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Use of the Empirical Hill Equation for Characterization of the Effect of Added Cations on the Viscosity of Aqueous Solutions of Partially Hydrolyzed Polyacrylamide

Richard E. Ellwanger, David A. Jaeger and Roland E. Barden*

Department of Chemistry and Division of Biochemistry, University of Wyoming, Laramie, Wyoming 82071, USA

SUMMARY

An empirical method based on the Hill equation has been developed to characterize the effects of added cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) on the viscosities of aqueous solutions of partially hydrolyzed polyacrylamide.

INTRODUCTION

Aqueous solutions containing partially hydrolyzed polyacrylamide are commonly used as viscosity-controlling "slugs" in enhanced oil recovery operations (DOSCHER 1977). Both laboratory and field tests have demonstrated that polymeric additives can increase oil recovery (DAVIS and JONES 1968, GOGARTY et al. 1970, HOWELL et al. 1979), but this technology is very complex and still the object of intense investigation in many laboratories. Systematic laboratory studies on some factors influencing the performance of polymer floods have been published (SZABO 1975).

The viscosity of the injected polymer solution is a key variable influencing performance. Several studies have shown that added salt has a significant effect on the viscosity of poly-ion solutions (MORAWETZ 1965). Solutions of partially hydrolyzed polyacrylamide may be subjected to increased electrolyte concentrations due to mixing with connate brine in the oil reservoir. Consequently, we investigated the effect of increasing concentrations of cations (i.e., counterions) on the viscosity of solutions of various polyacrylamides which were of interest as additives in oil-recovery operations. We collected numerous sets of data in these studies and thus searched for a convenient method of reducing the data to tables of information that could be readily evaluated. The report below describes the empirical method we adopted.

EXPERIMENTAL

Preparation of Partially Hydrolyzed Polyacrylamide.

* To whom correspondence should be addressed

The average molecular weight of the polyacrylamide used in the studies described here was in the million range. The polyacrylamide was provided by the Denver Research Center, Marathon Oil Company. Polyacrylamide was diluted with twice-distilled water to a 0.5% (w/v) solution. Sodium hydroxide (0.30 mole-equivalent) was added, and the solution was stirred overnight at 55° C. Approximately 30% of the amide groups are hydrolyzed by this procedure to give a solution with a carboxylate concentration of 2.0×10^{-2} M.

Viscosity Measurements. Samples (500 ml) of the partially hydrolyzed polyacrylamide solution were placed in a thermostated bath (Precision Scientific Company) and equilibrated to 25.0 ± 0.2°C. Viscosity measurements were obtained with a Brookfield Synchro-Lectric Viscometer (Model LVT) fitted with the #1 spindle.

In tests of the effect of increasing cation concentration on the viscosity, small aliquots of a concentrated stock solution of the cation under investigation were successively added to the polyacrylamide solution. A total of 5 ml of the concentrated stock solution was added to a polyacrylamide solution; further increases in cation concentration were achieved by the addition of solid salt. After each addition of salt, the solution was mechanically stirred for $\sim$1 min. The cations studied were Na^+, K^+, Mg^{2+}, and Ca^{2+} (as their chloride salts).

RESULTS AND DISCUSSION

In preliminary studies, the viscosity of the partially hydrolyzed polyacrylamide solution in the absence of added salt was measured as a function of the rotational speed of the viscometer spindle. The results indicated that the polyacrylamide solution is a non-thixotropic, pseudoplastic fluid. The viscosities, η (cp), reported in this paper were measured at 60 rpm, which lies within the straight-line section of the relationship between η and rotational speed.

As expected on the basis of analogous studies with other poly-ions (MORAWETZ 1965), addition of salt to a solution of partially hydrolyzed polyacrylamide causes a decrease in the measured viscosity. Results of a typical experiment are illustrated in Figure 1, where η is plotted versus the log of the concentration of added cation. It has been established via thermodynamic and transport measurements that a fraction of the counterions is bound to specific sites on polyions (RICE and NAGASAWA 1961). The curves in Figure 1 indicate that the measured viscosity is related to the degree of saturation of the cation binding sites on partially hydrolyzed polyacrylamide. That is, the viscosity decreases as the available binding sites on the poly-

anion become increasingly occupied by cations. Ulti-
mately, essentially all of the binding sites are occu-
pied by cations (i.e., the sites are saturated), and
further addition of cations does not cause a signifi-
cant decrease in viscosity. The mechanism by which
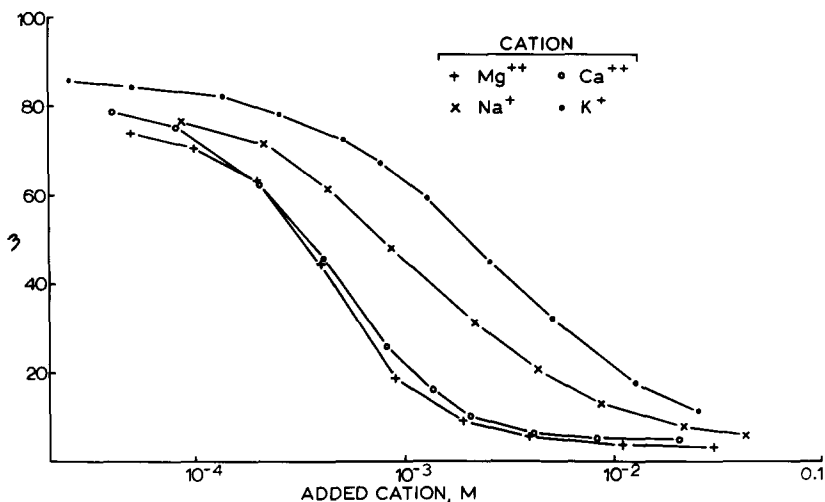added cations cause a decrease in viscosity is not

Figure 1. The viscosity of the solution of partially
hydrolyzed polyacrylamide as a function of the log of
the concentration of added cation.

fully understood. Presumably, the added cation shields
the fixed negative charges on the partially hydrolyzed
polyacrylamide, electrostatic repulsion is decreased,
and the polyanion consequently contracts and occupies
a smaller hydrodynamic volume (MORAWETZ 1965).
When several variables, such as cation type, poly-
mer concentration, average polymer size, etc., are
varied systematically, a large number of curves such
as those shown in Figure 1 is obtained. We desired
a convenient method for analyzing data of this type so
that characteristic parameters of each system could be
presented in a format which facilitates making critical
comparisons of the results from many experiments. A
modified form of the empirical Hill equation (eq. 1)
was found to be quite useful in our work. The Hill
equation (BROWN and HILL 1922-23), derived originally

$$\log\ (\eta_t - \eta_o)/\eta_o = n\ \log\ [C] - \log\ K \qquad (1)$$

to describe oxygen binding to hemoglobin, is used fre-
quently in examining multiple ligand binding to en-
zymes, particularly in assessing cooperativity among

binding sites (Cf. SCRUTTON 1974, ATKINSON 1966,
KOSHLAND, JR. 1970). In equation (1), η_t is the max-
imum observed change in viscosity upon addition of a
saturating amount of cation; η_o is the difference
between an observed viscosity and that obtained upon
addition of a saturating amount of cation; C is the
molar concentration of added cation; K is a complex
constant; and n is the Hill coefficient, which indi-
cates the degree to which a ligand bound at one site
influences binding events at other sites.

With equation (1), the log of the saturation
function $(\eta_t - \eta_o)/\eta_o$ is plotted versus the log of the
concentration of the ligand being tested. An illus-
trative example of this treatment is shown in Figure
2. Two characteristic constants are obtained with
this analysis. The first is the half-saturation con-
centration, $[C]_{0.5}$, defined as that concentration of
added cation which gives half of the maximum observed
change in viscosity such that $(\eta_t - \eta_o)/\eta_o = 1$. The
second is the slope of the line, the Hill coefficient
n. Of these $[C]_{0.5}$ is clearly the more valuable param-
eter.

Each curve shown in Figure 1 has been analyzed as
described above, and the respective characteristic con-
stants are summarized in the Table. The observed val-
ues for $[C]_{0.5}$ indicate that this sample of partially
hydrolyzed polyacrylamide is "sensitive" to rather low
concentrations of added cation and, further has a
three to four times greater affinity for divalent cat-
ions than for monovalent cations. For Na^+ and K^+ the
maximum change in viscosity (η_t) is approached as the
counterion concentration approaches the carboxylate
concentration $(2 \times 10^{-2}M)$ of the partially hydrolyzed
polyacrylamide.

TABLE

Summary of Half-Saturation Concentrations and Hill
Coefficients for the Different Added Cations

Added Cation	$[C]_{0.5}$	Hill Coefficient n
Na^+	1.4×10^{-3}	1.1
K^+	2.2×10^{-3}	1.0
Mg^{2+}	4.8×10^{-4}	1.7
Ca^{2+}	4.8×10^{-4}	1.7

If the binding sites for added cations are inde-
pendent of each other, the binding process conforms to
a Langmuir adsorption isotherm, and a Hill coefficient
of 1.0 is obtained. Thus, it is apparent that the
binding of Na^+ and K^+ to this sample of partially hy-
drolyzed polyacrylamide takes place as if the binding
sites are essentially independent of each other. On
the other hand, some kind of site-site interaction
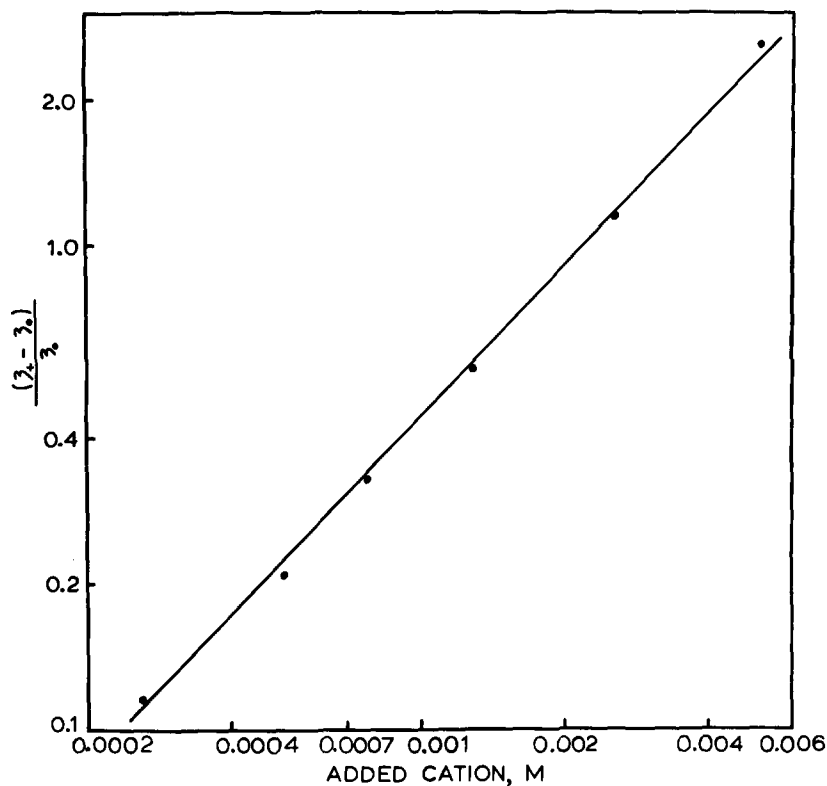does occur when divalent cations bind to this sample

$$\frac{(n_t - n_o)}{n_o}$$

ADDED CATION, M

Figure 2. A log-log plot of $(n_t - n_o)/n_o$ versus the concentration of added K^+ according to equation 1.

of partially hydrolyzed polyacrylamide, since the Hill coefficients obtained for the Mg^{2+} and Ca^{2+} systems approach 2. In this case binding events exhibit a positive cooperativity (Cf. KOSHLAND, JR. 1970). We conclude that once a divalent cation binds at one anionic site on the polyanion a second anionic site is sufficiently close so that each divalent cation tends to bind simultaneously to two anionic sites. However, the observation that the Hill coefficient for the divalent cations is 1.7, i.e., less than the theoretical value of 2.0, suggests that some divalent cations are not able to neutralize two anionic sites simultaneously. Presumably, some anionic sites do not have a neighbor site sufficiently close so that one divalent cation can interact with two sites at the same time.

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