

The Influence of Cations on the Dissociation Behaviour of Copolymers of Propene and Maleic Acid and Their Modified Products with Taurine In Salt-Free Solution

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ABSTRACT: Potentiometric and conductometric titrations were used to study the dissociation behaviour of poly(propene-co-maleic acid) and poly(propene-co-maleic acid) modified with various contents of taurine (2-aminoethanesulfonic acid) in salt-free solution. Copolymers of propene and maleic acid with different molecular weights were titrated with LiOH, NaOH, and KOH. The influence of molecular weight on pK_a is ascertainable in both the first and second dissociation step. Of the various alkali metal cations studied, lithium had the most significant effect on the dissociation behaviour. The acidic strength decreased in the order lithium > sodium \geq potassium. After insertion of sulfonic acid groups into poly(propene-co-maleic acid), the influence of strong acidic groups on the dissociation behaviour of carboxylic groups was studied. The contents of taurine were 10, 25, and 50 mol%. The second dissociation step was analyzed in this case. The pK_a values increased with increasing content of taurine for titrations with LiOH and KOH, but not NaOH. When NaOH was used, the pK_a decreases if the polymer was modified with 10% taurine. Higher taurine contents had no influence on the magnitude of pK_a . The results demonstrate the strong influence of short-range electrostatic interactions on the dissociation behaviour of weak polyacids. © 1999 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 37: 1949–1955, 1999

Keywords: poly(propene-co-maleic acid); potentiometric titration; aqueous solution; dissociation behaviour; taurine

INTRODUCTION

In aqueous polyelectrolyte solutions, dissociation behaviour is influenced by both the concentration of added salt and the types of counterions. Investigations of various maleic acid copolymers—such as those with styrene and α -methyl styrene,^{1,2} isobutene,³ propene,⁴ and alkyl vinyl ethers⁵—in salt solutions, have shown that increasing the concentration of added low molecular weight electrolyte decreases the pK_a values. The binding of counterions for these polyanions occurs in the following sequence: lithium > sodium > tetramethyl ammonium and lithium > sodium > potassium, respectively. Rinaudo⁶ reported the same

binding order for carboxymethylated derivatives of cellulose in salt-free solution, and, for polyethylene sulfonic acid, the exact opposite.

The purpose of this paper is to describe in detail the dissociation behaviour of alternating copolymers of propene and maleic acid, as well as copolymers modified with taurine, in salt-free solution. Of special interest is the interaction between the polyanion and different alkali metal cations (lithium, sodium, and potassium). The dependence of dissociation behaviour on molar mass was also studied.

EXPERIMENTAL

Materials and Methods

Preparation of Poly(propene-co-maleic acid)

Copolymers were prepared by precipitation polymerization in dichloroethane⁴ followed by hydro-

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Table I. Molecular Weights of the Investigated Poly(propene-co-maleic Anhydride)

Polymer	M_n [g/mol]	M_w [g/mol]
1	20,000	44,000
2	5,400	22,000
3	500	1,800

lysis in water at 60°C for 10 h. For titration, these stock solutions were diluted with water to 0.1N and 0.01N concentrations (C_p s). The former were titrated with 1N alkaline solutions—LiOH, NaOH, and KOH—and the latter with the same alkaline solutions at 0.1N concentration. Weight-average molecular weights (M_w s) of poly(propene-co-maleic anhydride) ranged from 1,800 to 44,000 g/mol (Table I).

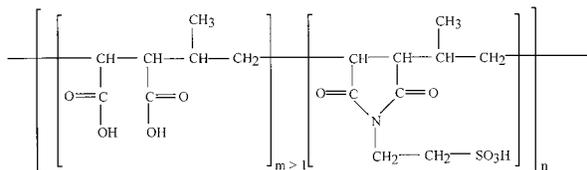
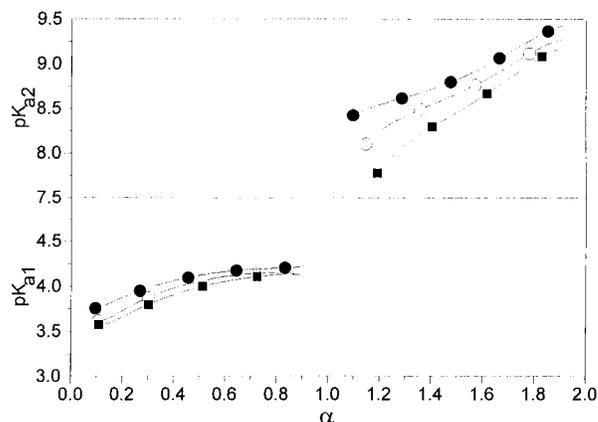
Preparation of Poly(propene-co-maleic acid) Modified with 2-Aminoethanesulfonic Acid (Taurine)

Poly(propene-co-maleic anhydride) of $M_n = 9,500$ g/mol and $M_w = 30,000$ g/mol was used as the starting compound. By adding sodium hydroxide, the monosodium salt of poly(propene-co-maleic acid) was converted with 10, 25, and 50 mol % of taurine. In a 200 mL steel autoclave, 10 mmol of polymer was converted with taurine in 30 mL water for 10 h at 140°C. The autoclave was flushed with nitrogen for three times before starting the reaction. Taurine content was determined by potentiometric titration; conversion of taurine exceeded 95% (Fig. 1).

Measurements

Potentiometric Titration

Potentiometric titrations were carried out with the computer-controlled titration system TPC 2000 with a pH electrode of type N 1042A from

**Figure 1.** Poly(propene-co-maleic acid) modified with 2-aminoethanesulfonic acid (taurine).**Figure 2.** Variation of pK_a with molar mass at $C_p = 0.1N$; titrant: NaOH. (●) Copolymer 1, $M_w = 44,000$ g/mol; (○) Copolymer 2, $M_w = 22,000$ g/mol; (■) Copolymer 3, $M_w = 1,800$ g/mol; frequency of symbols: 7–9.

Schott-Geräte GmbH (Germany). All titrations were carried out at $25 \pm 0.1^\circ\text{C}$ under nitrogen.

Conductometric Titration

The conductivity (Λ) of poly(propene-co-maleic acid) solutions was also measured with the TPC 2000 system equipped with a black platinized electrode. The cell constant was 1.07 cm^{-1} . Water was purified by ion exchange to conductivity $7 \times 10^{-6} \text{ S cm}^{-1}$. Titrations were carried out at 25°C under nitrogen. Since KCl diffusion from the glass electrode influences conductivity measurements, a different solution was used to measure pH and Λ .

RESULTS AND DISCUSSION

Influence of Molecular Weight on pK_a

The viscometric behaviour of hydrolyzed propene maleic anhydride copolymers of differing molecular weight varies in salt-free aqueous solutions.⁷ The dependence of intrinsic viscosity of copolymers on the degree of neutralization shows a maximum when weight-average molar mass exceeds 20,000 g/mol. Polymers with a degree of polymerization of 100 and higher usually show solution characteristics typical of a coil.

For our investigation, we chose oligomers with rod-like behaviour (DP: 7) and coiled polymers (DP: 77; DP: 286). For the former, intramolecular interactions of chain segments can be excluded. The dependence of pK_a on the degree of dissociation (α) is shown in Figure 2. Two dissociation

Table II. Values of pK_0 and ΔF_e for the Investigated Copolymers of Propene and Maleic Acid

Polymer	C_P [mmol/g]	Counterion	pK_{01}	ΔF_{e1} [kJ/mol]	pK_{02}	ΔF_{e2} [kJ/mol]	ΔpK
1			3.80	2.79	8.20	7.98	4.40
2	0.1	K ⁺	3.60	3.60	7.76	9.87	4.16
3			3.49	4.28	7.29	12.95	3.80
1			3.79	3.08	8.25	7.13	4.46
2	0.1	Na ⁺	3.63	3.93	7.91	8.67	4.28
3			3.55	4.33	7.53	11.24	3.98
1			3.76	3.14	8.16	4.10	4.40
2	0.1	Li ⁺	3.58	4.28	7.88	5.76	4.30
3			3.46	4.68	7.46	8.10	4.00
1			4.24	4.85	9.26	4.96	5.02
2	0.01	K ⁺	4.00	3.70	8.29	5.70	4.29
3			3.88	6.27	8.40	10.78	4.52
1			4.22	4.39	9.05	1.65	4.83
2	0.01	Na ⁺	4.06	5.76	8.71	5.70	4.65
3			3.89	8.56	8.74	7.42	4.85
1			4.21	4.50	8.97	2.39	4.76
2	0.01	Li ⁺	4.00	5.93	8.82	4.50	4.82
3			3.75	6.73	8.14	7.81	4.39

steps are clearly visible, as already shown for many maleic acid copolymers.^{8,9} Titration data were analyzed according to the previously reported method^{4,8} which involves the following relationships:

$$\alpha = \frac{[\text{MeOH}] + [\text{H}^+] - [\text{OH}^-]}{C_P} = \alpha_N + \frac{[\text{H}^+] - [\text{OH}^-]}{C_P} \quad (1)$$

$$pK_{a1} = \text{pH} - \log[\alpha/(1 - \alpha)] \quad (2)$$

$$pK_{a2} = \text{pH} - \log[(\alpha - 1)/(2 - \alpha)] \quad (3)$$

in which [MeOH] is the molarity of added titrant, [H⁺] and [OH⁻] are the molarities of free hydrogen and hydroxyl ion, respectively, C_P is the total molarity of the carboxyl group, and α_N the degree of neutralization. The [H⁺] was obtained by measuring pH and [OH⁻] was calculated from the ion product of water K_w (1.01×10^{-14} mol²/L² at 22°C).

Copolymers of poly(propene-*co*-maleic acid) contain erythro and threo configurations in a 20 : 80 ratio. Because each form dissociates in two steps, four dissociation constants are expected to emerge. In one study,¹⁰ polarographic measurements revealed three dissociation steps for poly(propene-*co*-maleic acid); in another,¹¹ four steps were detected for poly(ethene-*co*-maleic

acid). However, for the curve to show two separate dissociation steps, the difference between the two pK_a values had to exceed 2. Hence, our calculated pK_a values are only approximate. The determined intrinsic dissociation constants pK_0 are summarized in Table II. The value for pK_{01} was estimated by extrapolating pK_a values to $\alpha = 0$, using the $0.1 < \alpha < 0.9$ data because of the large errors in measurements for the $\alpha < 0.1$ and $\alpha < 0.9$ regions. The corresponding pK_{02} was determined for $1.1 < \alpha < 1.9$.

In both the first and second dissociation steps, the trend in pK_0 values indicates that acidic strength decreases with increasing molecular weight of the polymers, whereas the slope increases with lower molecular weight. (We will discuss the slopes in more detail later.)

In the first dissociation step, the pK_{01} values of polymers with different molar masses are relatively close. Distinct differences, however, are apparent in the second step in which, unlike in the first dissociation step, intramolecular interactions must play a dominant role.

In contrast to a polymer in which molecular weight is high enough to have no influence on dissociation, the dissociation of poly(propene-*co*-maleic acid) is a function of molecular weight. For other copolymers of maleic acid, the region of dependence should be different because of the

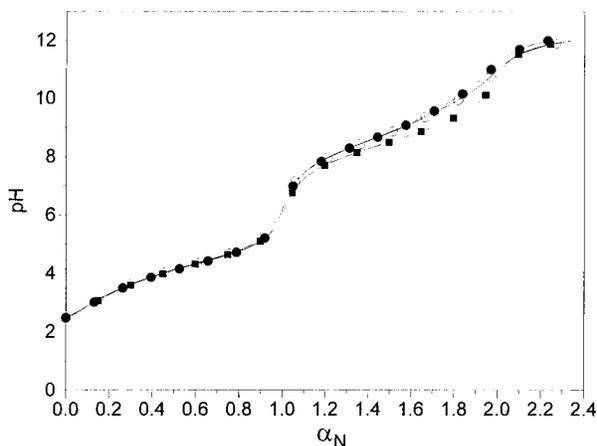


Figure 3. Titration curves of copolymer 1 with (●) KOH, (○) NaOH, and (■) LiOH at $C_P = 0.1N$; frequency of symbols: 7–9.

different intramolecular interactions. Because molecular weight distribution plays an important role in adsorption and complex formation, it is essential to pinpoint the region in which dissociation behaviour depends on molecular weight.

Dependence of pK_a on the Counterion

Potentiometric titration curves with LiOH, NaOH, and KOH titrants are shown in Figure 3 in which α_N , the degree of neutralization, is plotted against pH. Although the inflection points for all titrants are visible for the first dissociation step, the end point of LiOH titration for the second step is more pronounced than those of the other titrants, showing that the dissociation behaviour (in the absence of co-ions) is significantly influenced by the type of the counterion.

The potentiometric curves (Fig. 4) were analyzed as previously described. The pK_a with each titrant is plotted against α for two polymers with different molecular weights. The curves reflect the differences in pK_a values for the two dissociation steps (a1 and a2). In the range of the first step, the counterion had no measurable influence on dissociation behaviour in salt-free solution; the pK_{01} values of the curves were about the same (Table II).

As shown in Figure 4, however, a significant difference does appear among the titrants in the region of the second dissociation step, indicating that the type of the cation affects the acidic strength. The curves show that for each of the two copolymers, the pK_a value for a given value of α increases with the size of the cation. The size,

however, is related to the non-hydrated state of the counterions (cations), and cations in solution have a hydration layer. It is therefore possible that the solvation layer may be partly destroyed.

As mentioned previously, the tendency in the pK_a was found to be lithium < sodium \leq potassium for carboxylic groups in salt solution^{3,4,8,12} and salt-free solution.⁶ Consistent with these data, the acidic strength in our case was highest with LiOH titration. But for the sodium and potassium counterions, a visible difference between pK_a values is evident only when α exceeds 1.5.

The variation of pK_{02} is the result of the difference in slopes of the curves. To interpret the course of pK_a values, it is appropriate to explain the slopes, which provide a measure of the additional work (ΔF_e) to transfer protons (against the attraction of the negative charged polyion) from polyion to the bulk. The apparent dissociation constant (pK_a) is defined as follows:^{13,14}

$$pK_a = pK_0 + 0.434[\Delta F_e / RT] \quad (1)$$

where ΔF_e increases with increasing linear charge density on the chain. Different interactions between counterions and polyion are responsible for the different screening of negative charges on the polymer. Consequently, the contribution of ΔF_e to pK_a is smallest for lithium, as shown by the smallest slope of the pK_a curve (Fig. 4). The calculated ΔF_e values in Table II are similar in magnitude to those calculated by Rios et al.¹⁴ for maleic acid–vinylpyrrolidone copolymers in salt-free solution.

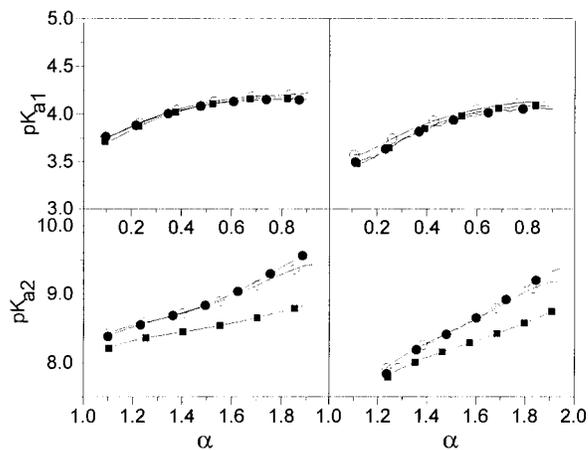


Figure 4. pK_a vs α on titration with (●) KOH, (○) NaOH, and (■) LiOH at $C_P = 0.1N$; a) copolymer 1 and b) copolymer 3; frequency of symbols: 7–9.

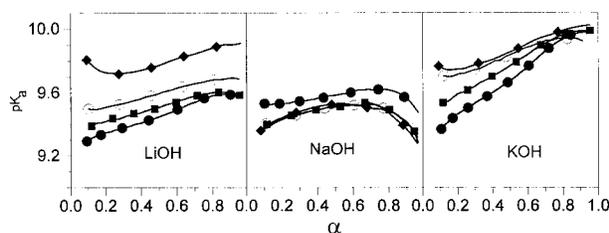


Figure 5. Variation of the apparent dissociation constant (pK_a) of poly(propene-*co*-maleic acid) modified with different contents of taurine; titration with a) LiOH, b) NaOH, and c) KOH; content of taurine: (●) 0%, (■) 10%, (○) 25%, (◆) 50%; $C_P = 0.00479$ mmol/g; frequency of symbols: 4–6.

Figure 5(a–c) shows the variation of pK_a with α for poly(propene-*co*-maleic acid) modified with taurine, and its dependence on the type of the counterion and percentage concentration of taurine. Since the order in which the alkali metal ions bind to the sulfonic acid groups of taurine is different from that of the carboxylic acid groups, it would be interesting to determine how a rising content of taurine influences the dissociation behaviour of the carboxylic groups.

In our experiments, taurine content (based on maleic anhydride units) in the copolymers ranged from 10% to 50%. The average distance of the sulfonic acid groups of the taurine was 50, 20 and 10 Å. Hence, the number of the maleic acid units between the taurine units were on average 9, 3 and 1. Only the second dissociation step was evaluated, since the first step includes the neutralization of both the first carboxyl group and the sulfonic acid group.

The influence of both the ionized carboxyl and sulfonic groups on the dissociation behaviour in

the second step is clear in Figure 5. Values for pK_0 and ΔF_e of the curves for each titrant are collected in Table III.

The calculated pK_0 values increase with the taurine content for both the LiOH and KOH curves. Since alkali metal ions bind to carboxyl and sulfonic groups with opposite preference, the increase in pK_a value is caused by interactions between the carboxyl group and its charged neighbors. The net charge of the sulfonic acid group is lower with the potassium than with the lithium counterion. Consequently, the increase of pK_a with the potassium must be caused primarily by the neighboring ionized carboxyl group. Therefore the value for ΔF_e is lower with higher taurine content. When lithium counterion is present, the increase in pK_a is caused mainly by ionized sulfonic groups around the corresponding carboxyl group. Only short-range intramolecular interactions play a role in dissociation behaviour changes. Weak interactions with the fifth-nearest neighbor can be observed. Interactions are most pronounced when each maleic acid unit is surrounded by sulfonic acid groups along the polymer chain.

Sodium counterions exert a different effect than either lithium or potassium. When the polymer chain contains 10% sulfonic acid groups, the pK_a decreases. A higher content of taurine did not influence the magnitude of pK_a . No explanation is available at this time for the strong decrease of the pK_a values at $\alpha > 0.7$. Systematic error can be excluded.

When taurine content exceeded 50%, it was impossible to accurately measure pK_a for the second dissociation step. This prevented us from describing the influence of higher taurine content on dissociation. These experiments show that within limits, it is possible, by modifying reactions, to

Table III. Values of pK_0 and ΔF_e for Poly(propene-*co*-maleic Acid) Modified with Taurine

Content of Taurine [%]	Titrant					
	LiOH		NaOH		KOH	
	pK_0	ΔF_e [kJ/mol]	pK_0	ΔF_e [kJ/mol]	pK_0	ΔF_e [kJ/mol]
0	9.26	2.28	9.49	1.03	9.29	4.16
10	9.35	1.77	9.41	0.97	9.45	3.65
25	9.45	1.77	9.41	0.97	9.61	2.51
50	9.61	1.94	9.43	1.08	9.64	2.34

control the influence of the type of counterion on polyacid dissociation behaviour.

Influence of the Polymer Concentration on pK_a Values

The data in Table II show that, for polymers at low concentrations, pK_a values increase in a manner that is independent of their structure in solution. The competing reaction between alkali metal counterions and protons seems to be relevant to this.¹⁴ Apparently the more dilute the polymer solution, the lower the exchange of protons by other cations, resulting in a decrease in the acidic strength. Moreover, the values for ΔF_e increase for $\alpha < 1.0$ for the same counterion with dilution. We have no explanation for why ΔF_e decreases with dilution in the second dissociation step.

For the 0.01N solutions, several ΔF_e values are lower than their ΔF_e counterparts. That is also inexplicable. One should assume that the tendency of protons to dissociate decreases with an increase in linear charge density along the polymer chain. For this reason the contribution of ΔF_e to pK_a should be greater (as for $\alpha < 1$).

This unusual behaviour must be attributed to specific effects of the polymers themselves—which are not considered when calculating pK_a values.

Conductometric Investigations on the Polymer Solutions

Conductometric measurements were carried out to define possible effects of concentration, molar mass, and counterion type on the autodissociation of propene–maleic acid copolymers. Van Leeuwen et al.¹⁵ have described the theoretical background of conductivity, a suitable method to determine concentrations of polymer in solution. The autodissociation constant (K) for polyacids can be estimated from the minima occurring in the initial part of conductometric titration curves. The basic equation is the following:

$$K = [\text{H}^+][\text{A}^-]/[\text{HA}] \quad (4)$$

If $[\text{HA}] = [\text{HA}]_0 - [\text{A}^-]$ and $[\text{OH}^-]_{\text{titrant}} = [\text{H}^+] = [\text{A}^-]$, then

$$pK = \log\{([\text{HA}]_0 - [\text{A}^-])/[\text{A}^-]^2\} \quad (5)$$

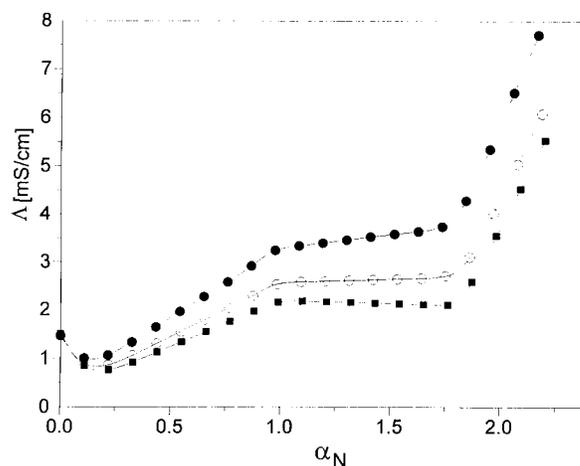


Figure 6. Typical conductometric titration curves with titrants (●) KOH, (○) NaOH, and (■) LiOH, copolymer 2, $C_p = 0.1$ mol/L; frequency of symbols: 7–9.

in which $[\text{OH}^-]_{\text{titrant}}$ represents the molarity of the titrant added at the minimum of the conductometric curve.

Figure 6 shows the dependence of conductivity (Δ) on the degree of neutralization for the three titrants. The calculated pK_a values obtained from the minima are shown in the pK_a columns of Table IV. Additionally pK_a from potentiometric titration can be calculated from the following equation:

$$pK_a = \text{pH} - \log[\alpha/(1 - \alpha)]. \quad (6)$$

The pK_a values obtained from conductometric curve minima are somewhat lower than those obtained from potentiometry. This means that the proton concentration calculated from conductometry exceeds that arrived at from potentiometric data. This is in accord with the expectation that protons, which reside in the counterion cloud of the polyelectrolyte, cannot be recorded by the glass electrode used in potentiometry.

The significant influence of cations on autodissociation was apparent from the observed shift of the minimum when LiOH was used for neutralization instead of NaOH or KOH. Obviously the different cations influence the dissociation in a region where Manning's charge density parameter is $\xi = 0.36$ ¹⁶. In this case, counterion condensation should not occur.

Conductometry can be used to investigate dissociation behaviour of dilute salt-free solutions of the polymers studied, particularly when glass electrodes cannot be used. It should also be possible to determine how the degree of autodissocia-

Table IV. Calculated pK_a -values of Autodissociation for Copolymers of Propene and Maleic Acid

Polymer	Counterion	C_P [mmol/g]	pK_a^A	pK_a^B	C_P [mmol/g]	pK_a^A	pK_a^B
1	K ⁺	0.1	3.41	3.86	0.01	3.97	4.39
	Na ⁺	0.1	3.26	3.86	0.01	3.85	4.37
	Li ⁺	0.1	3.16	3.84	0.01	3.73	4.39
2	K ⁺	0.1	3.19	3.69	0.01	3.70	4.16
	Na ⁺	0.1	3.02	3.74	0.01	3.73	4.29
	Li ⁺	0.1	2.98	3.71	0.01	3.60	4.22
3	K ⁺	0.1	3.02	3.60	0.01	3.63	4.15
	Na ⁺	0.1	3.02	3.67	0.01	3.57	4.12
	Li ⁺	0.1	2.90	3.62	0.01	3.42	4.07

^A Values from minimum of conductometric curves.

^B Values from interpolation of the pK_a -curves for corresponding degree of neutralization.

tion of polyacids in highly dilute solutions depends on polyacid concentration.

CONCLUSIONS

The dissociation behaviour of the investigated polyacids is influenced by the type of the counterion in salt-free solution. The acidic strength of the polyacids decreases according to the following: lithium > sodium \geq potassium. The same tendency is known in the dependence of the pK_a values on ionic strength.

Intramolecular and intermolecular interactions vary significantly with identical concentrations of polymer. The acidic strength decreases with increasing molecular weight. The difference is a function of the degree of neutralization.

Neighboring sulfonic acid groups influence the dissociation behaviour of the carboxyl groups. The influence depends on the type of counterion.

Conductometric measurements should particularly useful to further investigate the influence of substituents at the backbone of a polymer chain on dissociation, and to study the auto-dissociation behaviour at higher dilutions in salt-free solutions.

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