

Potentiometric Titration of Carboxyalkylated Poly Vinyl Alcohol with Mono-, Di-, and Trichloroacetic Acids with Alkali Metals and Quaternary Ammonium Bases

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Potentiometric titrations of the obtained first carboxyalkylated products were carried out with LiOH, NaOH, KOH, NH₄OH, N(CH₃)₄OH and N(C₂H₅)₄OH in deionized water and with mixtures of LiOH and tetraethylammonium hydroxide of varying proportions. The experimental results were expressed in terms of the modified Henderson-Hasselbach equation $\text{pH} = \text{pK}'a - n \log [(1 - \alpha/\alpha)]$. Appreciable shifts in the titration curves to lower pH values are observed, accompanied by increase in the values of calculated capacity of the polyelectrolyte, upon passing from N(C₂H₅)₄OH to N(CH₃)₄OH to NH₄OH to KOH to NaOH to LiOH. The values of pK'a (at $\alpha = 0.5$) and of n are found to increase with the size of counterion. The titration curves of the three polyelectrolytes with mixtures containing different proportions of LiOH and N(C₂H₅)₄OH in deionized water, show that the calculated values of capacity and the position of the curves were intermediate between those obtained with the single cations. At the same value of α , the value of pH increased with the per cent of N(C₂H₅)₄OH relative to LiOH.

INTRODUCTION

While the titration behaviour of low molecular weight acids and bases is independent of the nature of the base or acid used as a titrant, this is not the case with polymeric acids and bases. Here specific effects have been found to occur where different counterions are present. Some of these specific effects have been observed by Steinhard¹ and by Tanfard², who observed that the titration behaviour of proteins was dependent in part on the specific acid and base used. Differences in the viscometric behaviour of polyacrylic acid when neutralized with NaOH and with KOH are mentioned by Katchalsky³. A note by Greger, Luttinger and Loeb⁴ described the titration of polyacrylic acid with quaternary ammonium bases, and showed that pka (the negative logarithm of the average ionization constant) was 6.43 with KOH and 6.85 with N(C₂H₅)₄OH. This decrease in acid strength with increasing size of the counterion was also observed with crosslinked polyacrylic and polymethacrylic acids by Gregor, Hamilton, Becher and Bernstein⁵. Swelling measurements of these crosslinked gels showed that the entropy of the polymer chain decreased with increasing size of the counterion, at the same degree of neutralization.

EXPERIMENTAL

Materials

The carboxyalkylation reactions of polyvinyl alcohol with mono-, di- and trichloroacetic acid as well as the purification of the obtained products are carried out as reported elsewhere⁶. All the chemicals used were either of BDH or AnalaR grades.

Potentiometric Titrations

Weighed amounts of the pure polymer (1.0 gm/25 ml deionized water, or in aqueous NaCl solution) in the H-form was titrated at 25°C using the MOH solution upon vigorous shaking (M=Li, Na, K, NH₄, N(CH₃)₄ and N(C₂H₅)₄). The practically unchanged pH values stayed for 30 minutes after each addition, was recorded with the help of pH-meter (Orion Research Digital Ion analyzer 1501). The temperature was maintained in all the experiments at 25°C. First, second and third carboxyalkylation carried out as reported elsewhere⁷.

RESULTS AND DISCUSSION

The contribution presents detailed data on the titration of carboxyalkylated polyvinyl alcohol with mono-, di- and trichloroacetic acids (first carboxyalkylation) with LiOH, NaOH, KOH, NH₄OH, N(CH₃)₄OH and N(C₂H₅)₄OH in deionized water and with mixtures of LiOH and N(C₂H₅)₄OH of varying proportions. All potentiometric titrations were carried out in the absence of added salts. The experimental results for each titration curve could be expressed in terms of the modified Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}'a - n \log [(1 - \alpha)/\alpha]$$

where α is the degree of neutralization, or equivalents of base added per equivalent of acid present, n is a constant, and $K'a$ is the average ionization constant. Results given in Table 1 for carboxyalkylated polyvinyl alcohol (2.25 gm/25 ml deionized water) with mono-, di-, and trichloroacetic acid respectively with N(Et)₄OH, N(CH₃)₄OH, NH₄OH, KOH, NaOH and LiOH. In each case an appreciable shift in the titration curves to lower pH values is observed and also an increase in the values of capacity of the resin, upon passing from N(Et)₄OH to N(CH₃)₄OH to NH₄OH to KOH to NaOH to LiOH. From the plots of $\text{pH} + \log (1 - \alpha)/\alpha$ versus—Fig. (1) I, II, III, the values of $\text{pK}'a$ at $\alpha = 0.5$ are evaluated and the results given in Table 1 show that they increase with the size of counterion.

Upon applying Henderson-Hasselbalch plots for these titration curves the values of n and consequently the average values of $\text{pK}'a$ are calculated from the plots of pH versus $\log (1 - \alpha)/\alpha$, Fig. (2) I, II, III, Table 2. The

values of n and the slopes of the obtained curves are found to decrease with the size of counterion, whereas those of $pK'a$ increase. The pH shifts cannot be ascribed to specific salt effects, but rather to polyanion-counterion interactions. In the absence of neutral salt, the average ionization constants are nearly the same, and the significant increase in the average values of $pK'a$ begins from potassium ions. In all cases Henderson-Hasselbalch plots of the data gave plateau of nearly parallel lines for each polymer.

The carboxyalkylated polyvinyl alcohol with mono-, di-, and trichloroacetic acid were also titrated with mixture of bases (each mixture consists of a large and small counterion) and the results are given for titrations in

TABLE 1
VALUES OF pK AND K DERIVED FROM THE PLOTS OF
 $pH + \text{Log} \{(1 - \alpha)/\alpha\}$ VERSUS α

Polyacid	Apparent pK	K
<i>Polyvinyl alcohol with monochloroacetic acid titrant</i>		
with LiOH	4.8	1.582×10^{-5}
with NiOH	5.5	3.155×10^{-6}
with KOH	6.2	6.293×10^{-7}
with NH_4OH	8.5	3.151×10^{-9}
with $N(CH_3)_4OH$	9.1	7.913×10^{-10}
with $N(C_2H_5)_4OH$	9.8	1.578×10^{-10}
<i>Polyvinyl alcohol with dichloroacetic acid titrant</i>		
with LiOH	7.3	4.997×10^{-8}
with NaOH	8.2	6.288×10^{-9}
with KOH	8.9	1.254×10^{-9}
with NH_4OH	9.5	3.150×10^{-10}
with $N(CH_3)_4OH$	9.9	1.254×10^{-10}
with $(C_2H_5)_4OH$	10.2	6.283×10^{-11}
<i>Polyvinyl alcohol with trichloroacetic acid titrant</i>		
with LiOH	2.3	5.007×10^{-3}
with NaOH	2.4	3.977×10^{-3}
with KOH	2.8	1.583×10^{-3}
with NH_4OH	3.2	6.301×10^{-4}
with $N(CH_3)_4OH$	3.7	1.992×10^{-4}
with $N(C_2H_5)_4OH$	7.6	2.504×10^{-3}

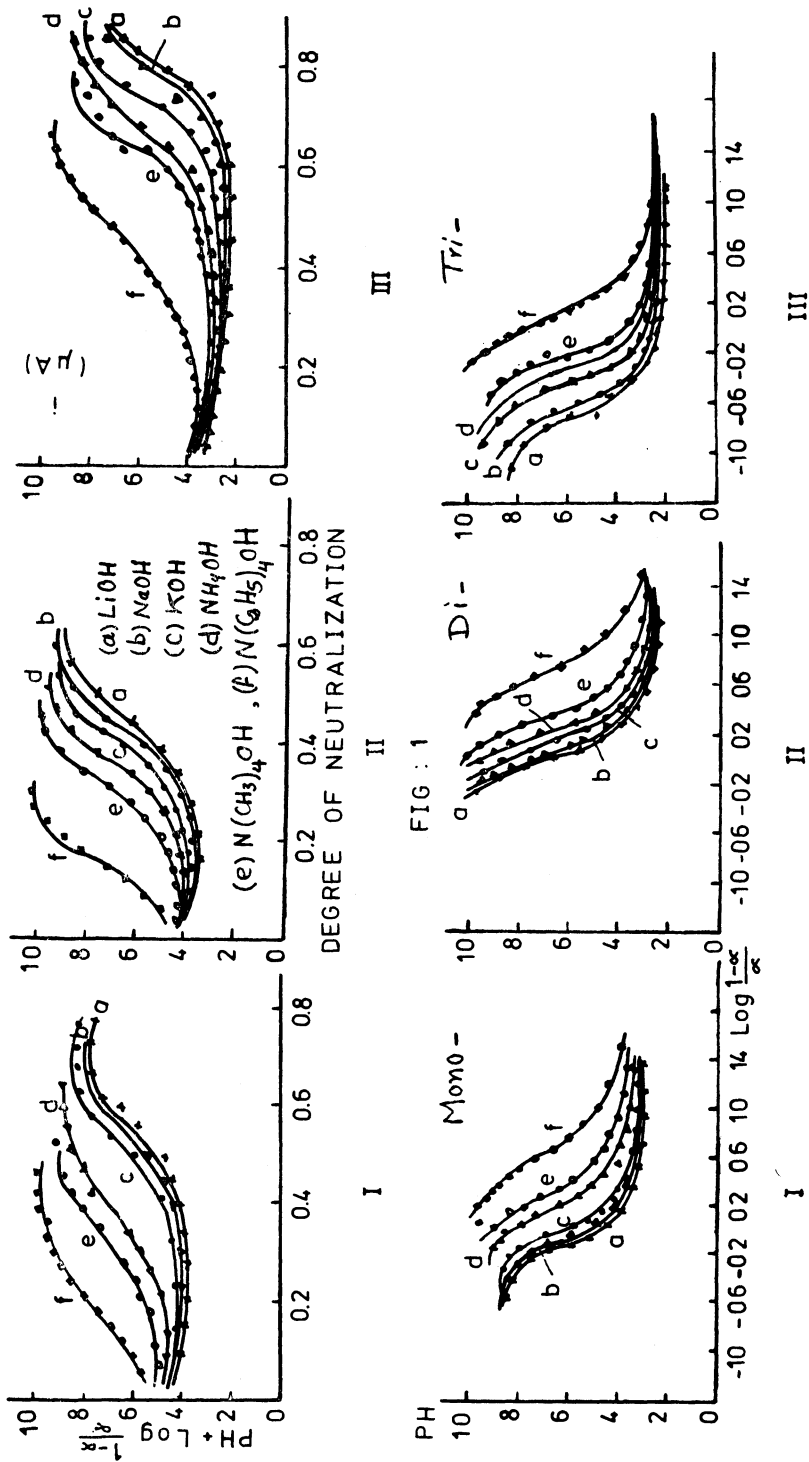


Fig. 2

TABLE 2
VALUES OF $pK'a$, $K'a$ and n DERIVED FROM THE
PLOTS OF pH VERSUS $\text{Log} \{(1-\alpha)/\alpha\}$

Polyacid	Average pKa	$K'a$	n
<i>Polyvinyl alcohol with monochloroacetic acid titrant</i>			
with LiOH	5.4	3.972×10^{-6}	11.9
with NaOH	5.6	2.506×10^{-6}	11.5
with KOH	6.5	3.154×10^{-7}	10.5
with NH_4OH	8.7	1.988×10^{-9}	9.5
with $\text{N}(\text{CH}_3)_4\text{OH}$	9.6	2.502×10^{-10}	9.0
with $\text{N}(\text{C}_2\text{H}_5)_4\text{OH}$	10.9	1.253×10^{-11}	7.0
<i>Polyvinyl alcohol with dichloroacetic acid titrant</i>			
with LiOH	7.5	3.152×10^{-8}	14.6
with NaOH	8.15	7.056×10^{-9}	14.0
with KOH	8.9	1.254×10^{-9}	13.5
with NH_4OH	9.8	1.278×10^{-10}	12.0
with $\text{N}(\text{CH}_3)_4\text{OH}$	11.04	9.078×10^{-12}	11.2
with $\text{N}(\text{C}_2\text{H}_5)_4\text{OH}$	13.6	2.498×10^{-14}	9.5
<i>Polyvinyl alcohol with trichloroacetic acid titrant</i>			
with LiOH	0.9	1.258×10^{-1}	8.6
with NaOH	1.8	1.584×10^{-2}	7.7
with KOH	2.1	7.936×10^{-3}	7.5
with NH_4OH	2.9	1.257×10^{-3}	7.
with $\text{N}(\text{CH}_3)_4\text{OH}$	3.5	3.158×10^{-4}	6.7
with $\text{N}(\text{C}_2\text{H}_5)_4\text{OH}$	6.6	2.505×10^{-7}	6.0

the absence of salts. Table 3 shows the titration curves for (0.25 gm./25 ml H_2O) of the three polyelectrolytes with mixtures containing different proportions of LiOH and $\text{N}(\text{C}_2\text{H}_5)_4\text{OH}$ in deionized water.

The discussion contained herein will concern itself primarily with qualitative aspects of these phenomena. The binding of Li and Na by carboxylic groups as compared to potassium is well known. The alkali metal acetates show activity coefficients which decrease with decreasing atomic weight. This has been interpreted as being due to the entrance of the carboxyl group into the hydration sphere. These effects are not observable in 0.01 M solutions of the acetates, but only in relatively concentrated solutions.

The mole fraction of LiOH in the mixed bases varied from 100% to 0%. The experimental results for each titration curve show that with increasing the size of the counterion, the determined values of n decrease while those of $pK'a$ increase. It is mentioned⁸ that increasing counterion size and the consequent increasing the distance of closing approach of the counterion to the chain makes for an increased chain potential.

The obtained curves and the calculated values of capacity Fig. 3 & 4 and Tables 3 & 4 were intermediate between those obtained with the single

TABLE 3
VALUES OF APPARENT pK , K DERIVED FROM THE
PLOTS OF $pH + \text{Log} \{(1-\alpha)/\alpha\}$ VERSUS α

Polyelectrolyte used	Mole fraction of counter ion	Apparent pK	K
Polyvinyl alcohol with monochloroacetic acid	$XLi^+ = 1$	4.8	1.532×10^{-5}
	$XLi^+(0.6) + XN(Et)_4OH(0.4)$	7.9	1.255×10^{-8}
	$XLi^+(0.5) + XN(Et)_4OH(0.5)$	8.1	7.917×10^{-9}
	$XLi^+ = \text{zero}$	9.8	1.578×10^{-10}
Polyvinyl alcohol with dichloroacetic acid	$XLi^+ = 1$	7.3	4.997×10^{-8}
	$XLi^+(0.6) + N(Et)_4OH(0.4)$	9.2	6.286×10^{-10}
	$XLi^+(0.5) + N(Et)_4OH(0.5)$	9.7	1.987×10^{-10}
	$XLi^+ = \text{zero}$	10.2	6.283×10^{-11}
Polyvinyl alcohol with trichloroacetic acid	$XLi^+ = 1$	2.3	5.007×10^{-3}
	$XLi^+(0.6) + XN(Et)_4OH(0.4)$	3.1	7.933×10^{-4}
	$XLi^+(0.5) + XN(Et)_4OH(0.5)$	3.4	3.975×10^{-4}
	$XLi^+ = \text{zero}$	7.6	2.504×10^{-8}

TABLE 4
VALUES OF $pK'a$, $K'a$ AND n DERIVED FROM THE PLOTS OF pH
VERSUS $[\text{Log}(1-\alpha)/\alpha]$

Polyelectrolyte used	Mole fraction of counter ion	Average $pK'a$	$K'a$	n
Polyvinyl alcohol with monochloroacetic acid	XLi	5.4	3.972×10^{-6}	11.9
	$XLi^+(0.6) + XN(Et)_4OH(0.4)$	8.2	6.288×10^{-9}	10.0
	$XLi^+(0.5) + XN(Et)_4OH(0.5)$	8.4	3.967×10^{-9}	9.7
	$XLi^+ = \text{zero}$	10.9	1.253×10^{-11}	7.0
Polyvinyl alcohol with dichloroacetic acid	$XLi^+ = 1$	7.5	3.152×10^{-8}	14.6
	$XLi^+(0.6) + XN(Et)_4OH(0.4)$	10.2	6.283×10^{-11}	12.0
	$XLi^+(0.5) + XN(Et)_4OH(0.5)$	10.9	1.253×10^{-11}	11.5
	$XLi = \text{zero}$	13.6	2.498×10^{-14}	9.5
Polyvinyl alcohol trichloroacetic acid	$XLi =$	0.9	1.258×10^{-1}	8.6
	$XLi^+(0.6) + XN(Et)_4OH(0.4)$	2.8	1.583×10^{-3}	7.1
	$XLi^+(0.5) + XN(Et)_4OH(0.5)$	3.3	5.005×10^{-4}	6.9
	$XLi^+ = \text{zero}$	6.6	2.505×10^{-7}	6.0

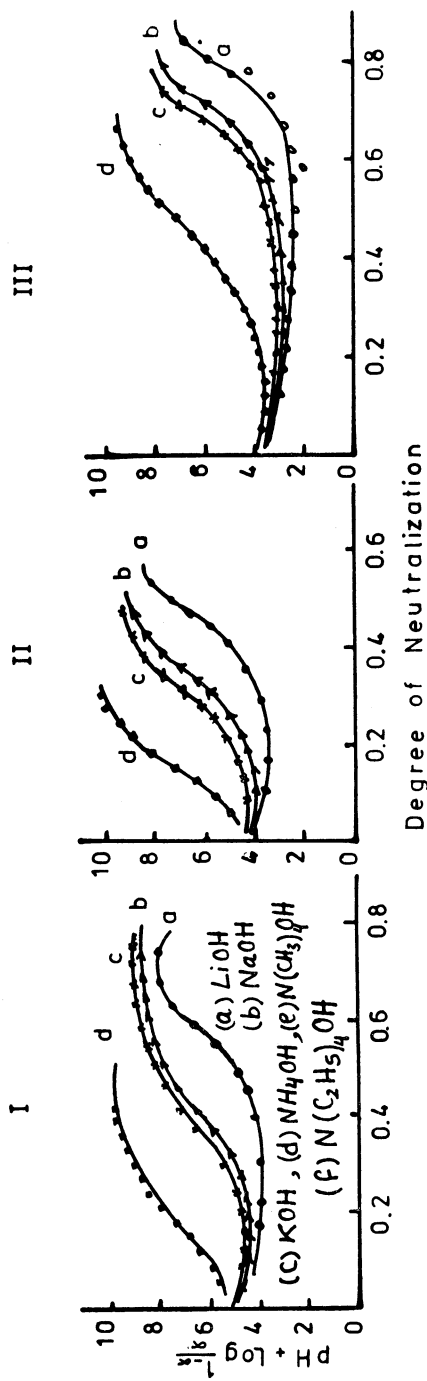


FIG : 3

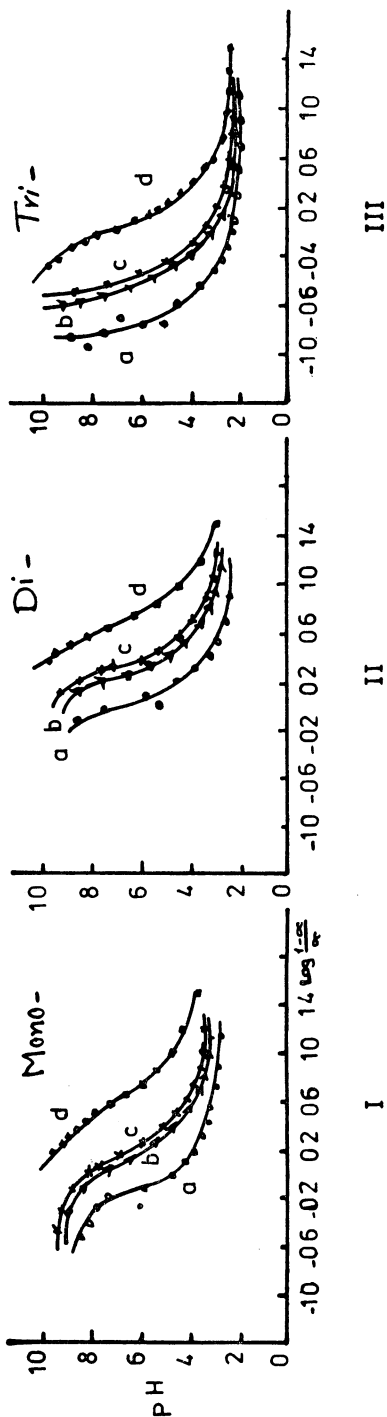


Fig. 4

cations. At the same value of α , the value of pH increases with the percentage of $N(C_2H_5)_4OH$ relative to $LiOH$. It is reported⁹ that the specific binding of Li is enhanced by the high chain potential of tetrabutylammonium polyacrylate.

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