

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY, CHICAGO 16, ILLINOIS]

## The Interaction of Polyvinylpyrrolidone with Aromatic Compounds in Aqueous Solution. III. A Model for the Molecular Expansions Caused by Anionic Cosolutes<sup>1</sup>

BY P. MOLYNEUX<sup>2</sup> AND H. P. FRANK

RECEIVED MAY 22, 1964

The expansion that occurs in the encompassed volume of an isolated neutral polymer molecule in aqueous solution when it binds ions from the electrolyte also present in the solution is treated theoretically from the viewpoint of the "free ionic excess"; the model used is restricted to cases where there is only a small concentration of bound ions within the polymer coil. The relations obtained are applied to data reported in the first two parts on the binding of aromatic anions by polyvinylpyrrolidone in aqueous solution, for which the assumption of low bound-ion concentration is shown to hold; there is general agreement between the theoretical model and the experimental data except that the apparent binding constants for expansion are less than those determined by dialysis by a fairly constant amount (*ca.* 30  $M^{-1}$ ).

### Introduction

In the previous parts<sup>1</sup> of this series we have reported experimental data on the interaction between three types of aromatic cosolutes (anionic, nonionic, and cationic) and polyvinylpyrrolidone (PVP) in aqueous solution; in this paper we develop a general theoretical treatment of the expansion in the encompassed volume of an initially neutral, random-coil polymer molecule when it binds ions predominantly of one charge (here the anions) from an electrolyte present with it in solution; the treatment is based largely upon the statistical thermodynamic theory of dilute solutions of neutral polymers and polyelectrolytes.<sup>3</sup> The simplification introduced in the present treatment is that the concentration of bound ions within the volume encompassed by the polymer molecule is always small; this is shown to hold for the interaction between PVP and the aromatic anions, and hence the theoretical relations obtained are tested using the data obtained for this interaction.

**Theoretical Treatment.** (i) **Derivation of the Free Ionic Excess.**—Consider an isolated polymer molecule immersed in an infinite bath of a strong electrolyte (here the cosolute NaA, molar concentration  $a$ ); this state is one for which data are readily attainable by taking measurements over a range of polymer concentrations and then extrapolating to *zero* polymer concentration. Since in this state there is an overwhelming excess of solution over polymer then any binding of the cosolute by the polymer (or indeed any other interaction between them) will have no effect on the cosolute concentration in the bulk of the solution. In addition, since the concentration of polymer in the region encompassed by the polymer molecule is quite low (for PVP in water at ambient temperature it is about 0.4%) then we can neglect the purely diluting effect that the polymer segments have on ionic concentrations in this region.

Assume that one of the ions (here, the anion  $A^-$ ) from the cosolute is bound by the chain according to the form of the Langmuir adsorption isotherm; also, assume that none of the cations ( $Na^+$ ) are directly bound by the chain itself but that they can be bound to previously attached anions, with this *counter-ion* binding also following the Langmuir isotherm.<sup>4</sup> If the binding con-

stants for these consecutive processes are  $K$  and  $K'$ , respectively, then the concentrations of bound anions and bound ion pairs within the molecule are

$$[A^-_b] = K[A^-_b]_\infty[A^-_f] / (1 + K[A^-_f] + KK'[A^-_f][Na^+_f]) \quad (1)$$

$$[NaA_b] = KK'[NaA_b]_\infty[Na^+_f][A^-_f] / (1 + K[A^-_f] + KK'[A^-_f][Na^+_f]) \quad (2)$$

where the subscripts  $f$  and  $b$  indicate free and bound species and the subscript  $\infty$  indicates the states in which all the adsorption sites are occupied solely by that species, with the size of the polymer coil the same as at the referred finite concentration (these "saturation" concentrations depend upon the polymer segment density, which varies both with the degree of expansion of the coil and with the distance from the centre of mass, and we should strictly specify both of these, but this can be left until a later stage).

Assuming that, if  $K'$  is not zero, all of the sites that will accept a bound anion will also accept a cation to form an ion pair, then

$$[A^-_b]_\infty = [NaA_b]_\infty \quad (3)$$

and hence the total bound anion concentration will be given by

$$[A^-_b]_{tot} = [A^-_b] + [NaA_b] \quad (4)$$

$$= K[A^-_b]_\infty[A^-_f](1 + K'[Na^+_f]) / (1 + K[A^-_f] + KK'[Na^+_f][A^-_f]) \quad (5)$$

(Note that if  $K'[Na^+_f] \ll 1$ , *e.g.*, at low cosolute concentrations, or in the absence of cation binding, this reduces to

$$[A^-_b]_{tot} = K[A^-_b]_\infty[A^-_f] / (1 + K[A^-_f]) \quad (6)$$

which is of the simple Langmuir form; the equilibrium dialysis data in part I<sup>1</sup> showed that over the cosolute concentration range used ( $10^{-3}$  to  $10^{-2}$   $M$ ) the binding of aromatic anions by PVP did obey this isotherm, and hence we can use the values of  $K$  and of  $[A^-_b]_\infty$  derived from the dialysis data in the later test of the model;

(4) It is possible that the binding of an anion by the polymer chain, by imbedding it in a medium largely composed of hydrocarbon groups and hence of low dielectric constant, may increase the purely electrostatic forces between such a bound anion and a cation in its vicinity and hence produce the appearance of site-binding of the cation; the introduction of the second Langmuir isotherm is an attempt to allow for such an effect; the whole concept of counter-ion site binding has been discussed by Rice and Nagasawa ("Polyelectrolyte Solutions," Academic Press Inc., New York, N. Y., 1961, Chapter 9).

(1) Parts I and II: P. Molyneux and H. P. Frank, *J. Am. Chem. Soc.*, **83**, 3169, 3175 (1961); note that eq. 4 in part I should read:  $\Delta H_b = \Delta H_2 + \Delta H_3 + \Delta H_4$ , and that the coordinate labels on Fig. 5 of this paper should be transposed.

(2) Correspondence should be addressed to School of Pharmacy, Chelsea College of Science and Technology, London, S.W. 3.

(3) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

for the viscometry (molecular size) experiments, however, the cosolute concentrations ranged up to 0.25  $M$ , in which region it is possible that the counter-ion binding may become important, so that we will retain the full form of eq. 1 in the subsequent treatment.)

Since the free ions within the volume encompassed by the polymer molecule are in equilibrium with those in the bulk of the solution, then assuming the mean ion activity coefficients inside and outside the coil are equal (since for the PVP data we will show that the corresponding concentrations lie within the limits  $a \gtrsim [A^-_f] \gtrsim 0.75a$ , and  $a \lesssim [Na^+_f] \lesssim 1.33a$ , then this assumption is valid)

$$[Na^+_f][A^-_f] = a^2 \quad (7)$$

Further, if the solution contains only ions derived from the cosolute NaA, and if the region inside the polymer molecule can be taken to be electrically neutral,<sup>5</sup> then

$$[Na^+_f] = [A^-_f] + [A^-_b] \quad (8)$$

If we use  $\Delta a$  to represent the excess concentration of free ions within the coil above that outside it (the "free ionic excess"), then

$$\Delta a = [Na^+_f] + [A^-_f] - 2a \quad (9)$$

Eliminating  $[A^-_b]$  from eq. 1, 7, and 8 gives

$$a^2/[A^-_f]^2 = 1 + \{K[A^-_b]_\infty / (1 + K[A^-_f] + KK'[Na^+_f][A^-_f])\} \quad (10)$$

and hence from eq. 7, 9, and 10

$$\Delta a = K^2[A^-_f]^3[A^-_b]_\infty^2 / \{(1 + K[A^-_f] + KK'a^2)(a + [A^-_f])\}^2 \quad (11)$$

It would now be desirable to obtain  $[A^-_f]$  as an exact explicit function from eq. 10 and substitute for it in 11, but this cannot be done without the relations becoming prohibitively complicated; it is more convenient to introduce a parameter,  $\zeta$ , given by

$$[A^-_f] = \zeta a \quad (12)$$

$\zeta$  can be evaluated quite accurately from eq. 10 by putting  $[A^-_f] = a$  and  $K' = 0$  on the right hand side, and it is found to differ little from unity and be essentially insensitive to large variations in  $a$ ,  $K$ , etc., as long as there are only a few ions bound to the polymer coil.<sup>6</sup> Substituting from (12) in (11), and introducing the simplifying approximation

$$(1 + \zeta)^2/4\zeta = 1 \quad (13)$$

(this is exact when  $\zeta = 1$ , and even for  $\zeta = 0.75$  the discrepancy is only 2%) we obtain

(5) If we choose the maximum possible difference, for the PVP case, between the ionic concentrations within and without the coil, *i.e.*  $[A^-_f] = 0.75a$ , then this leads to a maximum Donnan membrane potential of 7.3 mv. (coil negative); this in turn, assuming the molecule to be equivalent to a solid conducting sphere with its radius (and hence its capacity) equal to its mean radius of gyration, corresponds to a maximum average excess concentration of negative ions within the coil of about  $5 \times 10^{-5} M$ : for the experimental concentrations of  $10^{-3} M$  and above, this is a negligible deviation from electroneutrality.

(6) If we neglect the counter-ion binding term in eq. 10, then  $\zeta$  has a value lying between  $(1 + K[A^-_b]_\infty)^{-0.5}$  (for  $a = 0$ ) and unity (for  $a \rightarrow \infty$ ); thus, as long as  $K[A^-_b]_\infty$  is small,  $\zeta$  will never fall greatly below unity. For the PVP data the most strongly bound anion, 3-phenanthroate, has  $K = 300 M^{-1}$ ; since from the dialysis and light-scattering results (see below) the over-all average value of  $[A^-_b]_\infty$  for the unexpanded (water at 30°) polymer coil is about  $2.6 \times 10^{-3} M$ , then  $K[A^-_b]_\infty = 0.78$  and hence  $\zeta = 0.75$ ; this is thus the minimal value of  $\zeta$  for the PVP data.

$$\Delta a = K^2\zeta^2a[A^-_b]_\infty^2/4(1 + K\zeta a + KK'a^2)^2 \quad (14)$$

(ii) **Effect of the Free Ionic Excess on the Molecular Size.**—Let us now consider the effect that the presence of this ionic excess has on the configuration of the isolated polymer molecule. We will assume, conventionally, that the molecule has a spherically symmetrical Gaussian distribution of its segments about its center of mass, and we will consider it to be divided into concentric spherical shells, with the  $j$ th shell being at distance  $R_j$  from the center of mass and of thickness  $\delta R_j$ , both for the molecule in its *ideal* configuration.

Now the complete system of isolated polymer molecule and encompassed solution can be considered to be formed from the completely isolated molecule in its ideal state in two steps, consisting first of the expansion to its final configuration, followed secondly by a mixing step involving the introduction of this polymer molecule, together with any additional cosolute ions or molecules of solvent (or with the removal of either of these) into the infinite bath of cosolute solution; the free energy change for the total process,  $\Delta F$ , for one mole of polymer, will thus be given by

$$\Delta F = \Delta F_{\text{ex}} + \sum_j \Delta F_{M_j} \quad (15)$$

Partially differentiating with respect to the lineal expansion coefficient,  $\alpha$

$$\partial \Delta F / \partial \alpha = \partial \Delta F_{\text{ex}} / \partial \alpha + \partial \sum_j \Delta F_{M_j} / \partial \alpha = 0 \quad (16)$$

since the system is at equilibrium, so that

$$\partial \Delta F_{\text{ex}} / \partial \alpha = -\partial \sum_j \Delta F_{M_j} / \partial \alpha \quad (17)$$

The right hand side, referring to the expansion of the polymer coil from the ideal to the equilibrium configuration, is given by

$$\partial \Delta F_{\text{ex}} / \partial \alpha = 3\mathcal{R}T(\alpha - \alpha^{-1})/\mathcal{N} \quad (18)$$

where  $\mathcal{R}$  is the gas constant,  $T$  is the absolute temperature, and  $\mathcal{N}$  is Avogadro's number.

The left hand side of eq. 17 for the  $j$ th shell alone becomes, following Flory<sup>7</sup>

$$\partial \Delta F_{M_j} / \partial \alpha = 12\pi\alpha^2 R_j^2 \delta R_j (\mu_{1j} - \mu_1^*) / V_1 \quad (19)$$

where  $V_1$  is the molar volume of water and  $\mu_{1j}$ ,  $\mu_1^*$  are the chemical potentials of the water in the  $j$ th shell, and outside (*i.e.* at infinite distance from) the polymer coil; now the difference between these last two can be assumed, also following Flory, to consist of the sum of two parts, the one due to the difference between the concentration of polymer units within the shell and that (zero) outside the coil, and the other due to the corresponding difference in concentrations of free ions, *i.e.*

$$\mu_{1j} - \mu_1^* = -\mathcal{R}T \{ \psi(1 - \Theta/T)\phi_{2j}^2 + V_1(\Delta a)_j \} \quad (20)$$

where  $\psi$  is the entropy of dilution parameter for the polymer-solvent pair and  $\Theta$  is its ideal temperature,  $\phi_{2j}$  is the volume fraction of polymer in the  $j$ th shell, and  $(\Delta a)_j$  is the free ionic excess for this shell. This last term is introduced from a consideration of the relation for the effect of the ions alone on the chemical potential of the solvent, which in the most general case is

$$\mu_1 = \mu_1^0 + \mathcal{R}T \ln \gamma_1 x_1 \quad (21)$$

where  $x_1$  is the mole fraction of solvent and  $\gamma_1$  is its (mole fraction) activity coefficient; since the ionic concentrations within and without the coil are almost equal, we can put

$$\gamma_1^* = \gamma_1 \quad (22)$$

and hence for the effect of the ions alone

$$\mu_{1j} - \mu_1^* = RT \ln (x_{1j}/x_1^*) \quad (23)$$

Converting from mole fractions of solvent to those of ions (with the molar volume of the solution taken to be  $V_1$ ), expanding the logarithms in power series and neglecting all but the first terms (the series are in powers of terms such as  $2aV_1$ , which even with  $a$  as high as  $0.25M$  has a value of only about 0.01), leads to the second, ionic term on the right hand side of eq. 20. Substituting from eq. 20 in eq. 19 and summing over the whole molecule, we obtain

$$\sum_j \partial \Delta F_{Mj} / \partial \alpha = -12\pi\alpha^2 RT \psi V_1^{-1} (1 - \Theta/T) \cdot \int_0^\infty \phi_{2j}^2 R_j^2 dR_j - 12\pi\alpha^2 RT \int_0^\infty (\Delta a)_j R_j^2 dR_j \quad (24)$$

Flory has shown<sup>7</sup> that the first term on the right hand side, if evaluated assuming a Gaussian distribution of segments about the center of mass, has the value  $C_1/\alpha^4$  where  $C_1$  is a constant for a single sample of polymer in the same liquid as solvent at a fixed temperature. For the second term on the right hand side of eq. 24, if the Gaussian distribution of segments is given by

$$x_j = x(\beta'_\theta/\pi^{0.5})^3 \exp(-\beta'_\theta^2 R_j^2) 4\pi R_j^2 \delta R_j \quad (25)$$

(this corresponds primarily to the number of segments,  $x_j$ , in the  $j$ th shell in the *ideal* configuration, but expansion to another configuration will not change the identity, and hence will not change the number of units in this shell;  $x$  is the total number of segments in the molecule), and if at "saturation" there are  $n$  bound ions per segment, we have

$$[A^-]_{\infty,j} = nx(\beta'_\theta/\pi^{0.5})^3 \exp(-\beta'_\theta^2 R_j^2) / \mathfrak{N} \alpha^3 \quad (26)$$

and hence substituting from eq. 14 and 26 in eq. 24 and carrying out the integration

$$\sum_j \partial F_{Mj} / \partial \alpha = C_1/\alpha^4 - 3RTn^2 x^2 \beta'^3_\theta K^2 \zeta^2 a / (2\pi)^{1.54} \mathfrak{N}^2 \alpha^4 (1 + K\zeta a + KK'a^2) \quad (27)$$

If we introduce eq. 17 and 18 and note that when  $a = 0$  or  $K = 0$  the molecule has its configuration in pure water, *i.e.*,  $\alpha = \alpha_0$ , so that

$$C_1/\alpha_0^4 = 3RT(\alpha_0 - \alpha_0^{-1})/\mathfrak{N} \quad (28)$$

then referring all the  $\alpha$ -values explicitly to the corresponding cosolute concentration

$$n^2 x^2 \beta'^3_\theta K^2 \zeta^2 a / (2\pi)^{1.54} \mathfrak{N} (1 + K\zeta a + KK'a^2) = (\alpha_a^5 - \alpha_a^3) - (\alpha_0^5 - \alpha_0^3) \quad (29)$$

Now if  $[\eta]_\theta$ ,  $[\eta]_0$ , and  $[\eta]_a$  are the intrinsic viscosities of the polymer in water at the (undetermined) ideal temperature, in water at the experimental temperature, and in cosolute solution at the experimental temperature, then as long as the intrinsic viscosity is proportional to the cube of a linear dimension of the polymer molecule in solution, it follows that

$$[\eta]_0/[\eta]_\theta = \alpha_0^3 \quad (30)$$

and

$$[\eta]_a/[\eta]_\theta = \alpha_a^3 \quad (31)$$

The intrinsic viscosity ratio,  $V$ , which we have previously defined<sup>1</sup> as

$$V = [\eta]_a/[\eta]_0 \quad (32)$$

hence gives

$$\alpha_a = V^{0.33} \alpha_0 \quad (33)$$

so that substituting in (29)

$$n^2 x^2 \beta'^3_\theta K^2 \zeta^2 a / (2\pi)^{1.54} \mathfrak{N} (1 + K\zeta a + KK'a^2) = \alpha_0^3 \{ \alpha_0^2 (V^{1.66} - 1) - (V - 1) \} \quad (34)$$

Since all the quantities in this equation are either universal constants or are, in principle, determinable experimentally, then it serves as a convenient expression for testing the model.

**Application of the Model to the PVP Data.**<sup>1</sup>—The equilibrium dialysis data showed that the binding of the anions obeyed the Langmuir isotherm (6) at the low cosolute concentrations used (below  $10^{-2}M$ ) and there were no signs of deviation from this form due to, say, counter-ion binding (eq. 5); the site occupied  $10 (\pm 3)$  monomer units, *i.e.*  $n = 0.10 \pm 0.03$  (the binding constants,  $K$ , are set out in Table I).

Viscometry yielded values of the intrinsic viscosity ratio,  $V$ , for the cosolutes at various concentrations; the majority of the aromatic anionic cosolutes gave  $V$ -values greater than unity, showing that these cosolutes do cause the molecule to expand. Such cosolutes as sodium acetate and sodium chloride gave  $V$ -values close to unity, indicating lack of binding of either acetate, chloride, or most importantly, sodium ions by the coil itself.

The light-scattering data showed the molecules of polymer sample used had a  $z$ -average r.m.s. radius of gyration,  $\langle \bar{R}^2 \rangle_z^{0.5}$ , of 590 Å. (water at 30°); a linear relationship, expected on theoretical grounds, was obtained between  $\langle R^2 \rangle$  and the second virial coefficient  $A_2$ , as these both varied from one cosolute solution to another, and a short extrapolation to  $A_2 = 0$  gave the unperturbed r.m.s. radius of gyration,  $\langle \bar{R}_0^2 \rangle_z^{0.5}$ , as  $504 \pm 13$  Å.; from this value and from that for water at 30°

$$\alpha_0 = 1.17 \pm 0.03 \quad (35)$$

In addition, the  $z$ -average value of  $\beta'_\theta$  is given by:

$$\bar{\beta}'_{\theta,z} = 1.5^{0.5} \langle \bar{R}_0^2 \rangle_z^{-0.5} = 2.44 \times 10^5 \text{ cm.}^{-1} \quad (36)$$

The constancy of the ratio  $\langle \bar{R}^2 \rangle_z^{0.5} / V^{0.33}$ , at a value of  $596 \pm 13$  Å., indicates the concordance between the light scattering and the viscometry data, and the validity of eq. 30 and 31.

The light-scattering data also gave the weight average molecular weight of the polymer,  $\bar{M}_w$ , as  $1 \times 10^6$ ; assuming the sample to have a "most probable" distribution, then the  $z$ -average value,  $\bar{M}_z$ , is  $1.5 \times 10^6$  (the published value<sup>8</sup> of the number-average molecular weight,  $\bar{M}_n$ , of PVP K-90 is  $3.6 \times 10^5$ , compared with

(8) "PVP Polyvinylpyrrolidone," General Aniline and Film Corp., New York, N. Y., p. 2.

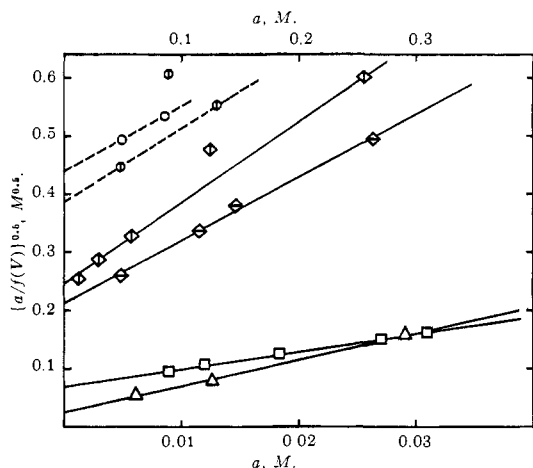


Fig. 1.—Anion key:  $\Delta$ , 3-phenanthroate;  $\square$ , biphenyl-4-carboxylate;  $\diamond$ , 2-naphthoate;  $\triangleleft$ , 1-naphthoate;  $\odot$ , *p*-toluate;  $\circ$ , benzoate. The lower concentration scale refers to the first two anions, the upper to the remainder.

$5 \times 10^5$  expected from  $\bar{M}_w = 1 \times 10^6$  and a "most probable" distribution); hence

$$\bar{x}_z = 1.5 \times 10^6 / 111 = 1.35 \times 10^4 \quad (37)$$

We can now combine some of the quantities in eq. 34 into an evaluable parameter

$$\Gamma = n^2 x^2 \beta'_\theta^3 / 4\mathfrak{N}(2\pi)^{1.5} = 0.70 M \quad (38)$$

using the  $z$ -average values (since  $x$  and  $\beta'_\theta$  move in opposite directions when we change the type of average, then  $\Gamma$  is likely to be much the same regardless of the average involved).

Since for the present case  $\alpha_0$  is fixed, we can represent the right hand side of eq. 34 by  $f(V)$ , so that this equation becomes, upon rearrangement and taking the square root

$$\{a/f(V)\} = (1 + K\zeta a + KK'a^2)/K\zeta\Gamma^{0.5} \quad (39)$$

Figure 1 shows plots of  $\{a/f(V)\}^{0.5}$  vs.  $a$  for the PVP data with the indicated cosolutes; where three or more experimental points were obtained for one cosolute the plots are close to linear, indicating that the term  $KK'a^2$  in eq. 39 is negligible, and hence that counter-ion binding does not occur to an appreciable extent (from the scatter of the experimental points about the lines,  $K'$  for the naphthoates is probably maximally  $1 M^{-1}$ , and for the biphenyl-4-carboxylate and 3-phenanthroate maximally  $10 M^{-1}$ ; the good linear fit obtained with the naphthoates up to the surprisingly high concentration of  $0.25 M$  gives us confidence in obtaining parameters from the lines through the two points each available for benzoate and *p*-toluate. (Two points in Fig. 1, one for 1-naphthoate and the other for *p*-toluate, are highly discrepant, and have been disregarded in the fitting of the lines; in both cases the points are high, and both gave low  $V$ -values in the original plots of  $V$  vs.  $a^1$ ; this is explicable as due to samples of cosolute solution used, which may either have been prepared in error from nonequivalent quantities of acid or base or may have absorbed atmospheric carbon dioxide leading to both free acid and base; since we have shown<sup>1</sup> both that the free aromatic acid causes shrinkage of the coil and that the presence of nonbound salts leads to a reduced expansion with aromatic anionic cosolutes, then

TABLE I

Cosolute anion	$I, M^{0.5} \times 10^2$	$S, M^{-0.5}$	$D, \%$	$S/I\zeta_0, M^{-1}$	$K, M^{-1}$	$K - S/I\zeta_0, M^{-1}$
3-Phenanthroate	2.25	4.62	3.0	274	300	26
Biphenyl-4-carboxylate	6.65	3.08	1.6	51	75	24
2-Naphthoate	21.0	1.09	1.8	5.4	37	32
1-Naphthoate	24.3	1.40	1.0	6.0	37 <sup>a</sup>	31
<i>p</i> -Toluate	38.4	1.29	...	3.5	33 <sup>a</sup>	29
Benzoate	43.7	1.11	...	2.6	33	30

<sup>a</sup> Estimated values; see text.

this would explain the discrepancies with these two points.

Table I shows the intercepts ( $I$ ) and the slopes ( $S$ ) of the lines in Fig. 1, together with the per cent standard deviations,  $D$ , of the ordinates from these lines; the last three columns of the table contain the derived values of  $S/I\zeta_0$ , the binding constants  $K$  previously determined by dialysis,<sup>1</sup> and the numerical differences between these two quantities. No data are available for  $K$  for either *p*-toluate or 1-naphthoate, and the figures given in the table are merely estimates from their similarity in molecular structure to benzoate and 2-naphthoate, respectively, but since there is little difference between the  $K$ -values for these last two it is unlikely that the estimates are uncertain to more than a unit or two.

Considering first the slopes of the lines, from eq. 39 we would expect

$$S = \Gamma^{-0.5} = 1.20 M^{-0.5} \quad (40)$$

Table I shows that for the four most weakly bound cosolutes the slopes are indeed close to this value, the mean for the four being  $1.25 \pm 0.15$  (one standard deviation)  $M^{-0.5}$ .

For biphenyl-4-carboxylate and 3-phenanthroate, however, the slopes are 2.6 and 3.9 times the predicted value; this discrepancy may be due in part to the higher numbers of bound ions and higher degrees of molecular expansion obtained with these cosolutes, but it is surprising that similar high slopes are not obtained for the naphthoates, where the  $V$ -values range up to 1.46. It seems more probable that the discrepancy is due to a shrinkage effect of the same type observed with nonionic cosolutes, since it involves low  $V$ -values for a given cosolute concentration. The anions do not, of course, have groups able to form direct hydrogen bonds with the polymer, and it was to the presence of such groups on the nonionic cosolutes that the major part of their shrinking ability was attributed; however, it was also observed that 2-naphthol gave more shrinkage than phenol at the same degree of coverage, and hence it appears that the larger aromatic system causes an enhanced cross-linking effect, the cross links in this case being attributable to further interaction between the absorbed aromatic system and another section of the same polymer molecule. For the anions we assume that only the two largest of these show this cross-linking ability; if we start in the (hypothetical) initial state with the same number and position of cross links as in the final equilibrium state, these not being altered during the subsequent (hypothetical) processes, then since the number of cosolute molecules involved in cross links is always small there would be no appreciable disturbance of the ionic equilibria, so that

the only change required would be a modification of eq. 18 into the form

$$\partial \Delta F_{ex} / \partial \alpha = \epsilon \cdot 3RT(\alpha - \alpha^{-1}) / \mathcal{N} \quad (41)$$

where the factor  $\epsilon$ , equal to unity in the absence of cross links and greater than unity when they are present, is introduced to take into account the lesser extensibility of a cross-linked chain; the sole result of this is to replace  $\Gamma$  by  $\Gamma/\epsilon$ , and hence to increase the slope (by a factor of  $\epsilon^{0.5}$ ), which is consistent with what is observed; on this basis  $\epsilon$  would be 7 for biphenyl-4-carboxylate and 15 for 3-phenanthroate.

Considering next the ratio  $S/I\zeta_0$  for the lines, from eq. 39 we would expect it to be equal to the value of  $K$  for the particular cosolute; Table I shows that this is not so, but that the values of  $S/I\zeta_0$  differ from  $K$  by an amount which is fairly constant at about  $30 M^{-1}$ . (It may seem somewhat arbitrary to use  $\zeta_0$  (*i.e.*, that for  $a = 0$ , as given in footnote 7) here in place of any other values of  $\zeta$ , but since the plots are linear they must hold down to  $a = 0$ , and additionally most of the approximations made in the theoretical treatment, as to activity coefficients, etc., become completely valid at  $a = 0$ .)

This situation is puzzling, since the agreement with theory up to this stage, *i.e.*, the linearity of the plots in Fig. 1 and the essential agreement between their slopes and the expected value, suggests that the broad outline of the present treatment is correct; further, if we trace back the source for the identification of  $S/I\zeta_0$  with  $K$ , we find that it derives directly from the formulation in eq. 1 of the anion binding (the counter-ion term being now completely neglected), and the assumptions of the statistical thermodynamic part of the treatment are not directly involved.

One possible explanation of the discrepancy is that the bound anions are not fixed on definite sites, but are

free to move along the chain while still attached to it; P. M. has shown<sup>9</sup> that if this *adsorbate mobility* is complete, then for small degrees of coverage the system obeys the Langmuir isotherm but the apparent binding constant obtained (*i.e.*, from dialysis) is twice its correct value; however, this would involve a constant *multiplicative* factor, rather than the constant *additive* factor that the present case requires; additionally, such mobility would lead to a similar twofold error in the site size,  $n$ , whereas the essential agreement between the predicted and the experimental slopes suggests that our experimental  $n$ -value (*i.e.* that from dialysis) is correct.

Alternatively, since what is observed is a lowering in the effective value of  $K$  for expansion as compared with that from dialysis, it is possible that some other type of counter-ion binding (*i.e.*, not expressed by a Langmuir-type formulation with binding constant  $K'$ ) is involved; for *any* form of counter-ion binding must reduce the free ionic excess, through converting bound anions into bound ion-pairs (assumedly inactive in changing the volume of the coil); this could readily be checked by using, say, lithium or potassium as the counter-ion in place of sodium.

In conclusion, it appears that it is possible to account for the expansive effect of the anionic cosolutes by the present treatment, but that owing either to mobility of the bound anions or to some kind of counter-ion binding, there is a fairly constant discrepancy between the equilibrium binding constants determined by dialysis and those corresponding to the molecular size data.

**Acknowledgments.**—We are grateful to Dr. P. J. Flory for comments on this paper in manuscript. This work was supported in part by National Institutes of Health Contract A2253(C1).

(9) P. Molyneux, *Nature*, **202**, 368 (1964).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO, TORONTO 5, ONTARIO]

## A Mechanism for Tropylium Ion Formation by Electron Impact

BY F. MEYER AND A. G. HARRISON<sup>1</sup>

RECEIVED JUNE 4, 1964

The formation of  $C_8H_9^+$  in the mass spectrum of methylethylbenzene is found to involve loss of the  $\beta$ -methyl and ring methyl in the ratio 5:1, while the formation of  $C_9H_{11}^+$  in the mass spectra of dimethylethylbenzenes is also found to involve loss of both the ring and  $\beta$ -methyls. A mechanism involving methyl loss from a substituted cycloheptatriene ion in which a selective  $7\alpha$ -hydrogen transfer has occurred is proposed to explain these results. The mechanism is consistent with the labeling studies on the fragmentation of ethylbenzene, cycloheptatriene, and toluene, and, in addition, accounts for the small preference for loss of the methyl hydrogen in the fragmentation of toluene.

### Introduction

The dissociative ionization of alkylbenzenes produces major ions of the general formula  $C_nH_{2n-7}$ . For the  $C_7H_7^+$  ion ( $n = 7$ ) extensive studies<sup>2</sup> with  $C^{13}$  and deuterium labeling have led to the conclusion that this ion, as formed from toluene,<sup>2a,b</sup> ethylbenzene,<sup>2a</sup>  $p$ -xylene,<sup>2c</sup> and several other benzyl derivatives,<sup>2d</sup>

does not retain the benzyl structure but has undergone ring expansion to form the symmetrical tropylium ion. The mechanism and timing of this ring expansion is not known. For toluene and xylene extensive scrambling of the ring and side-chain hydrogens occurs prior to formation of  $C_7H_7^+$ , suggesting that ring expansion occurs prior to the dissociation process. On the other hand, dissociative ionization of ethylbenzene to form  $C_7H_7^+$  involves only loss of the  $\beta$ - $CH_3$  and it is impossible to determine whether this group is lost before, during, or after ring expansion has occurred.

The next higher homolog,  $C_8H_9^+$ , has also received some attention. The mass spectrum of labeled  $p$ -

(1) Alfred P. Sloan Research Fellow 1962–1964.

(2) (a) P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957); (b) S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957); (c) S. Meyerson and P. N. Rylander, *J. Phys. Chem.*, **62**, 2 (1958); (d) H. M. Grubb and S. Meyerson, "Mass Spectra of Alkyl Benzenes," in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, Inc., New York, N. Y., 1963.