

Matsen³. According to Taft and Apker⁶, however, the ionization potential of graphite determined from the photoelectric emission is 4.48–4.88 eV. Thus the extrapolated value seems to be not unreasonable. In conclusion, we consider that a fairly reliable value of ionization potential can be estimated by means of equation 2 for most polycyclic aromatic hydrocarbons. It is interesting to note that, if we substitute for $h\nu$ in equation 2 the corresponding value for ethylene, 7.52 eV, and that for butadiene, 5.63 eV, we obtain as I_p 10.37 and 9.05 eV, respectively, which coincide approximately with the observed ionization potentials, 10.45 eV (ref. 9) for ethylene and 9.07 eV (ref. 10) for butadiene.

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¹ Watanabe, K., *J. Chem. Phys.*, **26**, 542 (1957).

² Wacks, M. E., and Dibeler, V. H., *J. Chem. Phys.*, **31**, 1557 (1959).

³ Matsen, F. A., *J. Chem. Phys.*, **24**, 602 (1956).

⁴ Braun, A., and Bush, G., *Helv. Phys. Acta*, **20**, 33 (1947).

⁵ Briegleb, G., and Czekalla, J., *Z. Electrochem.*, **63**, 6 (1959).

⁶ Kuroda, H., Kobayashi, M., Kinoshita, M., and Takemoto, S., *J. Chem. Phys.*, **36**, 457 (1962).

⁷ Kinoshita, M., *Bull. Chem. Soc. Japan*, **35**, 1609 (1962).

⁸ Taft, E., and Apker, L., *Phys. Rev.*, **99**, 1831 (1955).

⁹ Price, W. C., and Tuttle, W. T., *Proc. Roy. Soc. A*, **174**, 207 (1940).

¹⁰ Price, W. C., and Walsh, A. D., *Proc. Roy. Soc. A*, **174**, 220 (1940).

Concentration Effects in Measurements of Sedimentation Velocity and Viscosity of Deoxyribonucleic Acid Solutions

THE dependence on concentration of the hydrodynamic properties of DNA solutions has been the subject of some recent publications¹⁻⁴. It has been shown in particular¹, that under specified conditions the dependence on concentration of the reduced viscosity and the sedimentation coefficient of aqueous DNA solutions may be expressed by empirical formulae that are formally analogous to those found to apply for most uncharged polymer solutions, namely:

$$1/s = 1/s_0 (1 + \alpha[\eta]c) \quad (1)$$

$$\eta_{sp}/c = [\eta] (1 + k[\eta]c) \quad (2)$$

In these equations the symbols s and s_0 represent the sedimentation coefficients at concentration c and zero respectively. η_{sp}/c and $[\eta]$ are the corresponding reduced viscosity values and α and k are dimensionless constants.

These equations determined empirically for DNA solutions are useful for the estimation of the values $[\eta]$ and s_0 , and hence for the characterization of various DNA samples from single measurements of s and η_{sp} . The suggestion has also been made³ that the coefficients α and k in the above two equations should be regarded as interaction coefficients reflecting, in effect, the concentration dependence of the frictional coefficient in all transport processes involving the migration of macromolecules through viscous media. The purpose of this communication is to point out that the complexity of the physical situation in dilute polyelectrolyte and hence DNA solutions would not seem to justify such a generalized interpretation of the concentration dependence of the transport properties of their solutions.

The dependence of the sedimentation coefficient on solute concentration has been discussed in detail by Schachman⁵, who emphasized the importance of the effects of density and backward flow in addition to the effective viscosity of the medium. It would seem, accordingly, that identification of the coefficient α in equation 1 with an interaction parameter is controversial even for uncharged polymers. For charged macromolecules such as DNA, in addition to the foregoing factors the primary charge effect is also expected to influence the concentration dependence of the sedimentation velocity⁶

and to increase the difficulty of an exact interpretation of the coefficient α .

The magnitude of the coefficient k in equation 2 has been related successfully to solute-solute and solute-solvent interactions in uncharged polymer solutions⁷, assuming that the configuration of the polymer molecules is independent of their concentration in sufficiently dilute solutions. A similar interpretation of the coefficient k in dilute solutions of polyelectrolytes proves to be more difficult. The presence of charges on the macroions leads to increased hydrodynamic interactions between the solute particles, and this secondary electroviscous effect⁸ was shown to result in an increase in the value of k compared with solutions of corresponding uncharged molecules. However, in some polyelectrolyte solutions the magnitude of k was found to be several orders of magnitude greater⁹ than the k values usually encountered in uncharged polymer solutions. Such an increase in k with charge cannot be attributed to the secondary electroviscous effect alone, and attempts to explain these results generally contain a series of assumptions such as the inclusion of the volume of the electrical double layer in the effective hydrodynamic volume of the polyions.

More recently we have shown¹⁰ by considering the changes in counterion distribution with concentration of polyion that at high dilutions the polyions may contract with dilution, thus explaining the anomalously high values obtained for the gradient of the initial linear range of the concentration dependence of the reduced viscosity. Accordingly k , obtained experimentally from such data, cannot be regarded as an interaction parameter since the necessary condition for such an interpretation that the solute configuration is constant is not fulfilled. It should be pointed out that this interpretation of the coefficient k in dilute polyelectrolyte solutions is supported by the fact that the extremely high k values are generally associated with polyelectrolyte chains of highly flexible nature, while in similar circumstances polyelectrolytes of less flexibility, such as sodium carboxymethyl cellulose¹¹ and native, double helical DNA⁴, exhibit much lower values of k .

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¹ Eigner, J., Schildkraut, C., and Doty, P., *Biochim. Biophys. Acta*, **55**, 13 (1962).

² Ganguli, P. K., and Bhattacharyya, A. L., *Nature*, **196**, 1201 (1962).

³ Ganguli, P. K., *Nature*, **200**, 164 (1963).

⁴ Kurucsev, T., *Arch. Biochem. Biophys.*, **102**, 120 (1963).

⁵ Schachman, H. K., *Ultracentrifugation in Biochemistry*, 90 (Academic Press, Inc., New York, 1959).

⁶ Ref. 5, 225.

⁷ Cragg, L. H., and Bigelow, C. C., *J. Polymer Sci.*, **16**, 177 (1955).

⁸ Harnsen, G. J., Van Schooten, J., and Overbeek, J. T. G., *J. Colloid Sci.*, **10**, 315 (1955).

⁹ Goring, D. A. I., and Rezanovich, A., *J. Colloid Sci.*, **15**, 472 (1960).

¹⁰ Darskus, R. L., Jordan, D. O., Kurucsev, T., and Martin, M. L. (to be published).

¹¹ Goring, D. A. I., and Sitaramaiah, G., *Polymer*, **4**, 7 (1963).

Effect of Nitrous Oxide and Carbon Dioxide on the Sensitivity of a 'Small' Argon Detector for use in Gas Chromatography

PREVIOUS work¹ has shown that the combination of a Golay capillary column and a Lovelock 'small' argon detector² provides a convenient method for the rapid estimation of volatile anaesthetic agents. The resulting chromatogram can be displayed on a long-persistence cathode-ray tube, or, and preferably, on a suitable moving-coil pen recorder. The instrument described by Hill *et al.*¹ used a disk-type sampling valve having an