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Counterion Effect on the Titration Behavior of Poly(maleic acid)

Nobuhiko Muto, Tsuyoshi Komatsu, and Tsurutaro Nakagawa
Department of Polymer Science, Faculty of Science, Hokkaido University, Sapporo 060

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The potentiometric titration of poly(maleic acid) (PMaA) in aqueous solutions containing alkali metal salts and a tetramethylammonium salt was carried out at 25 °C, and the effect of the counterions on the titration behavior of PMaA was examined in detail. The acidity of the primary carboxylic groups of PMaA increases in the order of $(CH_3)_4N^+ < Li^+ < Na^+ < K^+$, whereas that of the secondary carboxylic groups increases with the decrease in the crystallographical radius of the counterions, in agreement with the results for ordinary polycarboxylic acids. The order of $K^+ > Na^+ > Li^+$ for the binding strength to the primary carboxylate groups of PMaA is interpreted in terms of the radius of the hydrated cations; it can be attributed to the stable ring structure of the monoanion of the maleic acid residue, resulting from the hydrogen bonding between two adjacent carboxylate groups.

It is well known that the titration behavior of weak polyelectrolytes is remarkably affected by the nature of the counterions. This can be ascribed to the polyion-counterion interaction caused by the high electrostatic potential around the macroions. Gregor *et al.*[1,2] investigated the effect of alkali metal ions and tetraalkylammonium ions on the titration behavior of poly(acrylic acid) and poly(methacrylic acid), and demonstrated that the acidity of those polymonocarboxylic acids decreases with the increase in the counterion size; that is, the alkali metal ions are bound to the polyanions in the order of $Li^+ > Na^+ > K^+$. Similar phenomena have been observed in connection with the viscosity,[3] the conductivity,[3,4] and the counterion activity[5] in such polyelectrolyte systems.

As for polydicarboxylic acids, several studies have been performed on counterion binding with maleic

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[1] H. P. Gregor and M. Frederick, *J. Polymer Sci.*, **23**, 451 (1957).

[2] I. Kagawa and H. P. Gregor, *ibid.*, **23**, 477 (1957).

[3] H. P. Gregor, D. H. Gold, and M. Frederick, *ibid.*, **23**, 467 (1957).

[4] K. Tamaki, M. Ozaki, M. Ogiwara, and I. Takemura, *Nippon Kagaku Zasshi*, **88**, 711 (1967).

[5] I. Kagawa and K. Katsuura, *J. Polymer Sci.*, **17**, 365 (1955).

acid copolymers,[6–9] though few papers have described the effect of alkali metal ions in detail. Recently, homopolymers of maleic anhydride have been prepared by the use of γ-irradiation[10] and radical initiators,[10–12] and the titration behavior of their hydrolysis products in added salt-free solutions has been briefly reported.[10,13] The counterion effect on the behavior, however, has still not been adequately examined.

The present authors have synthesized a homopolymer of maleic anhydride by radical polymerization in acetic anhydride and have carried out the potentiometric titrations of the hydrolysis product, namely, poly(maleic acid) (PMaA), in aqueous solutions containing added salts. The present study will deal with the effects of alkali metal ions (Li^+, Na^+, and K^+) and the tetramethylammonium ion on the titration behavior of PMaA. Especially, the binding of the alkali metal ions to the primary carboxylate groups of PMaA will be discussed.

Experimental

The PMaA sample was prepared by reference to the procedure of Lang *et al.*[10] as follows. Maleic anhydride was polymerized in an acetic anhydride solution containing 50 wt% monomer and 3 wt% α,α'-azobisisobutyronitrile at 80 °C for 48 hr. The reaction mixture thus became a deep purple color.[10] From the reaction solution diluted with methyl ethyl ketone, the polymer was separated by precipitation in toluene. The poly(maleic anhydride) was purified by reprecipitation and dried *in vacuo* at 60 °C. The product retained a slight purple tint.[10,12] Found: C, 47.03; H, 3.67; N, 1.23%. Calcd for $(C_4H_2O_3)_n$: C, 48.92; H, 2.20%. The molecular weight of the poly(maleic anhydride) was determined by means of vapor-pressure osmometry to be 2500. The intrinsic viscosity, $[\eta]$, in acetophenone was 0.082 dl/g at 25.0 °C. The anhydride polymer was hydrolyzed in water at 80—90 °C for 6 hr. The PMaA solution was standardized potentiometrically and stored in a polyethylene container at 5 °C.

The titrants, NaOH and $Ba(OH)_2$ solutions, were prepared so as to be carbonate-free. As added neutral salts, the nitrates of lithium, sodium, and potassium, and tetramethylammonium chloride were used. All the chemicals used were of a guaranteed reagent grade. The maleic and acetic anhydrides were purified by distillation. All the aqueous solutions were prepared by the use of deionized water.

The pH values were measured by the aid of a Yokogawa KPH-51A pH meter, with Toa Denpa HG-4005 glass and HC-205 calomel electrodes separated by a saturated KCl-agar salt bridge. The titrations were performed in a special titration vessel maintained at 25.0 °C under a nitrogen atmosphere. It was found that the acid-base equilibrium was not immediately attained in the region around and beyond the half-neutralization point of PMaA. Similar phenomena have been observed in the cases of other polyacids.[14,15] In this region, the solutions were stirred for 15 min—1 hr after each addition of a certain amount of the base, until the pH readings were ascertained to be constant; then the titrations were resumed. The repeated-titration curves were reproducible to within ±0.01 pH unit.

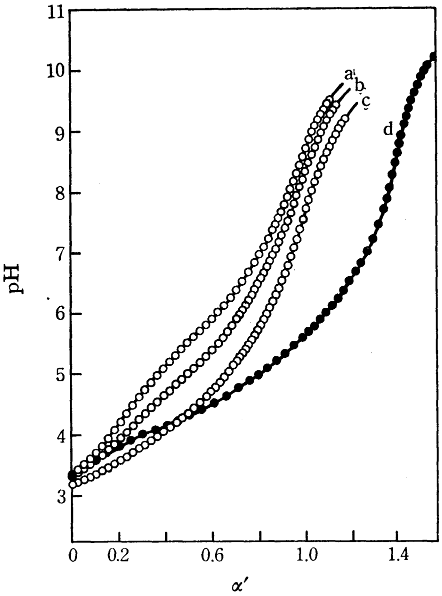

Fig. 1. The pH titration curves of 3.88×10^{-3} N PMaA (in the primary carboxylic groups) with NaOH in water (a), in 0.01 mol/l $NaNO_3$ (b), in 0.1 mol/l $NaNO_3$ (c), and with $Ba(OH)_2$ in water (d).

Results and Discussion

Figure 1 shows the pH titration curves of PMaA with NaOH and $Ba(OH)_2$ in water or in the presence of $NaNO_3$, where α' is the degree of the neutralization of the primary carboxylic groups of PMaA. Each titration curve with NaOH (open circles) has an inflection point at the same degree of neutralization ($\alpha'=1.0$), which corresponds to the equivalent point of the primary carboxylic groups, regardless of the ionic strength. It has been found that the carboxylic groups of PMaA as well as those of the ethylene–maleic acid copolymer[6] dissociate in two distinct steps.[10,13] The titration curve with $Ba(OH)_2$ (solid circles) had the end point for the total (primary and secondary) carboxylic groups at $\alpha'=1.4$. This indicates that, in the present PMaA sample, part of the secondary carboxylic groups (60%) are lost or are turned into some nonionic forms by side reactions in the course of the polymerization; as a result, there are many single carboxylic groups besides vicinal ones derived from the anhydride units. This finding is similar to that of Braun *et al.*,[12] who carried out the radical homopolymerization of maleic anhydride in organic solvents.

Figure 2 illustrates the titration curves of PMaA with

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[6] B. J. Felber, E. M. Hodnett, and N. Purdie, *J. Phys. Chem.*, **72**, 2496 (1968).

[7] B. J. Felber and N. Purdie, *ibid.*, **75**, 1136 (1971).

[8] A. J. Begala and U. P. Strauss, *ibid.*, **76**, 254 (1972).

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[10] J. L. Lang, W. A. Pavelich, and H. D. Clarey, *J. Polymer Sci., Sec. A*, **1**, 1123 (1963).

[11] R. M. Joshi, *Makromol. Chem.*, **53**, 33 (1962).

[12] D. Braun, I. A. A. El Sayed, and J. Pomakis, *ibid.*, **224**, 249 (1969).

[13] I. Sakurada, Y. Sakaguchi, S. Hōrin, and H. Uehara, *Kobunshi Kagaku*, **27**, 74 (1970).

[14] H. P. Gregor, L. B. Luttinger, and E. M. Loeble, *J. Phys. Chem.*, **59**, 34 (1955).

[15] N. Muto, T. Komatsu, and T. Nakagawa, *Nippon Kagaku Zasshi*, **92**, 43 (1971).

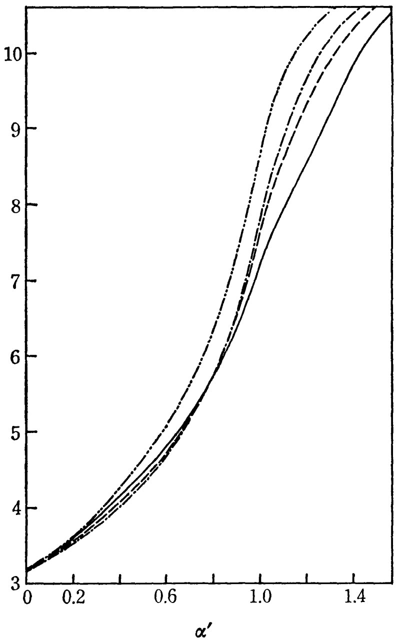

Fig. 2. The pH titration curves of 3.88×10^{-3} N PMaA with NaOH in 0.1 mol/l $LiNO_3$ (——), $NaNO_3$ (------), KNO_3 (-·-·-), and $(CH_3)_4NCl$ (-··-··-).

NaOH in 0.1 mol/l solutions of four kinds of 1-1 salts. The first equivalent point is independent of the sort of added salt as well. Since, in these titrations, the added salt concentration (0.1 mol/l) is much higher than that of polyacid (*ca.* 10^{-3} N primary carboxylic groups), the dissociation behavior of PMaA must be substantially influenced by the cations of added salts, in spite of the use of NaOH as a titrant in all cases.

The effect of the four kinds of cations in the first dissociation step seems to differ from that in the second one. In the second dissociation step ($\alpha' \geq 1.0$), the pH values at a given α' decrease in the order of $(CH_3)_4N^+ > K^+ > Na^+ > Li^+$, in agreement with the cases of ordinary polycarboxylic acids.[1] On the other hand, in the first dissociation step a peculiar effect of the alkali metal ions is observed; that is, the pH values at a given α' decrease in the order of: $(CH_3)_4N^+ > Li^+ > Na^+ > K^+$ in the region of $\alpha' \leq 0.8$. It has been found that, in the titrations of the ethylene–maleic acid copolymer with KOH and $(CH_3)_4NOH$,[6] the pH values decrease in the order of: $(CH_3)_4N^+ > K^+$ over the whole range of α'. This fact indicates that the potassium ion is bound to the polymer in a certain way.[6] Lang *et al.*[10] carried out similar titrations of PMaA with LiOH, NaOH, KOH, and $(CH_3)_4NOH$, but they made no reference to the specific effect of the alkali metal ions in the first dissociation step.

In order to characterize this counterion effect, the apparent acid-dissociation constants (K) were calculated from the titration curves according to this equation:

$$pK = pH + \log\frac{1-\alpha}{\alpha} \tag{1}$$

where α is the degree of dissociation of the primary carboxylic groups of PMaA. The α values were determined from the electroneutrality condition in acidic solutions:

$$\alpha = \frac{[NaOH]+[H^+]}{[A_t]} = \alpha' + \frac{[H^+]}{[A_t]} \tag{2}$$

where $[A_t]$ represents the total concentration of the primary carboxylic groups; the $[H^+]$ values were calculated from the measured pH values, with a correction for the activity coefficient ($\gamma_{H^+} = 0.83$ at the ionic strength of 0.1[16]). It is well known that the apparent dissociation constant for weak polyacids continuously decreases with the increase in α. This effect is connected with the increasing difficulty in the removal of

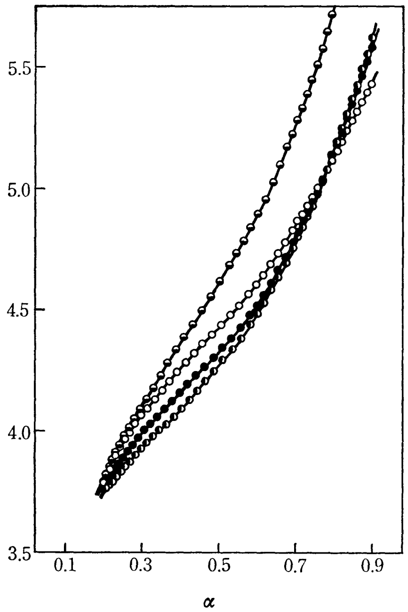

Fig. 3. The dependence of pK on α, calculated from the curves in Fig. 2. ○: $LiNO_3$, ●: $NaNO_3$, ◐: KNO_3, and ◒: $(CH_3)_4NCl$.

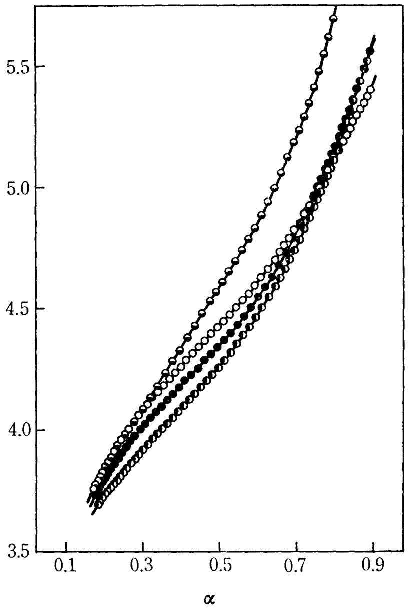

Fig. 4. The pK *vs.* α curves of 5.82×10^{-3} N PMaA with NaOH in 0.1 mol/l $LiNO_3$ (○), $NaNO_3$ (●), KNO_3 (◐), and $(CH_3)_4NCl$ (◒).

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[16] J. Kielland, *J. Amer. Chem. Soc.*, **59**, 1675 (1937).

protons from polyions with the increase in the charge on a polymer chain.[17]

Figures 3 and 4 show the pK *vs.* α curves. The latter was obtained at a polyacid concentration higher by 50% than the former. The curves with the same added salt are virtually superposed on each other, irrespective of the polymer concentration. In the case of poly(acrylic acid),[18] it has been found that the pK_{av} (pK at $\alpha=0.5$) values at the same ionic strength are, in fact, constant over the concentration range of 10^{-3}—10^{-1} N polyacid.

TABLE 1. THE pK_{av} VALUES OF THE PRIMARY CARBOXYLIC GROUPS OF PMaA IN 0.1 mol/l ADDED SALTS

Counterion	Polyacid concentration[a)] 3.88 mN	5.82 mN
$(CH_3)_4N^+$	4.61	4.59
Li^+	4.43	4.43
Na^+	4.33	4.35
K^+	4.27	4.27

a) In the primary carboxylic groups.

It is noticeable that, in the region of $\alpha \leq 0.8$, the pK values at a given α decrease in the order of: $(CH_3)_4N^+ > Li^+ > Na^+ > K^+$, and that the p$K$ curves in the presence of the alkali metal ions deviate most from each other in the region of $0.4 \leq \alpha \leq 0.5$. Table 1 summarizes the pK_{av} values of the primary carboxylic groups determined in Figs. 3 and 4. The differences in pK_{av} with the alkali metal ions (0.06—0.10 pK unit) are sufficiently larger than the estimated uncertainty on pK (0.02), not to mention the differences in the effect between the $(CH_3)_4N^+$ ion and the others. In such a case, the extent of the lowering in the pK or the increment in acidity gives a measure of the interaction between carboxylic groups and counterions.

On the basis of the assumption that no $(CH_3)_4N^+$ ions are bound to carboxylate groups in the PMaA–$(CH_3)_4NCl$ system, the degree of binding (θ) of the alkali metal ions (M^+) with the primary carboxylate groups (A^-) was calculated from the titration curves. The θ is defined by the equation:

$$\theta = \frac{[MA]}{[A_t]} = \frac{[A_t]-[HA]-[A^-]}{[A_t]} \tag{3}$$

where [HA] and [A^-] are the concentrations of the undissociated and dissociated primary carboxylic groups respectively, and where [MA] is that of the primary carboxylate groups bound to the alkali metal ions. In Eq. (3), [HA] is found to be:

$$\begin{aligned}[HA] &= [A_t] - [NaOH] - [H^+] \\ &= [A_t](1-\alpha') - [H^+] \end{aligned} \tag{4}$$

from the conservation and electroneutrality conditions. The [A^-] values in the 0.1 mol/l MNO_3 solutions are determined by the use of the reference curve for the 0.1 mol/l $(CH_3)_4NCl$ solution (Fig. 5). After the determination of the (pH+log[HA]) values for the 0.1 mol/l MNO_3 solutions at the same concentration of PMaA, the appropriate [A^-] concentrations in the MNO_3 solutions can be found in the reference graph. The scheme with the reference curve has been devised by Mandel *et al.*;[19] their method of calculation for the formation curves of metal-polyacid complexes from the titration curves is a modification of the method proposed by Gregor *et al.*[14]

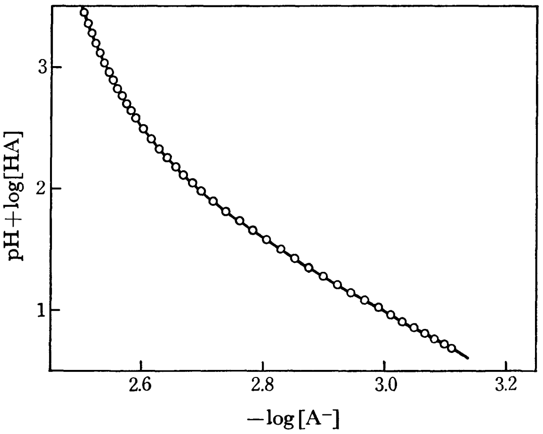

Fig. 5. The reference plot of 3.88×10^{-3} N PMaA in 0.1 mol/l $(CH_3)_4NCl$, for calculation of θ.

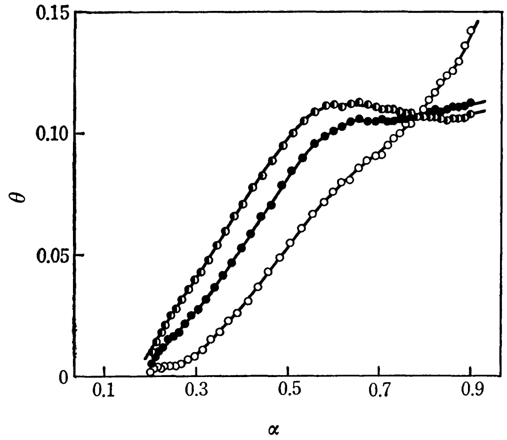

Fig. 6. The dependence of θ on α, calculated from the curves in Fig. 2. ○: Li^+, ●: Na^+, and ◐: K^+.

The dependence of θ on α is shown in Fig. 6. In the region of $\alpha \leq 0.8$, the binding strength was in the order of $K^+ > Na^+ > Li^+$, whereas in the region of $\alpha \geq 0.8$ the order was reversed. With the increase in α, the θ values in the cases of the K^+ and Na^+ ions were saturated so as to be practically constant (0.10—0.11) in the region of $\alpha \geq 0.5$. On the other hand, the θ values for Li^+ ions monotonously increased with α and grew much higher than those for other ions beyond $\alpha=0.8$. Since, in the present PMaA sample, the equivalent point of the total carboxylic groups was found at $\alpha'=1.4$, roughly half of the total carboxylic groups are dissociated at the above-mentioned point of $\alpha=0.8$. That is to say, the dissociation behavior in the region of

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[17] J. Th. G. Overbeek, *Bull. Soc. Chim. Belges,* **57**, 252 (1948).

[18] J. V. McLaren, J. D. Watts, and A. Gilbert, *J. Polymer Sci., Ser. C,* **16**, 1903 (1967).

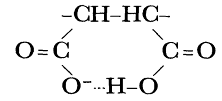
[19] M. Mandel and J. C. Leyte, *ibid., Ser. A,* **2**, 2883 (1964).

$\alpha \leq 0.8$ may be influenced predominantly by the typical primary carboxylic groups in the maleic acid residues, and then in the region of the larger α values the single and the secondary carboxylic groups may dissociate. Thus, the present results indicate that the mode of the binding of the alkali metal ions to the primary carboxylate groups of PMaA differs from that to the secondary and the single carboxylate groups.

The binding order of $Li^+ > Na^+ > K^+$ with the secondary carboxylate groups of PMaA (Fig. 2) agrees with the results for ordinary polymonocarboxylates[1,3,4] and for the secondary carboxylate groups of maleic acid copolymers.[8] The latter were obtained in connection with dilatometric studies of the binding of Li^+ and K^+ ions to the carboxylate groups in 0.2 mol/l $(CH_3)_4NCl$ solutions.[8] The results can be explained in terms of the crystallographical ionic radius of alkali metals;[2] that is, the smallest Li^+ ion is bound to the largest extent.

It is noteworthy that the binding strength of the alkali metal ions to the primary carboxylate groups is in the order of: $K^+ > Na^+ > Li^+$. In general, the binding strength of ion pairs increases with the decrease in a certain ionic-size parameter as far as the same valence type is concerned. The order of the binding strength with the primary carboxylate groups can, therefore, be interpreted in terms of the radii of the *hydrated* alkali metal ions, which increase in the order of: $K^+ < Na^+ < Li^+$. In other words, in the first dissociation step of PMaA the so-called solvent-separated ion pairs between hydrated cations and carboxylate groups are predominant, not the so-called contact ion pairs interpreted in terms of the crystallographical ionic radii of the counterions.[2]

It can be presumed that the specific counterion binding to the primary carboxylate groups results from the peculiar structure of the maleic acid polymers, in which the local density of ionizable groups on the main polymer chain is much higher than that in ordinary polycarboxylic acids; hence, the interaction between neighboring groups must be considerable. Recently, Strauss *et al.* measured by dilatometry the volume changes associated with the binding of the hydrogen ion to the anions of maleic acid copolymers in 0.2 mol/l $(CH_3)_4NCl$ solutions,[8] and pointed out that the monoanion of the maleic acid residue has the following structure:



involving cooperative hydrogen bonding by two adjacent carboxylate groups.[8,20] Felber *et al.*,[7] who measured the heats of the protonation of the ethylene–maleic acid copolymer, have proposed the same structure in the first ionization process, too. In a monomeric maleic acid molecule, the intramolecular hydrogen bond of the hydrogen maleate anion has been confirmed.[21,22]

It is considered that, in the first dissociation step of PMaA, the monoanion of the maleic acid residue probably has a stable ring structure resulting from the hydrogen bond, in which a single electronic charge is distributed by resonance over a wide range. Therefore, the primary carboxylate groups, which would be bound to the alkali metal ions by nature, are more tightly bound to the protons of the secondary carboxylic groups. The present findings that hydrated alkali metal ions are more loosely bound to the primary carboxylate groups can be attributed to such a chelation of a proton with two adjacent carboxylate groups. In the second dissociation step, the intramolecular hydrogen bond almost disappears; hence, the contact ion pairs between alkali metal ions and carboxylate groups become predominant.

Finally, the potentiometric titration method has been found to be very useful in detecting such subtle differences in the modes of short-range interaction as the binding of counterions to polyelectrolytes. Similar studies will be performed on the titration behavior of other dicarboxylic acid polymers.

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20) A. W. Schultz and U. P. Strauss, *J. Phys. Chem.*, **76**, 1767 (1972).

21) S. Nagakura, *J. Chim. Phys.*, **61**, 217 (1964).

22) J. J. Christensen, R. M. Izatt, and L. D. Hansen, *J. Amer. Chem. Soc.*, **89**, 213 (1967).