duced from their electric dichroism work on PBIC that the source of the rigidity is a combination of first, a high potential barrier to rotation from the planar amide configuration, and, second, steric interference of the *n*-alkyl side chain and the carbonyl group. In the presence of a polar solvent, we speculate that the potential barrier to rotation from a planar amide configuration is reduced. This solvent effect indicates that steric effects alone cannot account for the rigidity of the PBIC and POIC molecules.[28]

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Determination of the Thermodynamic Parameters of Selectivity on Polyelectrolytes by Potentiometry and Microcalorimetry

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ABSTRACT: The free energy of selectivity between different monovalent and divalent counterions is obtained by potentiometry between 14 and 65°; by microcalorimetry, the enthalpy is determined by exchange at 25°. From both sets of results, ΔH is confirmed and ΔS is given as a function of the nature of the counterions. The experiments were performed on a carboxymethylcellulose with a substitution degree $\overline{DS} = 2.49$.

The selectivity of a polyanion is directly related to its charge density and to the nature of the ionic site (-COOH or -SO$_3$H) and that of the counterions. By potentiometric titration, the affinity sequence is clearly described and is found to be Li > Na > K > Cs > TEA (tetraethylammonium) for monovalent counterions on carboxymethylcellulose.[1] The enthalpy change (obtained by microcalorimetry) accompanying the exchange of two counterions depends on the counterions and is directly related to the charge density.[2] A theoretical treatment may be proposed with the Lifson-Katchalsky rodlike model to interpret the electrostatic contribution[3,4] but no theory explains the selectivity.

In this communication, the results obtained by both techniques are given and used to calculate the thermodynamic parameters which characterize the selectivity of a carboxymethylcellulose (CMC) with a charge parameter $\lambda = 3.44$; λ is defined by the relation $\lambda = \alpha\epsilon^2/DbkT$, with ϵ protonic charge, α number of ionic sites per monomeric unit, b length of a monomeric unit, D dielectric constant, and kT Boltzmann term.

Experimental Section

The potentiometric titrations are followed with a Sargent S 30,000 potentiometer using a combination electrode S 300-72-15 (Sargent) for pH determinations at 14, 25, 35, 45, 55, and 65 ± 0.1°.

The titration experiments with monovalent counterions were all performed by titrating solutions 5×10^{-3} N in H-CMC with 0.1 N base XOH ($X^+ = TEA^+, Li^+, K^+$) there being no added salt. With divalent counterions the titrations are carried out with 0.04 N base $X(OH)_2$ ($X^{2+} = Ca^{2+}, Ba^{2+}, Sr^{2+}$). The acidic form H-CMC is obtained by passage of the sodium salt solution through an ion-exchange column (Amberlite IR 120 H^+).

The free energy of exchange $\Delta G(T)$ is given by the potentiometric area between the both neutralization curves concerned ($TEA^+ \rightarrow Li^+$; $TEA^+ \rightarrow K^+$; $K^+ \rightarrow Li^+$; $Na^+ \rightarrow Ca^{2+}$; $Na^+ \rightarrow Sr^{2+}$; $Na^+ \rightarrow Ba^{2+}$); experimentally, the ΔG values are found to be independent on the polymer concentration. During titration of a polyacid, the pH values are related to the change of the electrostatic free energy ΔG_{el} by the following expression

$$\mathrm{pH} = \mathrm{p}K_0 - \log\,[(1-\alpha)/\alpha] + 0.434\Delta G_{el}/kT$$

in which K_0 is the intrinsic constant of ionization and α the degree of neutralization. The electrostatic free energy per ionizable site at the degree of ionization α is given by

$$G_{el}(\alpha) = 2.3kT\int_0^{\alpha}\{\mathrm{pH} + \log\,[(1-\alpha)/\alpha] - \mathrm{p}K_0\}\mathrm{d}\alpha$$

corresponding to the area under the graph $\{\mathrm{pH} + \log\,[(1-\alpha)/\alpha] - \mathrm{p}K_0\}$ *vs.* α.[5] As a consequence, the area between two curves of neutralization gives directly the free energy (per charged carboxyl) of transfer of fully charged polymer from a solution in which it has one counterion to a solution in which it has another counterion.

Microcalorimetric measurements were performed at 25° with a Calvet microcalorimeter standard model manufactured by D.A.M. Lyon (France). To eliminate the dilution effects, a differential technique is employed in which same additions of reactant are made at the same time in two identical cells, one of which contains the polyelectrolyte solution and the second one pure water.

The ΔH of exchange is obtained with monovalent counterions by addition of 1 N XCl to 40 ml of a 10^{-2} N TEA-CMC solution. With divalent counterions, addition of 0.5 N XCl$_2$ solution are made to 40 ml of a 5×10^{-3} N Na-CMC solution. The ΔH by monomeric unit is found experimentally to be independent on the polymer concentration.

The ΔH of exchange is also obtained by a second method which consists of adding 1 N HCl solution at the same time in two identical cells one of which contains a 10^{-2} N TEA-CMC solution and the second a 10^{-2} N X-CMC solution;[2] these experimental conditions correspond directly to those used in potentiometry.

The ΔH values obtained in both ways are in good concordance. The results are expressed in calories per equivalent ionic site.

Experimental Results and Discussion

The data obtained by potentiometry are given in Table I as a function of the temperature; experimental curves are presented on Figures 1 and 2 for monovalent and divalent counterions.

For monovalent cations, one can directly observe that

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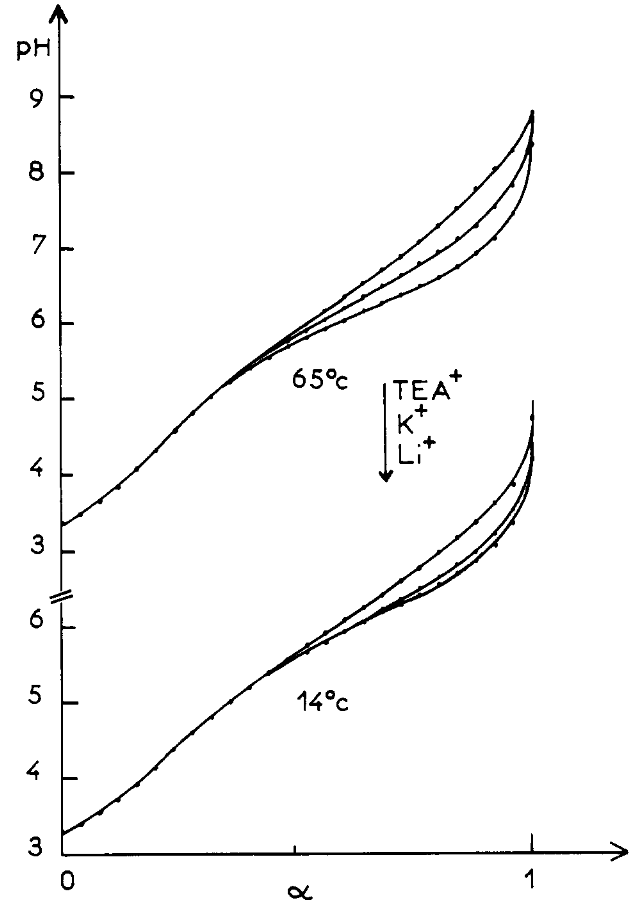

Figure 1. Titration of H-CMC ($\overline{DS}$ = 2.49; *c* 5 × 10^{-3} *N*) by TEAOH, KOH, and LiOH (all 10^{-1} *N*).

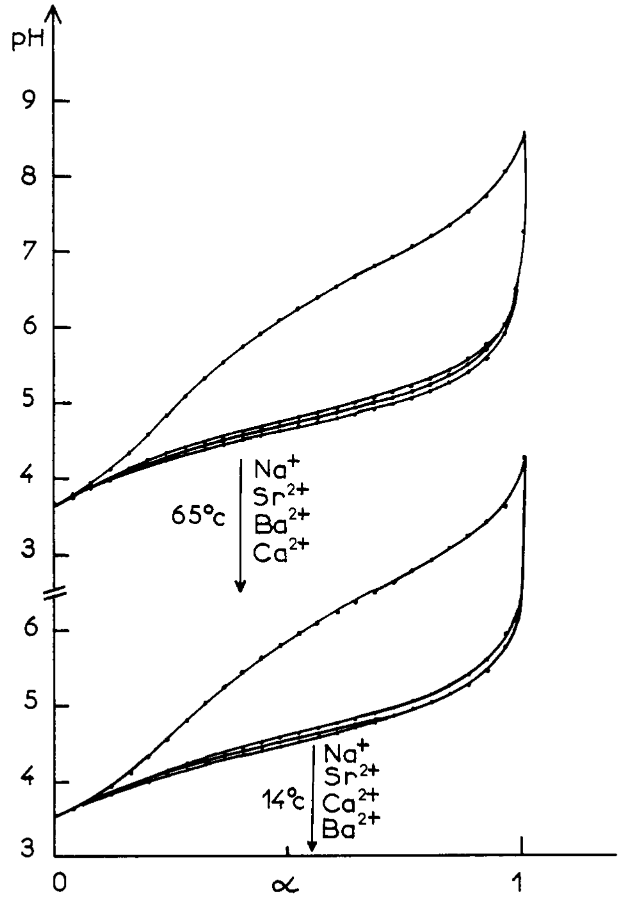

Figure 2. Titration of H-CMC ($\overline{DS}$ = 2.49; *c* 2 × 10^{-3} *N*) by NaOH, $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$ (all 4 × 10^{-2} *N*).

Table I
Free Energy of Exchange as a Function of Temperature

Temp (°C): Exchanges	14	25	35	45 ΔG^a	55	65
$TEA^+ \rightarrow Li^+$	−258	−307	−309	−350	−385	−422
$TEA^+ \rightarrow K^+$	−205	−220	−204	−201	−209	−206
$K^+ \rightarrow Li^+$	−53	−87	−105	−149	−176	−216
$Na^+ \rightarrow Ca^{2+}$	−1532	−1641	−1725	−1830	−1902	−1998
$Na^+ \rightarrow Sr^{2+}$	−1455	−1584	−1623	−1720	−1770	−1880
$Na^+ \rightarrow Ba^{2+}$	−1555	−1648	−1705	−1770	−1830	−1915

[a] $Cal \cdot site^{-1}$.

Table II

Exchanges	ΔH^a	ΔS^b
$TEA^+ \rightarrow Li^+$	+628	+3.10
$TEA^+ \rightarrow K^+$	−231	−0.08
$K^+ \rightarrow Li^+$	+860	+3.18
$Na^+ \rightarrow Ca^{2+}$	+901	+8.34
$Na^+ \rightarrow Sr^{2+}$	+694	+7.57
$Na^+ \rightarrow Ba^{2+}$	+330	+6.61

[a] $Cal \cdot site^{-1}$. [b] $Cal \cdot deg^{-1} \cdot site^{-1}$.

$\Delta G_{TEA\text{-}K}$ is quasi-independent of the temperature but that the selectivity for Li^+ increases. The values of ΔG as a function of *T* are given on Figure 3.

The slopes are negative for TEA-Li and K-Li but null or slightly positive for TEA-K. For divalent counterions, the sequence of selectivity changes with the temperature and at 25° there is practically no selectivity between Ba^{2+} and Ca^{2+}. The values of $\Delta G(T)$ are given on Figure 4. A linear regression analysis is used to obtain the ΔS and ΔH values (see Table II). The results confirm the sequence of affinity generally observed: $Li^+ > K^+ \sim TEA^+$ and $Ca^{2+} > Sr^{2+} > Ba^{2+}$, when $T > 85°$ in concordance with the ionic radius. The values can be compared to the microcalorimetric data given in Table III. From ΔG given by potentiometry and ΔH by calorimetry at 25°, ΔS is directly deduced (see Table III). The concordance between the values obtained with monovalent counterions by both techniques is very good; with divalent counterions, to eliminate precipitation, the concentration of the solution has to be low and the precision is lower.

The influence of the nature of the counterions is shown by the variation of ΔG, ΔH, and ΔS of exchange. The particular entropic contribution can be attributed to a modification of hydration corresponding to site binding;[6] this hypothesis has been proposed by Strauss for polyelectrolyte systems;[7] for example, in the case of Li^+, the release of free water corresponding to the site binding corresponds to the most important increase of entropy by reference to the nonspecific counterion TEA. These results confirm those obtained by ultrasonic absorption[8] or ΔV measurements.[9] With divalent counterions, the tightness of the binding leads to a large entropy change; the combination

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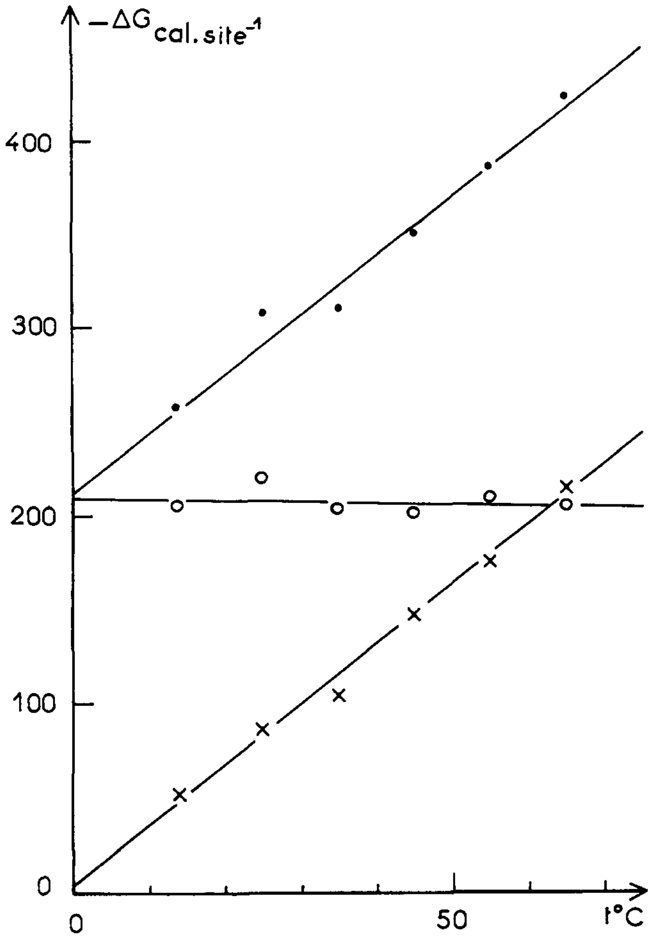

Figure 3. Free energy of exchange as a function of the temperature XCMC ($\overline{DS}$ = 2.49; c 5 × 10^{-3} N): (●) $TEA^+ \rightarrow Li^+$; (○) $TEA^+ \rightarrow K^+$; (x) $K^+ \rightarrow Li^+$.

Table III

Exchanges	ΔG^a Potentiometry 25°	ΔH^a Calorimetry	ΔS^b
$TEA^+ \rightarrow Li^+$	−307	+580	+2.97
$TEA^+ \rightarrow Na^+$	−237	+177	+1.24
$TEA^+ \rightarrow K^+$	−220	−247	−0.10
$TEA^+ \rightarrow Cs^+$	−165	−292	−0.72
$K^+ \rightarrow Li^+$	−87	+827	+3.07
$Na^+ \rightarrow Ca^{2+}$	−1641	+770	+8.1
$Na^+ \rightarrow Sr^{2+}$	−1584	+450	+6.85
$Na^+ \rightarrow Ba^{2+}$	−1648	+170	+6.1

[a] Cal·site^{-1}. [b] Cal·deg^{-1}·site^{-1}.

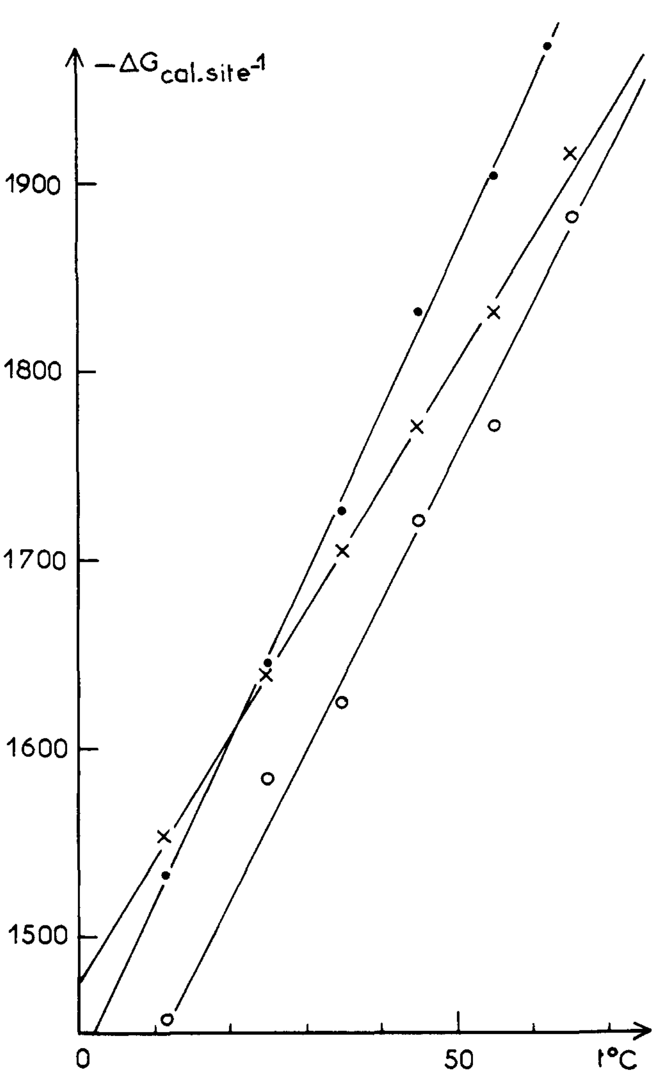

Figure 4. Free energy of exchange as a function of temperature of XCMC ($\overline{DS}$ = 2.49; c 2 × 10^{-3} N): (●) $Na^+ \rightarrow Ca^{2+}$; (○) $Na^+ \rightarrow Sr^{2+}$; (x) $Na^+ \rightarrow Ba^{2+}$.

of large ΔS with the ΔH values leads to affinity sequence depending on the temperature. This dependence is clearly demonstrated by potentiometry and gives respectively

$Ba^{2+} > Ca^{2+} > Sr^{2+}$ for $T < 25°$

$Ca^{2+} > Ba^{2+} > Sr^{2+}$ for $25° < T < 85°$

$Ca^{2+} > Sr^{2+} > Ba^{2+}$ for $T > 85°$

From our experimental results, the conclusion is that potentiometry, which is a useful classical technique, is convenient to determine the thermodynamic parameters characterizing the site binding on polyelectrolyte; this evidence results from the good concordance between calorimetric and potentiometric data.