Notes

The Temperature Coefficient of the Unperturbed Dimensions of Polyoxyethylene

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In a recent publication,[1] de Candia, Vittoria, Bianchi, and Patrone have reported experimental values of the temperature coefficient d ln $\langle r^2\rangle_0/\mathrm{d}T$ of the unperturbed dimensions of polyoxyethylene (POE) chains. These results were estimated from thermoelastic (force–temperature) measurements on POE networks in swelling equilibrium with a diluent, and from viscosity–temperature data on relatively short POE chains in thermodynamically good solvents. The values of the temperature coefficient of $\langle r^2\rangle_0$ obtained by these two methods were found to be in serious disagreement with each other, and also with the result obtained previously by us[2] from thermoelastic measurements on POE networks at constant diluent concentration. Although not mentioned by de Candia, Vittoria, Bianchi, and Patrone, their recent results are also at variance with those of an earlier investigation previously reported by de Candia.[3]

De Candia *et al.*[1] have interpreted the disagreement of their recent results with ours to mean that, at least for this polymer, thermoelastic measurements cannot be relied upon for determination of d ln $\langle r^2\rangle_0/\mathrm{d}T$. In spite of much evidence to the contrary,[4] these authors suggest further that contributions from *inter*molecular interactions are the source of the discrepancy between the results they obtained by these two methods. We wish to point out that, inasmuch as the temperature coefficient is very small, values obtained by experiment are particularly susceptible to vitiation unless experimental conditions are carefully chosen and the measurements are conducted with the utmost pains to minimize sources of error.

The thermoelastic behavior of networks at swelling equilibrium is subject to large effects from the change of volume of the open system (network) with temperature. Hoeve and one of the present authors[5] showed that if the solvent medium is so chosen as to render the volume independent of the temperature, then the observed stress–temperature coefficient should lead directly to d ln $\langle r^2\rangle_0/\mathrm{d}T$. Otherwise arduous corrections for dilational effects are required.

De Candia *et al.* found the temperature coefficient of swelling of cross-linked POE in acetone to be "nearly zero." No limits of error were given. Under the assumption that this change is in fact zero, their temperature coefficient of the retractive force of POE networks in acetone led to[1] d ln $\langle r^2\rangle_0/\mathrm{d}T = -0.14 \times 10^{-3}\ \mathrm{K}^{-1}$, compared with our value[2] of 0.23 (±0.02) $\times 10^{-3}\ \mathrm{K}^{-1}$. They obtained an even lower value, $-0.28 \times 10^{-3}\ \mathrm{K}^{-1}$, by treating their data according to an approximate equation due to Bashaw and Smith.[6] This equation is a limiting expression accurate only at high dilution, *i.e.*, for very highly swollen networks, and certainly not at the volume fraction $v_r = 0.36$ in the experiments quoted. Bashaw and Smith were explicit in citing the limitations of their approximate equation. The latter of the two values obtained by de Candia and coworkers may therefore be dismissed.

From their plot of swollen length in acetone against temperature from *ca.* 30–65°, it would appear that the fractional change in length with temperature might be as great as $\pm 0.2 \times 10^{-3}\ \mathrm{K}^{-1}$. For the mean extensions in their measurements, this would convey an uncertainty of *ca.* $\pm 0.5 \times 10^{-3}\ \mathrm{K}^{-1}$ in d ln $\langle r^2\rangle_0/\mathrm{d}T$, which exceeds the disparity between their result and ours obtained by the more precise method involving measurements on a closed system, *i.e.*, one of constant composition. It is apparent that constancy of volume with temperature must hold stringently if d ln $\langle r^2\rangle_0/\mathrm{d}T$ is to be obtained straightforwardly from force–temperature measurements on open systems. The thermoelastic results previously obtained by de Candia[3] on POE networks of constant composition give d ln $\langle r^2\rangle_0/\mathrm{d}T = 0.48$ (±0.06) $\times 10^{-3}\ \mathrm{K}^{-1}$, a value which is positive, in agreement with our result,[2] but somewhat larger than the value we have obtained.

For the estimation of d ln $\langle r^2\rangle_0/\mathrm{d}T$ from intrinsic viscosities $[\eta]$ of dilute solutions, de Candia and coworkers[1] carried out measurements on solutions of polymers of low molecular weight, M_n = 400 to 4000, in acetone and in dioxane over temperature intervals within the range 25–55°. They identified d ln $\langle r^2\rangle_0/\mathrm{d}T$ with (2/3)d ln$[\eta]/\mathrm{d}T$ on the premise (i) that for these low polymers the expansion factor α should differ little from unity and hence be independent of temperature. Although not explicitly acknowledged, the further assumption (ii) that the hydrodynamic volume is directly proportional to $\langle r^2\rangle^{3/2}$ is required. Beech and Booth[7] have shown that this latter assumption (ii) fails for POE polymers below $M_n \approx 10^4$. The departure from asymptotic hydrodynamic behavior should be expected to vary with the viscosity of the solvent, and hence contribute to d ln $[\eta]/\mathrm{d}T$.

The solvents used probably do not mix athermally with POE, and neither of them is a Θ solvent. Although the expansion due to excluded volume doubtless is small for these low polymers, it is unwarranted for the present purpose to regard it as negligible: even a change in α by 1% over a temperature interval of 30° would seriously affect d ln $[\eta]/\mathrm{d}T$. Hence, assumption (i), though acceptable as a basis for estimating $\langle r^2\rangle_0$ [if assumption (ii) were valid], is unacceptable for the estimation of d ln $\langle r^2\rangle_0/\mathrm{d}T$. Inasmuch as neither premise i nor ii is warranted, the values of this coefficient obtained by de Candia *et al.* from measurements of temperature coefficients of intrinsic viscosities carry no weight whatever.

Finally, we would point out that the value of d ln $\langle r^2\rangle_0/\mathrm{d}T$ we previously reported for POE does not stand alone, unsupported by other substantial evidence. The conformational energies adjusted to reproduce $\langle r^2\rangle_0$ and its tem-

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perature coefficient afford the basis for calculation of a number of other configuration-dependent properties of POE chains that are in good agreement with experiment. Examples are the dipole moments,[8] temperature coefficients of the dipole moments,[9] and optical anisotropies.[10] These conformational energies also give satisfactory results when used to calculate statistical properties of poly(trimethylene oxide)[11] and poly(tetramethylene oxide),[12] two other polymers in the series $[-(CH_2)_mO-]_x$ of which POE is a member. The internal consistency of this broad range of results lends strong support to the overall scheme and to the reliability of the principal quantities employed, including especially the value of $d \ln \langle r^2\rangle_0/dT$ previously given[2] for POE.

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Communications to the Editor

On the Selective Interaction of Monovalent Counterions with Polycarboxylates in Water

A variety of evidence indicates that the mode and extent of monovalent counterion binding in aqueous solutions of synthetic polyelectrolytes is a function of the size and/or hydration of the counterions as well as of the nature of the fixed charges along the macroion chains.[1-6]

Data accumulated so far permit a thermodynamic account of the observed "selective" interactions in terms of free-energy differences. However, contrary to the case of the selective uptake of ions by ion exchangers for which direct microcalorimetric experiments have been carried out,[7a-c] no information is presently available concerning enthalpy and entropy changes associated with the "site-binding" of different monovalent counterions by polyions in dilute aqueous solution.

We report here the results of calorimetric and potentiometric experiments from which informations of the type mentioned above may be deduced in the case of two polycarboxylic acids, poly(maleic acid), (MA), and the maleic acid-ethylene (1:1) copolymer, (MAE), for three counterions: Li^+, Na^+, and $(CH_3)_4N^+$. The MAE sample used in this study has been described in earlier reports.[8] The MA homopolymer was prepared by γ ray initiated polymerization of a 50% v/v maleic anhydride-acetic acid mixture.[9] Purification and full characterization of the MA sample are being reported elsewhere.[10] The elemental analysis of the sample was in good agreement with expectations and its intrinsic viscosity in butanone at 25° was 0.1 dl/g.[10] (Lang *et al.*[9] have described a MA sample with $[\eta] = 0.127$ dl/g in butanone at 25° having a $\bar{M}_w = 23{,}000$ measured by light scattering.)

The apparatus and experimental techniques used in the calorimetric and potentiometric experiments have already been illustrated in detail.[8,11]

Our calorimetric data display the dependence of the differential enthalpy of dissociation ΔH_{diss} (kcal/mol of protons) on the degree of neutralization, α, for both MA and MAE partially neutralized with LiOH, NaOH, and $(CH_3)_4NOH$, respectively, in water at 25°.

Data of Figure 1 clearly indicate that the enthalpy of dissociation of the two polycarboxylates depends strongly on the chemical composition of the chain, the charge density, *and* on the nature of counterions. Particularly striking is the case of MA for which we find that ΔH_{diss} is always positive in the range of α values considered ($\alpha = 1$ corresponds to half neutralization of the polyelectrolytes) and, more interestingly, that the ΔH_{diss} increases as the counterions are changed in the order $(CH_3)_4N^+ \rightarrow Na^+ \rightarrow Li^+$ for α greater than *ca.* 0.2. At $\alpha = 0$, the three curves for MA merge, yielding an approximate value for the enthalpy of ionization of the discharged polymer of *ca.* 0.6 kcal/mol of H^+.

On the other hand, in the case of MAE, the excess enthalpy of ionization, *i.e.*, the difference between experimental data and the extrapolated ΔH_{diss} value for $\alpha = 0$ (*ca.* 0.3 kcal/mol of H^+) is always negative, the results exhibiting furthermore only a minor dependence on the type of the ion neutralizing the fixed charges.

In any case, the difference between the calorimetric data for both MA and MAE at any given α with different counterions yield the difference in the enthalpy of the polyelectrolyte-solvent mixture due to the diverse macroions-counterions interactions.

For MA, for example, the replacement of protons by Li^+ ions and with $(CH_3)_4N^+$ ions, respectively at $\alpha = 0.5$

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