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Phase Separation Behavior in Neutralized Poly(maleic acid) Aqueous Solutions

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ABSTRACT: Aqueous solutions of poly(maleic acid) (PMA) exhibit a phase separation when neutralized with monovalent bases, prior to the complete neutralization, irrespective of the presence or absence of added salts. The values of the critical degree of neutralization (α_τ) at which the precipitation develops were measured for the PMA aqueous solutions neutralized with various kinds of monovalent counterions, as a function of polymer (C_p) and added salt concentrations (C_s). It was found that, at constant C_s, α_τ decreases sharply with increasing C_p and that, at constant α_τ, the critical NaCl concentration ($\bar{C}_s$) decreases linearly with increasing C_p. This phenomenon is attributable to the strong binding of monovalent counterions to ionized sites of a polyion and can be analyzed in terms of a site-binding model. The phase separation was shown to occur even in a salt-free solution when the amount of strongly bound Na^+ became a certain value, $C_p\gamma$, where $\gamma = 0.58$. Addition of monovalent salts facilitates the phase separation. At a low degree of neutralization, PMA was found to be quite soluble, in accordance with the neutralization dependence of the solubility of its monomer unit, maleic acid, which was also examined together with that of fumaric acid.

Introduction

The solubility of polyelectrolytes is one of their most important and fundamental physicochemical properties. The phase separation, precipitation, or so-called "coacervation" in polyelectrolyte aqueous solutions containing small ions seems to be the result of numerous interactions. There have been so far very limited experimental and theoretical studies on this problem,[1-13] compared with those on the other properties, because of its complexity. Addition of neutral salts to a polyelectrolyte solution induces a conformational change of the polyelectrolyte chains through a decrease in long-range electrostatic interaction[14] and hence reduces its solubility. The solubility is also decreased by the dehydration of a charged site due to counterion binding and by the "salting-out" resulting from the decrease in the activity of water molecules in the presence of salts, respectively. The studies reported on the precipitation of polyelectrolyte solutions can be classified into the three following categories:[11] (1) the liquid–liquid phase separation characterized by the Θ-point in a polyelectrolyte–water system containing mainly monovalent counterions,[7-10] (2) the precipitation induced mainly by multivalent counterions in the polyelectrolyte solutions,[1,3-5] and (3) the polyelectrolyte complex coacervation between oppositely charged polyelectrolytes.[12,13]

It has widely been accepted that the water affinity to low molecular weight organic carboxylic acids increases with neutralization, when neutralized with an alkali-metal hydroxide. This tendency may also hold for the corresponding solutions of weak polyacids. The solubility of the polyelectrolyte in water should increase with neutralization, since the alkali-metal ions are usually bound atmospherically to a polyion, and the fraction of dissociated protons in the weak polyacid solutions is usually low, resulting in a relatively lower solubility of the acid form. Several experimental results have supported this fact. For example, the solubility of poly(acrylic acid) (PAA) increased steeply with neutralization, when the monovalent cations are used as counterions.[1] For strongly bound multivalent counterions such as Mg^{2+}, Ca^{2+}, Ba^{2+}, and La^{3+}, however, PAA solutions easily produced the precipitation and their solubilities in the high pH region decreased steeply with neutralization.[1,4,5] Various studies have revealed that there are a number of factors affecting the phase separation behavior of the polyelectrolyte solution, such as the type of counterions and co-ions used, concentration of salts (C_s), degree of neutralization (α), strength of counterion binding, type of solvents, temperature, polymer concentration (C_p), molecular weight, and molecular weight distribution, similarly to the nonionic polymer solutions.[11,15-17]

Strauss et al. reported a very interesting behavior that the concentrated solutions of alternating copolymers of maleic acid with hexyl- and octylvinyl ethers, containing *only monovalent counterion*, produced the precipitation, prior to the complete neutralization in the presence of large amounts of salts.[6] They interpreted this phenomenon in terms of the "*monovalent counterion–polyion complexes*" having a specific negative water affinity. Other maleic acid copolymers such as copolymers with ethylene, ethyl vinyl ether,[18] and isobutylene,[19] however, never produced the precipitation by using monovalent counterions at higher neutralization. This means that not only the charge density and distribution of the charged sites on the polyelectrolytes but also their molecular structure and the balance between hydrophobic and hydrophilic interactions may be closely related to their phase separation behavior.

Our previous studies revealed that *dilute solutions* of poly(maleic acid) (PMA) and its stereoisomer, poly(fumaric acid) (PFA), both of which have a charge density exactly twice as high as PAA, containing small amounts of monovalent salts exhibited a phase separation, on the course of neutralization.[20] Interestingly, the precipitation occurred even for salt-free solutions of PMA and PFA and was strongly dependent on the type of cations used, as

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well as on C_p and C_s.[20,21] The accuracy and reproducibility of the cloud point were confirmed by back-titration with HCl.[20] Although the preliminary results for this phenomenon were first reported by Lang et al.,[22] they did not put into practice further studies. We became interested in the reason why both salt-free and added salt dilute solutions of PMA separate into two phases in the high pH region, in spite of containing *only monovalent counterions*.

The present paper describes the details of the phase separation behavior of PMA solutions under several types of counterions, as a function of C_p and C_s, and discusses the effect of the monovalent counterion on the solubility of polyelectrolytes with high charge density, using a site-binding model. In addition, the solubilities of their monomer analogs, maleic acid and fumaric acid, were measured with special attention to the dependence of their solubilities on the neutralization.

Experimental Section

The details of the synthesis and characterization of the PMA sample have been reported in the previous papers.[20,21] The number-average molecular weight (M_n) was 1.7×10^4. Further fractionation has not been carried out in the present study, although the phase separation behavior might be sensitive to its molecular weight.[11,20] The solutions for measurements were prepared by passing through a mixed bed of ion-exchange resins just before use. The C_p was determined by potentiometric titration.[20] The twice-recrystallized and carefully dried LiCl, NaCl, NaBr, NaI, $NaClO_4$, KCl, RbCl, CsCl, and $(n\text{-}C_4H_9)_4NBr$ were used for the present experiments. The corresponding hydroxides were prepared as CO_2-free solutions from the saturated ones.

The phase separation experiments were carried out at 25.0 ± 0.1 and 40.0 ± 0.1 °C under an Ar atmosphere. The conditions for the precipitation were determined by adding the solutions of alkali-metal hydroxide to the PMA solutions of known C_p and C_s. The addition of base was continued until the precipitation was found and kept at least for 1 h. It was confirmed that, after this point, the precipitate in solution increased with further neutralization and the solutions separated into liquid–liquid or liquid–solid phases. The time needed to determine one point was approximately 6 h. It should be stressed here that the precipitation at this point has been kept over for a month. In practice, the critical degree of neutralization (a_r) at which the precipitation develops was determined by measuring scattered light intensities at an angle of 90°, using a modified Brice–Phoenix universal light scattering photometer, Model 1000-D, with a He–Ne laser as a light source. The scattered intensities were recorded automatically by using a recorder. Since the appearance of precipitation brought about a sharp increase of the scattered intensity, a_r could be determined correctly from an inflection point in a curve which was made by plotting the average intensities against the degree of neutralization. The cell containing a sample solution was thermostated and stirred during the measurement. The error and reproducibility of a_r was confirmed to be within 1%. The measurements were made on solutions ranging in C_p from 5 to 750 mN and in C_s from 0 to 4.0 N.

Results

In Figure 1, the values of the critical degree of neutralization, a_r, at various C_s were plotted against C_p. Surprisingly, the phase separation took place even *at salt-free solutions*, since other ordinary weak polyacid solutions never produce a precipitation in this C_p region, and this contradicts the wealth of data indicating that neutralization with alkali-metal ion increases the water affinity to the polyacids. This experimental result implies that the solubility of the polyelectrolyte does not necessarily increase when neutralized with monovalent base. Taking into account the fact that the phase separation also occurred in the corresponding solutions of PFA,[20,21] this may be a specific phenomenon for the solutions of PMA and PFA having charge densities twice as high as an ordinary weak acid such as PAA. The a_r in the salt-free solution first decreased steeply with C_p up to $C_p = 0.1$ N and then decreased gradually. Interestingly, similar curves were also obtained for the added salt solutions, although the addition of salts to the salt-free solution at the same C_p decreased a_r, i.e., the solubility. Therefore, the phase separation is concluded to be produced by neutralization followed by counterion binding, irrespective of the presence or absence of added salts in solutions, as will be discussed later.

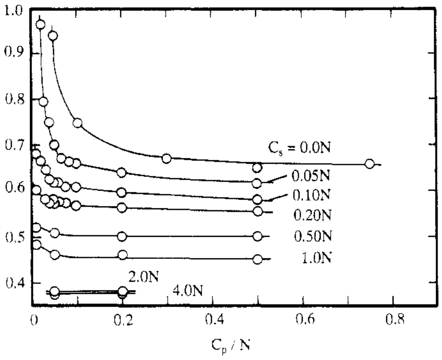

Figure 1. Plots of the critical degree of neutralization, a_r, of the PMA solutions with various NaCl concentrations against the polymer concentration, C_p, at 25 °C.

Table I. Critical Phase Separation Points (a_r) for Various Added Salt Solutions[a]

salt	base	C_s/N	temp/°C	a_r	pH
LiCl	LiOH	0.50	25	>1.0	
LiCl	NaOH	0.50	25	0.82	7.90
NaCl	NaOH	0.50	25	0.52	6.54
NaCl	NaOH	0.10	25	0.61	
NaCl	NaOH	0.10	40	0.65	
$NaClO_4$	NaOH	0.10	25	0.61	
NaBr	NaOH	0.50	25	0.51	
NaI	NaOH	0.50	25	0.52	
KCl[b]	KOH	0.50	25	0.55	
KCl[b]	NaOH	0.50	25	0.53	7.20
RbCl[b]	RbOH	0.50	25	>1.0	
RbCl[b]	NaOH	0.50	25	>1.0	
CsCl[b]	CsOH	0.50	25	>1.0	
CsCl[b]	NaOH	0.50	25	>1.0	
$(n\text{-}Bu)_4NBr$	$(n\text{-}Bu)_4NOH$	0.50	25	>1.0	
$(n\text{-}Bu)_4NBr$	NaOH	0.50	25	0.76	9.95

[a] $C_p = 9.92$ mN. [b] The solutions once produced the precipitation in the region of $a < 0.5$, but the precipitate dissolved completely again at $a = 0.5$.

The values of a_r for the various kinds of added salt solutions were listed in Table I. Clearly, the phenomenon is highly sensitive to the counterions but not to the coions used, that is, the solutions containing only Na^+ or K^+ separated into two phases, but no phase separation occurred with Li^+, Rb^+, Cs^+, and $(n\text{-}C_4H_9)_4N^+$ under the same conditions. Interestingly, the solutions containing much larger amounts of Li^+ and $(n\text{-}C_4H_9)_4N^+$ than C_p produced precipitation when neutralized with NaOH, whereas the corresponding solutions containing RbCl and CsCl did not produce precipitation. This may be closely related to the difference in the selectivity of the bound counterions and the tendency of "salting-out" or "salting-in" of added salts.

It should be emphasized here that the solutions containing K^+, Rb^+, and Cs^+ were clearly different from those containing other counterions. The former solutions once produced the precipitation in the region of $0.1 < a < 0.5$,

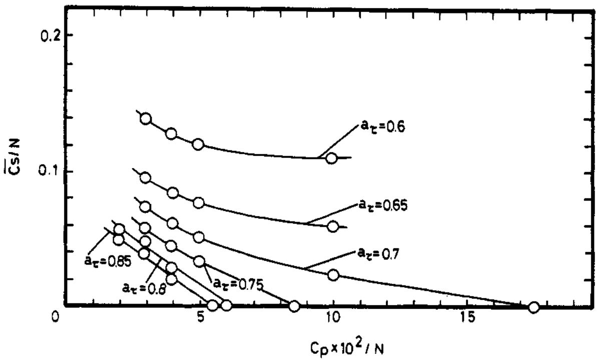

Figure 2. Critical NaCl concentration, $\bar{C}_s$, as a function of C_p at various α_r's at 25 °C.

but the precipitate dissolved completely again at $\alpha = 0.5$. The precipitate itself produced in the low α region was different from that in the region higher than $\alpha = 0.5$; the former was like a white powder but the latter like a finely dispersed gel. Therefore, the mechanism of the precipitation may be different between the low α region and the high α region. Also an increase in temperature usually increases the solubility to some extent, as seen in this table.

In Figure 2, the critical added salt concentration, $\bar{C}_s$, at various α_r's were plotted against C_p. The following empirical equation between $\bar{C}_s$ and C_p was proposed by Michaeli:[4]

$$\bar{C}_s = a + bC_p \tag{1}$$

where a is the term representing free ions, and bC_p is related to the fraction of bound ions to a single polyion. The positive values of b were reported in many polyelectrolyte–multivalent counterion systems, such as PAA–Ag^+, PAA–Mg^{2+}, PAA–Ca^{2+}, PAA–Ba^{2+}, PAA–La^{3+},[1] poly(methacrylic acid)–Ca^{2+},[4] and poly(maleic acid-*alt*-styrene)–Ca^{2+}.[5] Namely, the added monovalent salt enhances the solubility, probably due to the partial replacement of the bound multivalent ions by monovalent ions. The present study revealed, however, that the values of b are clearly negative. This result means that the phase separation behavior in the PMA–Na^+ system is largely different from that in the systems mentioned above. In this case, the addition of NaCl seems to decrease the solubility of the PMA–Na^+ complex through a decrease of the activity of the hydrated water molecules, that is, a salting-out effect, rather than the further increase of the binding of monovalent ions with increasing C_s, as in the former systems. The linearity of $\bar{C}_s$ on C_p seems to hold for the large values of α_r, e.g., larger than 0.8, but the initial slopes of these curves are more or less alike. For $\alpha_r < 0.75$, the slope becomes lower and the curves are deviated from the linearity with increasing C_p, given by eq 1. Probably this profile is due to the existence of multiple effects on the precipitation of PMA, other than the salting-out.

In Figure 3, $\bar{C}_s$ of PMA was plotted against α_r at C_p = 50 mN, and that of PAA[1] at the same C_p was also presented for comparison. The $\bar{C}_s$ of PAA increased monotonically with α_r, and above $\alpha_r = 0.5$ the solution did not exhibit the precipitation until $\bar{C}_s$ became a saturated solution of NaCl. In remarkable contrast to the case of PAA, $\bar{C}_s$ of PMA is very high at $\alpha_r = 0.38$ but steeply decreased with increasing α_r. Also, the PMA solution above $\alpha_r = 0.5$ could be little dissolved in the presence of NaCl. A quite sharp decrease in $\bar{C}_s$ with α_r was also found in the solutions containing multivalent counterions.[1,5] The high solubility of PMA at low α may be closely related to that of its monomer analogue, maleic acid, as will be discussed later.

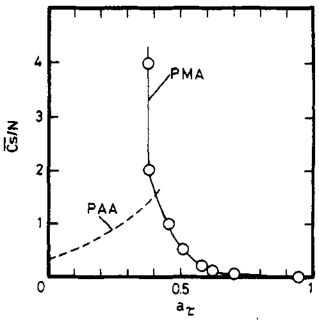

Figure 3. Plot of $\bar{C}_s$ against α_r at C_p = 50 mN. The broken lines were reproduced from ref 1.

Discussion

Precipitation in electrolyte solutions can be considered to occur through three processes: (1) approach of a cation to an anion by electrostatic attraction, (2) elimination of solvated molecules from ions, and (3) formation of ionic binding between oppositely charged ions. The solubility of low molecular weight salts may be determined exclusively by electrostatic interaction between charges, judging from the dependence of the solubility of the solute on the dielectric constant of the solvents.[23] On the other hand, the solubility of polyelectrolytes might become very low, if process 1 plays a dominant role, since the polyion produces a higher electrostatic field in the vicinity of its backbone than do the small ions to attract large amounts of surrounding counterions. The solubility of polyelectrolytes, however, seems to be not so low, compared with that of the corresponding solution of low molecular weight organic carboxylic acid. This means that the solubility of the polyelectrolyte may be, more or less, affected by processes 2 and 3 in addition to the counterion condensation, although they cannot be distinguished from each other. Precipitation in the polyelectrolyte solutions, therefore, is highly sensitive to the polyelectrolyte–counterion systems.[11]

The most characteristic phenomenon in the present study is the fact that the phase separation takes place even in *salt-free dilute solutions*. It seems reasonable to suppose that this precipitation results from the strong counterion binding, site binding, between a counterion and an ionized group of a polyion, as suggested by Strauss et al.[6] In fact, the abnormal high relaxation rates of sodium counterions in the salt-free PMA solutions above $\alpha = 0.5$ were observed by ^{23}Na-NMR relaxation measurement, compared with those in PAA solution.[24] The existence of strong interaction between PMA and Na^+ cannot be described by ordinary polyelectrolyte theory. In this theory the alkali-metal counterions are assumed to be atmospherically bound to a polyion. Our results, however, can be interpreted in terms of a site-binding model. Such a model led us to obtain precious information about the phase separation behavior in PMA solutions.

The following simple binding equilibrium is assumed between an ionized site on a polyelectrolyte chain and a neutralized sodium ion in a salt-free solution:

$$-COO^- + Na^+ \overset{K_b}{\rightleftharpoons} -COO^-Na^+ \tag{2}$$

where K_b is a binding constant and can be expressed as

$$K_b = \frac{\beta}{C_p \alpha (1 - \beta)^2} \tag{3}$$

In this equation, β is the degree of site binding by counterions. Taking into account that free $-COO^-$ has a high water affinity but $-COO^-Na^+$ has a very low water

Table II. Values of K_b, γ, and β_c Estimated Using Equations 5 and 6

C_s/N	K_b/N^{-1}	γ	β_c[a]	β_c[b]
0.0	206 ± 50	0.58 ± 0.02	0.6_6	0.8_5
0.05	61 ± 10	0.52 ± 0.01	0.7_4	0.8_1
0.10	42 ± 10	0.50 ± 0.01	0.8_1	0.8_3
0.20	20 ± 5	0.46 ± 0.01	0.8_0	0.8_1
0.50	10 ± 3	0.42 ± 0.01	0.8_3	0.8_4
1.0	5 ± 3	0.38 ± 0.01	0.8_3	0.8_3

[a] C_p = 0.05 N. [b] C_p = 0.20 N.

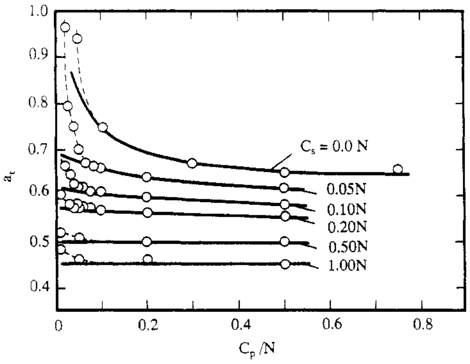

Figure 4. Comparison of the experimental a_τ's with theoretical curves (solid lines) calculated from eqs 5 and 6. The values of K_b and γ used are listed in Table II.

affinity, as suggested by Strauss,[6] the solubility of the polyelectrolyte should mainly be determined by the values of a and β. Now, if one assumes that the precipitation develops when the amounts of $-COO^-Na^+$, $C_p a \beta$, become a certain constant value, $C_p \gamma$, the relation between the critical values of a and β, a_τ and β_c, where the precipitation develops, is given by

$$\beta_c = \gamma / a_\tau \tag{4}$$

and a_τ is expressed by substituting eq 4 for β in eq 3, as

$$a_\tau = \gamma + [\gamma/(K_b C_p)]^{0.5} \tag{5}$$

Similarly, a_τ for the added salt solutions can be defined as follows:

$$a_\tau = \gamma - X/2 + [X^2/4 + \gamma/(K_b C_p)]^{0.5} \tag{6}$$

where $X = C_s/C_p$ and the additivity for the concentration of the sodium ions in added salt solutions was assumed.[25,26] If $C_s^2 > 4\gamma C_p/K_b$, eq 6 can be approximately rewritten as

$$a_\tau = \gamma + \gamma/(K_b C_s) \tag{7}$$

This equation means that a_τ at high C_s does not depend on C_p, in agreement with the experimental results shown in Figure 1. The values of K_b, γ, and β_c estimated by a curve fitting were listed in Table II, and a comparison of the calculated curves with the experimental data was shown in Figure 4. The theoretical curves calculated from this model are in agreement with the experimental data in the limited C_p region above C_p = 0.1 N over all C_s solutions. The disagreement in the region below C_p = 0.1 N may be due to the simple additivity between neutralized counterions from a polyion and added salts in eq 6. Probably, the net C_s acting in a binding equilibrium may be a function of C_p and should be low at low C_p. In order to improve the agreement between theoretical and experimental values of a_τ in the low C_p region, we considered the contribution from a Donnan term.[9] Such a contribution was, however, found to be negligibly small in low C_p region.

The value of K_b was found to decrease monotonically with increasing C_s, except for that in a salt-free solution. This may be due to the fact that K_b is an apparent binding constant and is closely related to the electrostatic potential (ψ) at a binding site of a polyion. Correspondingly, the value of γ also decreased monotonically with increasing C_s. That is, an increase of C_s reduces the solubility.

In Table II, we conclude that, even in a salt-free solution, phase separation occurs when about 58% of added Na^+ to neutralize is strongly bound to ionized sites of polyion, and the addition of NaCl facilitates the phase separation. From eq 6, $\bar{C}_s$ can be written as follows:

$$\bar{C}_s = \frac{\gamma}{(a_\tau - \gamma)K_b} - (a_\tau - \gamma)C_p \tag{8}$$

Clearly, this equation predicts that $\bar{C}_s$ decreases linearly with increasing C_p, since always $a_\tau > \gamma$. The experimental $\bar{C}_s$ decreased with C_p at high a_τ but deviated from linearity at low a_τ, as shown in Figure 2. This may be due to the fact that γ is a function of C_s, as shown in Table II.

The amounts of atmospherically bounded monovalent counterions seem to increase with a decrease in the radius of counterion, shown by measurements of intrinsic viscosity[27] and potentiometric titration.[28] The effect of counterion species on the precipitation, however, did not follow the order of the ionic radius of the counterion and was largely specific, as shown in Table I. The following order of specificity was obtained in this study: $Na^+ < K^+ \gg (n\text{-}Bu)_4N^+, Li^+ > Rb^+, Cs^+$. This is consistent with one reported by Eisenberg et al.[8] Here, it may be interesting to compare the present results with those of potentiometric titration[20] and the counterion activity coefficient.[29] The values of the negative logarithm of the apparent dissociation constant (pK_a) at $a > 0.5$ largely increased with the size of the cations, which means that the electrostatic potential increases with the size of the cations.[20] In other words, the smaller the size of the cation becomes, the greater is the amounts of bound counterion. This may be consistent with the present results, except for the case of Li^+.

The anomalous character of Li^+ seems due to the difference in the binding character of the ion bound species, $-COO^-M^+$; that is, the strong ionic binding accompanying the precipitation cannot be formed for the smaller counterions. Another reason why a PMA solution containing LiCl did not produce precipitation at C_s = 0.5 N may be interpreted in terms of the experimental fact that the solubility of LiCl in water is very high compared with that of other salts.[30] In the experiments of sodium ion activity and electrical conductivity of PMA in a salt-free solution, the bound sodium ions were fairly labile for $a > 0.5$ in a dilute, salt-free solution.[29] This seems to contradict the present results, but a_τ increases steeply with decreasing C_p in the region of $C_p < 0.1$ N, in which the measurement of activity and electrical conductivity were carried out. Therefore, we can conclude that the counterion binding manner of a PMA molecule for high C_p may be largely different from that for low C_p.

Mandel and co-workers[31] reported that a partially neutralized PAA with CH_3ONa in methanol exhibited a conformational transition at a low degree of neutralization, comparing with the effect of Li^+. They ascribed this phenomenon to a collapse of the chains into a compact particle when the neutralization proceeded, possibly due to ion pairing as well as change in the solvent quality. Their report may be instructive to understand the present data, although the charge density and the precipitation conditions are different. Another difference is in the viscosity behavior. In our case,[20] we did not observe a drastic decrease in viscosity as a function of the degree of

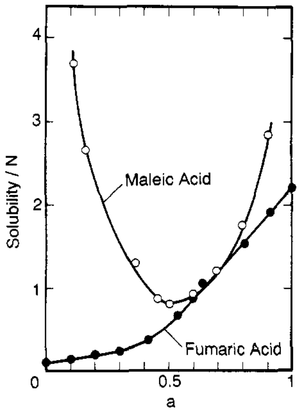

Figure 5. Plots of the solubilities of maleic acid and fumaric acid against the degree of neutralization at 25 °C.

neutralization. These results indicate that the conformational change is not verified as a cause of the ion binding. Further studies concerning ion specificity, especially the effect of Li^+, are presently undertaken in our laboratory in order to clarify the present results.

Finally, the solubilities of the monomer analogs of PMA, maleic acid, and its stereoisomer, fumaric acid, in water were shown in Figure 5, as a function of neutralization. Surprisingly, the solubility curve of maleic acid should be clearly different from that of fumaric acid. The solubility curve of fumaric acid consists of two modes, i.e., a lower increase with a in the region for $a \leq 0.5$ and a higher increase for $a \geq 0.5$.

In remarkable contrast to the solubility curve of fumaric acid, the solubility of maleic acid decreases steeply with a until $a = 0.5$ and exhibits a minimum at $a = 0.5$ and then increases with a. Maleic acid at $a = 0$ is about 100 times as soluble as fumaric acid (0.10 N).[32] On the other hand, the solubilities of maleic acid in the vicinity of $a = 0.5$ are nearly the same as those of fumaric acid. This result implies that the difference in the configuration strongly affects the solubility. The very high solubility of maleic acid at $a = 0$ may be due to the high water affinity to a solute molecule with adjacent carboxyl groups[33,34] and due to the low pK_1, compared with fumaric acid. Therefore, we conclude that the solubility of low molecular weight organic dicarboxylic acid does not necessarily increase, nor does it increase linearly with neutralization. The high solubility of PMA in the region of $a < 0.5$ which was shown in Figure 3 is thought to be due to the high water affinity of monomer units, although we do not have an explicit answer about the abnormal high solubility of maleic acid at $a = 0$. We can also conclude that the phase separation of PMA and PFA in the region of high a is a phenomenon characteristic of polyelectrolyte with a high charge density, since the solubilities of both hydrogen sodium maleate and the corresponding fumarate increase with further neutralization above $a = 0.5$.

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