Calorimetric studies of the neutralization of polygalacturonic acid

D. Rudan-Tasič *, C. Klofutar

Department of Food Science and Technology, Biotechnical Faculty, University of Ljubljana, 61000 Ljubljana, Slovenia

Abstract

Calorimetric data are reported on the enthalpy of neutralization of polygalacturonic acid obtained during its neutralization by either tetraalkylammonium or alkaline hydroxide solution. Thermometric curves are evaluated and discussed in terms of six equivalent equations, and the successive enthalpies of neutralization of previously chosen oligomeric subunits of polygalacturonic acid are determined. Together with the potentiometric data, this information provides a complete thermodynamic picture of the effect of the size of the alkyl group and the nature of the counterion on the dissociation behaviour of the polyacid in dilute aqueous solutions.

1. Introduction

In a previous paper from this laboratory, potentiometric measurements of the dissociation of polygalacturonic acid (PGA) in the presence of either tetraalkyl-ammonium or alkaline ions in aqueous solution were reported [1]. These results suggest that PGA can be successfully treated in terms of appropriately chosen oligomeric subunits containing six carboxylic groups. To assess the thermodynamics of the dissociation of PGA, accompanied by the interaction of the polycarboxylate group with counterions, more complete, calorimetric results were collected and added to the potentiometric data.

---

* Corresponding author.

A set of neutralization data for PGA obtained in the titration and partial neutralization of this polyacid using standardized tetraalkylammonium hydroxide $((C_4H_9)_4NOH, (CH_3)_4NOH)$ or alkaline hydroxide (LiOH, NaOH, KOH) are now reported. The linear titration curves produced by a thermometric method are discussed in terms of n equivalent equations for a polyprotic acid H_nA, the pK values of which are comparable, neutralized by a strong base [2].

2. Experimental

The specifications of the PGA employed and the preparation of its aqueous solutions were described previously [1]. Stock solutions of the hydroxides were purchased from Merck and Fluka Chemie.

Calorimetric measurements were made using an LKB 8700 precision calorimetry system with a chart recorder output. A Sargent recorder was applied. The description of the system used and the evaluation of the calorimetric data are given in Ref. [3]. The volume of the reaction vessel was 25 cm^3. The bath temperature and starting temperature of all the runs was 298.15 K. The system was tested by measuring the heat of solution of KCl in water at 298.15 K. The value determined of 17.391 ± 0.055 kJ mol^{-1} is close to the value given in the work of Somsen et al. [4].

The heat of neutralization of PGA was measured by the glass ampoule technique. A known amount of a strong base of known concentration was sealed in a glass ampoule of 1 cm^3 volume. After thermostating, the ampoule was broken in 20 cm^3 of PGA of known concentration in monomoles per dm^3 and the heat released in the neutralization process was simultaneously recorded. The pH of the solution in the calorimetric vessel was recorded after each addition of hydroxide using a pH meter (Radiometer, type pH M4d) and a glass combined electrode (Radiometer, type GK 2501 C).
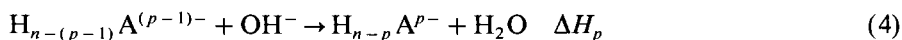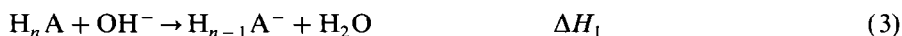
The total heat effect q_n obtained by the addition of a strong base to the solution of PGA, was in all cases corrected for the heat of dilution of the base and other physical effects q_{mix}, and for the heat of dilution of the polyelectrolyte q_d

$$q_n = q + q_d + q_{mix} \tag{1}$$

where q denotes the heat of neutralization of PGA. Values of q_{mix} had been determined previously for each hydroxide in our laboratory; q_d was provided on the basis of literature data [5].

3. Results and discussion

The basis of the thermometric approach has been given in detail in Ref. [2]. The authors used the following notations for the successive enthalpies of neutralization of a polyprotic acid H_nA [1]
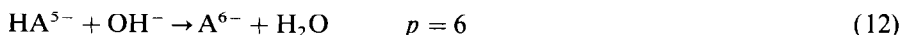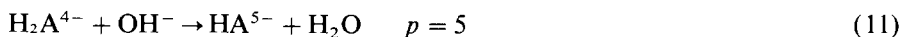
$$H^+ + OH^- \rightarrow H_2O \qquad\qquad\qquad\qquad \Delta H_0 \qquad\qquad (2)$$

$$H_nA + OH^- \rightarrow H_{n-1}A^- + H_2O \qquad\qquad \Delta H_1 \qquad\qquad (3)$$

$$H_{n-(p-1)}A^{(p-1)-} + OH^- \rightarrow H_{n-p}A^{p-} + H_2O \quad \Delta H_p \qquad\qquad (4)$$

$$HA^{(n-1)-} + OH^- \rightarrow A^{n-} + H_2O \qquad\qquad \Delta H_n \qquad\qquad (5)$$
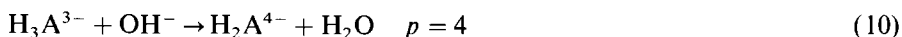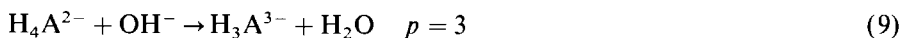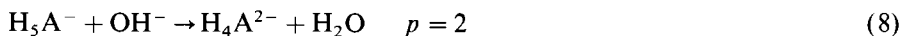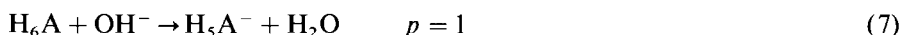
After introducing an auxiliary notation for the concentrations of the various species which may be present in solution at a definite point of neutralization and considering some assumptions, e.g. that only the first acidity of H_nA is sufficiently great, so that before the beginning of addition of hydroxide the aqueous solution contains only the H^+ of concentration $[H^+]_0$, and H_nA and $H_{n-1}A^-$ entities, the authors then derived a relation formulating n equivalent equations for the thermometric titration curve of a polyprotic acid H_nA neturalized by a strong base [2]

$$-q = c_b v \Delta H_p + [H^+]_0 V_0 (\Delta H_0 - \Delta H_1) + c_a V_0 \sum_{i=1}^{p} (\Delta H_i - \Delta H_p)$$

$$- [H^+](V_0 + v)\Delta H_0 + ([H^+] - [OH^-])(V_0 + v)\Delta H_p$$

$$- \sum_{i=1}^{p} \bar{c}_i (\Delta H_i - \Delta H_p)(V_0 + v) + \sum_{i=p+1}^{n} c_i (\Delta H_i - \Delta H_p)(V_0 + v) \qquad (6)$$

where V_0 denotes the volume (dm^3) of the polyacid solution, c_a the concentration of polyacid in monomoles per dm^3, i.e. mol H^+ per dm^3, c_b the concentration of the hydroxide solution (mol dm^{-3}), v the volume of hydroxide solution added (dm^3), and c_i and $\bar{c}_i$ are auxiliary concentration notations mentioned before (see Ref. [2]). The first three terms in Eq. (6) correspond to a line segment in a thermogram, $-q = f(v)$, with slope $c_b \Delta H_p$, i.e. proportional to the enthalpy of neutralization of the pth acidity.

Following the previous potentiometric treatment of PGA, its dissociation behaviour may be described by oligomeric subunits containing $N = 6$ acidic groups [1]. In this case the equations giving the calorimetric balances of the successive reactions ($1 \leqslant p \leqslant n = N$) for the subunit

$$H_6A + OH^- \rightarrow H_5A^- + H_2O \qquad p = 1 \qquad\qquad (7)$$

$$H_5A^- + OH^- \rightarrow H_4A^{2-} + H_2O \qquad p = 2 \qquad\qquad (8)$$

$$H_4A^{2-} + OH^- \rightarrow H_3A^{3-} + H_2O \qquad p = 3 \qquad\qquad (9)$$

$$H_3A^{3-} + OH^- \rightarrow H_2A^{4-} + H_2O \qquad p = 4 \qquad\qquad (10)$$

$$H_2A^{4-} + OH^- \rightarrow HA^{5-} + H_2O \qquad p = 5 \qquad\qquad (11)$$

$$HA^{5-} + OH^- \rightarrow A^{6-} + H_2O \qquad p = 6 \qquad\qquad (12)$$

may be written (Eq. (6))

$p = 1, n = 6$

$$\begin{aligned}
-q = & \; c_b v \Delta H_1 + [\mathrm{H}^+]_0 V_0 (\Delta H_0 - \Delta H_1) - [\mathrm{H}^+](V_0 + v)\Delta H_0 \\
& + ([\mathrm{H}^+] - [\mathrm{OH}^-])(V_0 + v)\Delta H_1 + [\mathrm{H_4A^{2-}}](V_0 + v)(\Delta H_2 - \Delta H_1) \\
& + [\mathrm{H_3A^{3-}}](V_0 + v)(\Delta H_3 + \Delta H_2 - 2\Delta H_1) \\
& + [\mathrm{H_2A^{4-}}](V_0 + v)(\Delta H_4 + \Delta H_3 + \Delta H_2 - 3\Delta H_1) \\
& + [\mathrm{HA^{5-}}](V_0 + v)(\Delta H_5 + \Delta H_4 + \Delta H_3 + \Delta H_2 - 4\Delta H_1) \\
& + [A^{6-}](V_0 + v)(\Delta H_6 + \Delta H_5 + \Delta H_4 + \Delta H_3 + \Delta H_2 - 5\Delta H_1)
\end{aligned} \tag{13}$$

$p = 2, n = 6$

$$\begin{aligned}
-q = & \; c_b v \Delta H_2 + [\mathrm{H}^+]_0 V_0 (\Delta H_0 - \Delta H_1) + c_a V_0 (\Delta H_1 - \Delta H_2) \\
& - [\mathrm{H}^+](V_0 + v)\Delta H_0 + ([\mathrm{H}^+] - [\mathrm{OH}^-])(V_0 + v)\Delta H_2 \\
& - [\mathrm{H_6A}](V_0 + v)(\Delta H_1 - \Delta H_2) + [\mathrm{H_3A^{3-}}](V_0 + v)(\Delta H_3 - \Delta H_2) \\
& + [\mathrm{H_2A^{4-}}](V_0 + v)(\Delta H_4 + \Delta H_3 - 2\Delta H_2) \\
& + [\mathrm{HA^{5-}}](V_0 + v)(\Delta H_5 + \Delta H_4 + \Delta H_3 - 3\Delta H_2) \\
& + [\mathrm{A^{6-}}](V_0 + v)(\Delta H_6 + \Delta H_5 + \Delta H_4 + \Delta H_3 - 4\Delta H_2)
\end{aligned} \tag{14}$$

$p = 3, n = 6$

$$\begin{aligned}
-q = & \; c_b v \Delta H_3 + [\mathrm{H}^+]_0 V_0 (\Delta H_0 - \Delta H_1) + c_a V_0 (\Delta H_1 + \Delta H_2 + 2\Delta H_3) \\
& - [\mathrm{H}^+](V_0 + v)\Delta H_0 + ([\mathrm{H}^+] - [\mathrm{OH}^-])(V_0 + v)\Delta H_3 \\
& - [\mathrm{H_6A}](V_0 + v)(\Delta H_1 + \Delta H_2 - 2\Delta H_3) - [\mathrm{H_5A^-}](V_0 + v)(\Delta H_2 - \Delta H_3) \\
& + [\mathrm{H_2A^{4-}}](V_0 + v)(\Delta H_4 - \Delta H_3) + [\mathrm{HA^{5-}}](V_0 + v)(\Delta H_5 + \Delta H_4 - 2\Delta H_3) \\
& + [\mathrm{A^{6-}}](V_0 + v)(\Delta H_6 + \Delta H_5 + \Delta H_4 - 3\Delta H_3)
\end{aligned} \tag{15}$$

$p = 4, n = 6$

$$\begin{aligned}
-q = & \; c_b v \Delta H_4 + [\mathrm{H}^+]_0 V_0 (\Delta H_0 - \Delta H_1) + c_a V_0 (\Delta H_1 + \Delta H_2 + \Delta H_3 - 3\Delta H_4) \\
& - [\mathrm{H}^+](V_0 + v)\Delta H_0 + ([\mathrm{H}^+] - [\mathrm{OH}^-])(V_0 + v)\Delta H_4 \\
& - [\mathrm{H_6A}](V_0 + v)(\Delta H_1 + \Delta H_2 + \Delta H_3 - 3\Delta H_4) \\
& - [\mathrm{H_5A^-}](V_0 + v)(\Delta H_2 + \Delta H_3 - 2\Delta H_4) - [\mathrm{H_4A^{2-}}](V_0 + v)(\Delta H_3 - \Delta H_4) \\
& + [\mathrm{HA^{5-}}](V_0 + v)(\Delta H_5 - \Delta H_4) + [\mathrm{A^{6-}}](V_0 + v)(\Delta H_6 + \Delta H_5 - 2\Delta H_4)
\end{aligned}$$

$$\tag{16}$$

$p = 5, n = 6$

$$
\begin{aligned}
-q = &\; c_b v \Delta H_5 + [\mathrm{H^+}]_0 V_0 (\Delta H_0 - \Delta H_1) \\
&+ c_a V_0 (\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - 4\Delta H_5) \\
&- [\mathrm{H^+}](V_0 + v)\Delta H_0 + ([\mathrm{H^+}] - [\mathrm{OH^-}])(V_0 + v)\Delta H_5 \\
&- [\mathrm{H_6A}](V_0 + v)(\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - 4\Delta H_5) \\
&- [\mathrm{H_5A^-}](V_0 + v)(\Delta H_2 + \Delta H_3 + \Delta H_4 - 3\Delta H_5) \\
&- [\mathrm{H_4A^{2-}}](V_0 + v)(\Delta H_3 + \Delta H_4 - 2\Delta H_5) - [\mathrm{H_3A^{3-}}](V_0 + v)(\Delta H_4 - \Delta H_5) \\
&+ [\mathrm{A^{6-}}](V_0 + v)(\Delta H_6 - \Delta H_5)
\end{aligned} \tag{17}
$$

$p = 6, n = 6$

$$
\begin{aligned}
-q = &\; c_b v \Delta H_6 + [\mathrm{H^+}]_0 V_0 (\Delta H_0 - \Delta H_1) \\
&+ c_a V_0 (\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 - 5\Delta H_6) \\
&- [\mathrm{H^+}](V_0 + v)\Delta H_0 + ([\mathrm{H^+}] - [\mathrm{OH^-}])(V_0 + v)\Delta H_6 \\
&- [\mathrm{H_6A}](V_0 + v)(\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 - 5\Delta H_6) \\
&- [\mathrm{H_5A^-}](V_0 + v)(\Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 - 4\Delta H_6) \\
&- [\mathrm{H_4A^{2-}}](V_0 + v)(\Delta H_3 + \Delta H_4 + \Delta H_5 - 3\Delta H_6) \\
&- [\mathrm{H_3A^{3-}}](V_0 + v)(\Delta H_4 + \Delta H_5 - 2\Delta H_6) \\
&- [\mathrm{H_2A^{4-}}](V_0 + v)(\Delta H_5 - \Delta H_6)
\end{aligned} \tag{18}
$$

where $[\mathrm{H_6A}]$, $[\mathrm{H_5A^-}]$, $[\mathrm{H_4A^{2-}}]$, $[\mathrm{H_3A^{3-}}]$, $[\mathrm{H_2A^{4-}}]$, $[\mathrm{HA^{5-}}]$ and $[\mathrm{A^{6-}}]$ denote the concentrations of the species, respectively. For the value of the enthalpy of ionization of water (Eq. (2)), $\Delta H_0 = -55.7895$ kJ mol^{-1} was used [6].

Taking into account the values of the overall dissociation constants of appropriately chosen oligomeric subunits of PGA, β_i at 298.15 K [1] and the pH values measured after each breaking of the ampoule, the mole fraction of the subunit species with i dissociated protons x_i could be calculated at each degree of neutralization, i.e. at each volume of the hydroxide solution added [1]. Finally the concentration of the species may be defined via the relation [7]

$$
x_{\mathrm{H}_{n-p}\mathrm{A}^{p-}} = \frac{(\mathrm{H}_{n-p}\mathrm{A}^{p-})}{c_0} \quad i = p \tag{19}
$$

where one should consider the following mass balance equation for c_0

$$
c_0 = [\mathrm{H}_n\mathrm{A}] + [\mathrm{H}_{n-1}\mathrm{A}^-] + \ldots + [\mathrm{A}^{n-}] = \frac{c_a V_0}{V_0 + v} \tag{20}
$$

A system of m linear equations (m denotes the number of experimental points) with six parameters ΔH_p ($1 \leqslant p \leqslant 6$) was obtained by using one of the equations, Eqs. (13)–(18) at each point of neutralization of PGA by the selected hydroxide.

Table 1
The values of the concentrations of the species of the oligomer subunits of PGA at different volumes of strong base added ($c_{LiOH} = 0.22$ mol dm^{-3}), together with experimental q_{ex} and calculated q_{cal} heats of neutralization for PGA ($c_a = 10.64$ mmol dm^{-3}) at 298.15 K

$v \times 10^3$ in dm^3	$[H^+]$ in mol dm^{-3}	$c \times 10^3$ in mol dm^{-3}							$-q_{ex}$ in J	$-q_{cal}$ in J
		$[H_6A]$	$[H_5A^-]$	$[H_4A^{2-}]$	$[H_3A^{3-}]$	$[H_2A^{4-}]$	$[HA^{5-}]$	$[A^{6-}]$		
0.0593	1.096×10^{-3}	3.077	4.584	2.748	0.191	0.011	0.000	0.000	0.689	0.703
0.1136	8.318×10^{-4}	2.265	4.455	3.513	0.317	0.032	0.000	0.000	1.378	1.362
0.2121	4.751×10^{-4}	0.979	3.517	5.055	0.842	0.137	0.000	0.000	2.653	2.631
0.3208	1.950×10^{-4}	0.118	1.655	5.562	2.162	0.827	0.073	0.000	3.950	3.964
0.4409	9.333×10^{-5}	0.031	0.541	3.811	3.103	2.468	0.437	0.021	5.440	5.441
0.6160	3.162×10^{-5}	0.000	0.426	0.826	1.993	4.656	2.426	0.382	7.435	7.436
0.7337	1.479×10^{-5}	0.000	0.000	0.144	0.749	3.767	4.199	1.406	8.904	8.904
0.9036	5.370×10^{-7}	0.000	0.000	0.000	0.000	0.031	0.998	9.154	11.102	11.102

Table 2
The successive enthalpies of neutralization (kJ mol^{-1}) for PGA obtained by different hydroxides at 298.15 K

Hydroxide	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H_3$	$-\Delta H_4$	$-\Delta H_5$	$-\Delta H_6$
LiOH	56.966	56.648	56.652	56.913	56.865	56.738
NaOH	58.261	57.956	58.565	58.628	58.425	58.306
KOH	59.047	59.046	59.318	59.385	59.457	59.494
$(CH_3)_4NOH$	56.873	56.733	56.849	56.980	56.926	56.899
$(C_4H_9)_4NOH$	55.929	57.299	57.427	58.133	57.956	57.637

The criterion for the choice of the pth equation was the maximum concentration of the species $H_{n-p}A^{p-}$ at the degree of neutralization investigated (italic data in Table 1). The overdetermined system of m linear equations was solved using the matrix form by the QR method [8]. This procedure of determining the successive enthalpies of neutralization ΔH_p was carried out for all the neutralization systems mentioned and the results are given in Table 2. The recalculated values of the heats of neutralization are, within experimental error, equal to the experimental data (see, for example, Table 1); the average difference ($q_{ex} - q_{cal}$) for all measurements was found to be ± 0.050 J. From Table 2 it follows that the values of the successive enthalpies of neutralization of the discussed polyacid and presented as sub-units containing six carboxylic groups, are equal for each particular hydroxide. Their average values amount to $\overline{\Delta H} = -56.797 \pm 0.136$ kJ mol^{-1} for LiOH, $\overline{\Delta H} = -58.357 \pm 0.242$ kJ mol^{-1} for NaOH, $\overline{\Delta H} = -59.291 \pm 0.199$ kJ mol^{-1} for KOH, and $\overline{\Delta H} = -56.877 \pm 0.084$ kJ mol^{-1} for $(CH_3)_4NOH$. In the case of $(C_4H_9)_4NOH$, there is a clear difference between the dissociation of the first proton and the succeeding ones. Actually three stages of neutralization can be distinguished: $\Delta H_1 = -55.929$ kJ mol^{-1}, $\overline{\Delta H_{2-3}} = -57.363 \pm 0.064$ kJ mol^{-1}, and
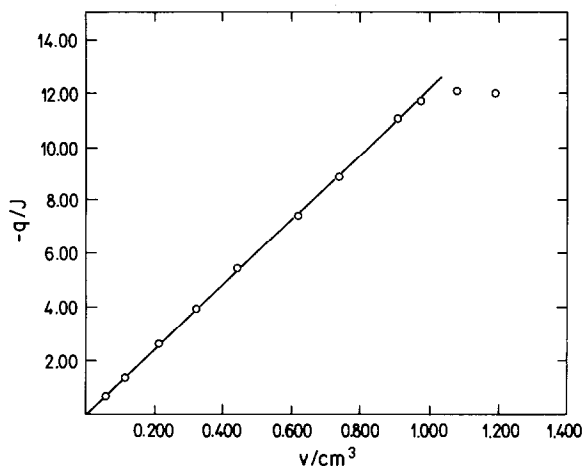
Fig. 1. Thermogram of the neutralization of PGA ($c_a = 10.64$ mmol dm^{-3}, $V_0 = 20 \times 10^{-3}$ dm^3) by a lithium hydroxide solution ($c_b = 0.22$ mol dm^{-3}).
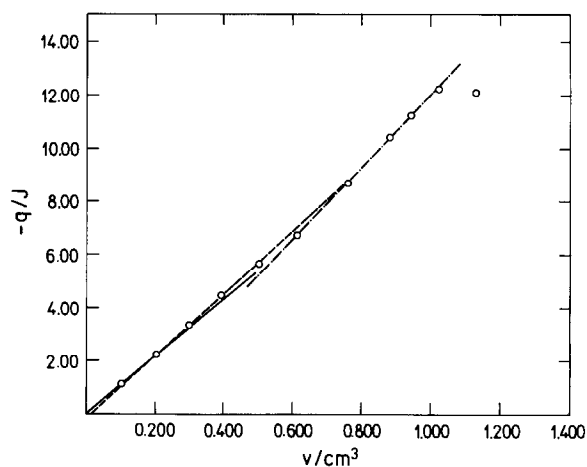

Fig. 2. Thermogram of the neutralization of PGA ($c_a = 10.57$ mmol dm^{-3}, $V_0 = 20 \times 10^{-3}$ dm^3) by a tetrabutylammonium hydroxide solution ($c_b = 0.21$ mol dm^{-3}).

$\overline{\Delta H}_{4-6} = -57.909 \pm 0.251$ kJ mol^{-1}. These can be identified with the three linear segments in the thermogram (Fig. 2) and can be contrasted with the monotonous thermometric curve for an alkaline hydroxide (Fig. 1).

The observed order in the case of alkaline hydroxides corresponded to the potentiometric one. Thus we can explain the influence of the size and nature of the counterion on the acid–base properties of PGA on the basis of the formation of contact ion pairs between an alkaline ion and the carboxylate group [1], which explanation also provides an understanding of the differences seen in Table 2. Thus, all the heat effects caused by the changes in the numbers and strengths of bonds

made and broken during the neutralization process are reflected in the heat of neutralization, including the binding of counterions by the macroion.

For tetraalkylammonium hydroxides, the individual size and structural properties of the tetraalkylammonium ions are probably the reason for their different behaviour in the process of neutralization of PGA, as has already been detected from potentiometric measurements [1].

Acknowledgement

References

[1] D.R. Tasič, Thermochim. Acta, 246 (1994) 11.
[2] M.A. Bernard and J.L. Burgot, Anal. Chem., 51 (1979) 2122.
[3] B.J. Birch, The Use of an LKB 8700 Precision Calorimetry System with Chart Recorder Output, in LKB Application Note, LKB-Procucter, Stockholm, November 15, 1972.
[4] G. Somsen, J. Coops and M.W. Tolk, Recl. Trav. Chim. Pays-Bas, 82 (1963) 231.
[5] A. Cesaro, A. Ciana, F. Delben, G. Manzini and S. Paoletti, Biopolymers, 21 (1982) 431.
[6] C.S. Leung and E. Grunwald, J. Phys. Chem., 74 (1970) 687.
[7] R. Levie, J. Chem. Educ., 70 (1993) 209.
[8] B. Noble and J.W. Daniel, Applied Linear Algebra, 3rd edn., Prentice Hall, London, 1988, p. 175.