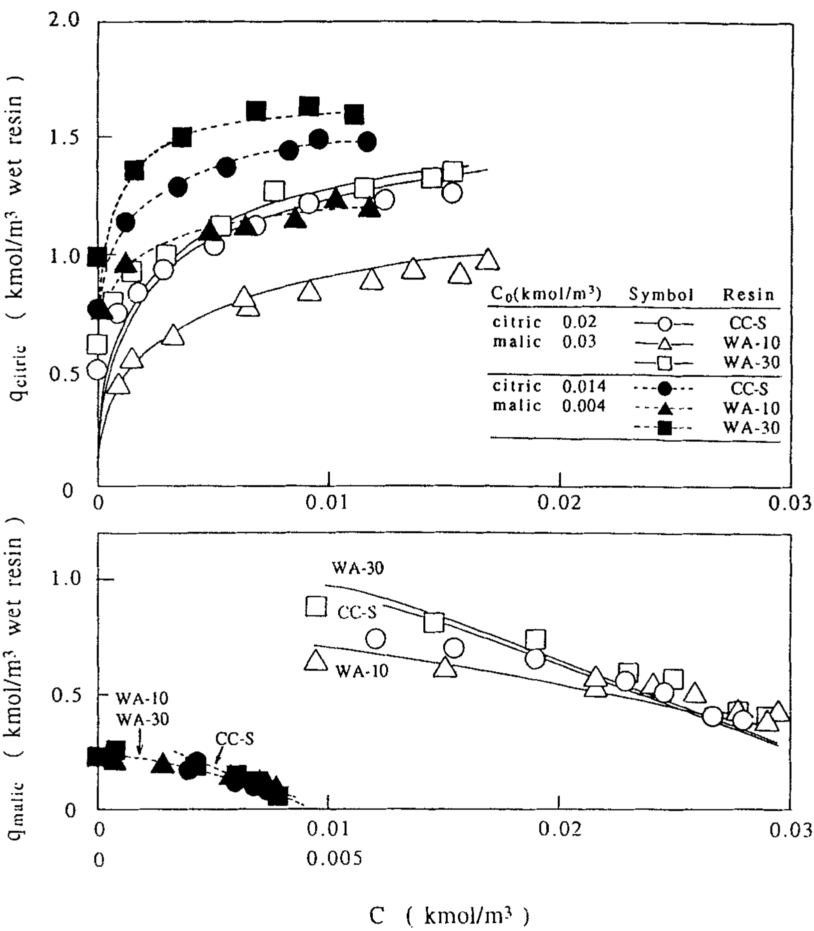


FIG. 6 Equilibrium isotherms for adsorption of binary system (citric and malic acids without ethanol) on CC-S, WA-10, and WA-30. T = 293 K.

lines calculated according to the Markham–Benton equation (12):

$$q_A = \frac{q_0 K_A C_A}{1 + K_A C_A + K_B C_B} \tag{14}$$

$$q_B = \frac{q_0 K_B C_B}{1 + K_A C_A + K_B C_B} \tag{15}$$

$$X_A = \frac{C_A}{C_A + C_B} \tag{16}$$

$$Y_A = \frac{q_A}{q_A + q_B} \tag{17}$$

$$K_{AB} = K_B/K_A \tag{18}$$

$$\frac{1}{Y_A} = 1 - K_{AB} + \frac{K_{AB}}{X_A} \tag{19}$$

TABLE 6
Experimental Markham–Benton Constants and Saturation Capacities in Binary Systems

Solution C_0 (kmol/m^3)	Resin	K_A (m^3/kmol)[a]	K_B (m^3/kmol)[b]	K_{AB} (—)	q_0 (kmol/m^3)	q_0/Q (—)
(Citric + malic) – water:						
C_{A0} = 0.02	CC-S	5000	550	0.11	1.64	0.53
C_{B0} = 0.03	WA-10	5000	1000	0.20	1.35	0.57
	WA-30	7000	800	0.11	1.71	0.61
C_{A0} = 0.014	CC-S	5000	550	0.11	1.55	0.49
C_{B0} = 0.004	WA-10	5000	1000	0.20	1.30	0.55
	WA-30	7000	800	0.11	1.71	0.61
(Citric + malic) – (ethanol[c] + water):						
C_{A0} = 0.02	CC-S	5000	550	0.11	1.75	0.56
C_{B0} = 0.03	WA-10	5000	1000	0.20	1.50	0.63
	WA-30	7000	800	0.11	1.90	0.68
C_{A0} = 0.014	CC-S	5000	550	0.11	1.55	0.50
C_{B0} = 0.004	WA-10	5000	1000	0.20	1.35	0.57
	WA-30	7000	800	0.11	1.75	0.62
Plum wine:						
C_{A0} = 0.014	CC-S	5000	550		1.00	0.32
C_{B0} = 0.004	WA-10	5000	1000		0.60	0.25
	WA-30	7000	800		1.10	0.39

[a] A: Citric acid.
[b] B: Malic acid.
[c] The concentration of ethanol was 1920 mol/m^3, which was the same as the plum wine.

where C_A and C_B are the concentrations of citric and malic acids in the liquid phase (kmol/m^3), respectively, q_A and q_B are the resin-phase concentrations of citric and malic acids (kmol/m^3), respectively, and K_A and K_B are the equilibrium constants for citric and malic acids (m^3/kmol), respectively. The data correlate reasonably well by the Markham–Benton equations (Eqs. 14 and 15). The experimental equilibrium constants and the saturation capacities are listed in Table 6. The equilibrium constants are independent of the initial concentrations of citric and malic acids, but

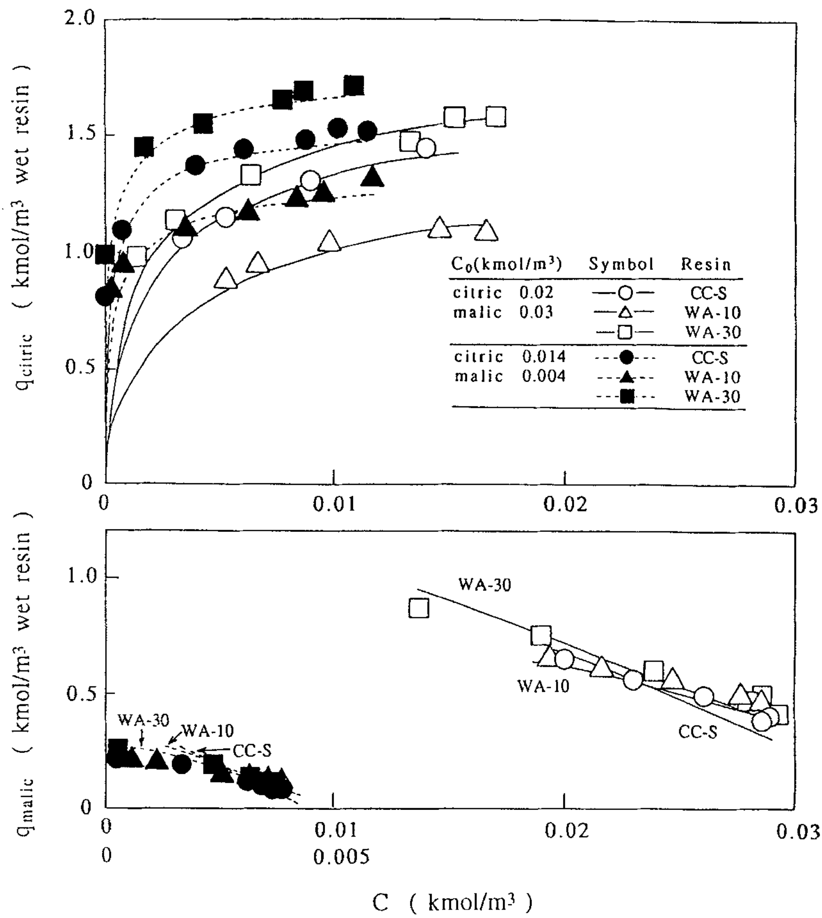


FIG. 7 Equilibrium isotherms for adsorption of binary system (citric and malic acids with ethanol–water solution) on CC-S, WA-10, and WA-30. T = 293 K. Concentration of ethanol was 1.92 kmol/m^3.

the saturation capacities depend on them only slightly. The equilibrium constants for citric acid in a binary system are larger than in a single component system, but those for malic acid are smaller. Therefore, these resins have higher selectivity for adsorption of citric acid than for malic acid. The saturation capacities did not show a large difference between single component and binary systems.

Figure 7 shows the equilibrium isotherms in a binary system of citric and malic acids for the case with 1920 mol/m^3 ethanol in the solution. The solid and dotted lines are theoretical lines calculated according to Eqs. (14) and (15). The equilibrium constants and the saturation capacities are listed in Table 6. The ethanol does not affect the equilibrium constants, but it does increase the saturation capacities a little.

Figure 8 shows the $X-Y$ diagram for citric and malic acids. The theoretical lines were calculated according to Eq. (19). The values of K_{AB} for CC-S and WA-30 were both 0.11, and that of WA-10 was 0.2. They are not affected by ethanol. CC-S and WA-30 show a higher selectivity for the adsorption of citric acid than does WA-10.

The Adsorption of Citric and Malic Acids from Plum Wine

Figure 9 shows the equilibrium isotherms for the adsorption of citric and malic acids on CC-S, WA-10, and WA-30 from plum wine. The solid

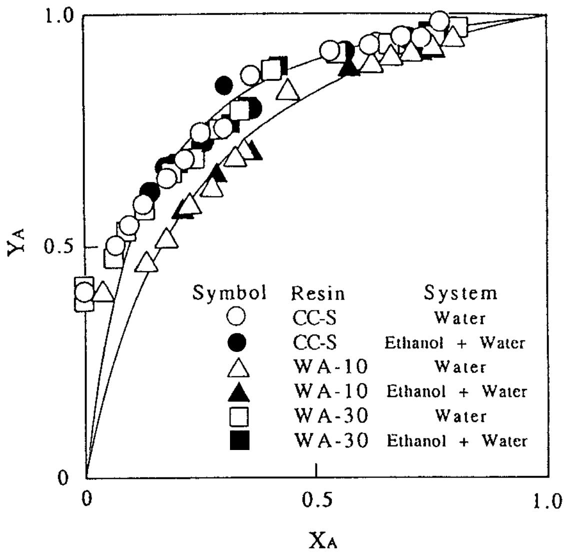


FIG. 8 $X-Y$ diagram on citric–malic system. K_{AB} = 0.11 (CC-S and WA-30), K_{AB} = 0.2 (WA-10).

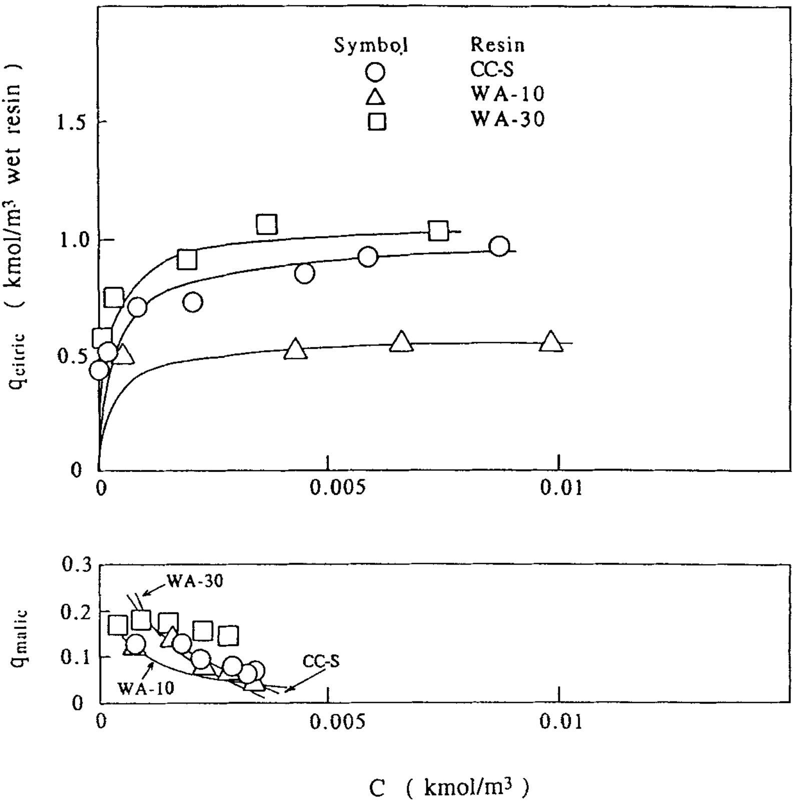


FIG. 9 Equilibrium isotherms for adsorption of citric and malic acids on CC-S, WA-10, and WA-30 from plum wine. C_{A0} = 0.014 kmol/m^3, C_{B0} = 0.004 kmol/m^3.

lines were calculated according to the Markham–Benton equations (Eqs. 14 and 15), and the equilibrium constants for the ethanol aqueous solution system as given in Table 6 were applied. The experimental values correlate reasonably well with Eqs. (14) and (15) except for malic acid on WA-30. The saturation capacities of CC-S, WA-10, and WA-30 were 0.65, 0.44, and 0.63 times that in the binary system with ethanol (C_{A0} = 0.014 kmol/m^3, C_{B0} = 0.004 kmol/m^3), respectively. q_0/Q was smaller than that in the binary system because CC-S, WA-10, and WA-30 adsorbed not only citric and malic acids but also glucose and other organic acids in plum wine. However, the equilibrium isotherm for the adsorption of organic acids in plum wine on the resins could be adequately approximated by the adsorption of citric and malic acids in binary systems.

CONCLUSION

The adsorption of organic acids on the weakly basic resins CC-S, WA-10, and WA-30 appears technically feasible even for an ethanol-containing solution and wine.

The ability to adsorb organic acids was in the order WA-30 > CC-S > WA-10. However, WA-30 added a strong smell of amino contaminants to the plum wine.

The equilibrium isotherms for a single component system of citric acid or malic acid were little affected by the initial concentration and by ethanol, and the equilibrium data correlated well by the Langmuir equation. The equilibrium constants for citric acid were the same as those for malic acid.

Equilibrium data for binary component systems of citric and malic acids were correlated reasonably well by the Markham–Benton equation. The equilibrium constants were little affected by the initial concentration and by ethanol. The equilibrium constants for citric acid were much larger than those for malic acid.

CC-S, WA-10, and WA-30 adsorbed organic acids, especially citric and malic, from plum wine very well. The equilibrium data for the adsorption of citric and malic acids in systems with several components could be adequately approximated by the Markham–Benton equation.

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