STATISTICAL-MECHANICAL STUDIES OF THE $\alpha \rightleftarrows \beta$ TRANSFORMATION IN KERATIN

IV. The Hill Model

HARVEY B. HAUKAAS, ROBERT SCHOR, *and* CARL W. DAVID

From the Department of Physics and Institute of Materials Science and the Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268

ABSTRACT The relationship between the two-dimensional Hill model and the David-Schor extension of the one-dimensional Zimm-Bragg model for the $\alpha \rightleftarrows \beta$ transformation in keratins is developed. On the basis of the assumptions of the David Schor model, it appears unlikely that the Hill model in its present form can give detailed agreement with the experimental tension-length isotherms.

INTRODUCTION

Keratin fibers exhibit remarkable elastic properties in which the molecular chains can be assumed to have undergone a 2–1 reversible extension (1, 2). One of the most noteworthy features of the elasticity of keratins is the rapid change of length with respect to applied tension in the yield region which is the α-β transformation. In this note we display the relationship between two models of this transformation: The two-dimensional model of Hill (3) and the David-Schor (4) extension of the Zimm-Bragg (5) model.

In previous work, we have considered a one-dimensional model for the stretching of keratin fibers (4, 6, 7). It was shown by a Monte Carlo simulation that good agreement to the experimental stretching data was obtained by using only the geometry of the polypeptide chain and a reasonable hydrogen bond potential (5). We have required that the theory predict the behavior of the tension-length isotherms in the transition region as well as in the limits of zero and large applied tension.

DISCUSSION

It may be possible in the future to generalize the David-Schor model to a two-dimensional one which could take into account the statistical mechanical equilibrium of inter- and intrachain hydrogen bonds. The only existing two-dimensional model for finite external tension, however, is that of Hill (3) who does not explicitly introduce a nucleation parameter σ. The cooperative nature of the transformation in the Hill model is dependent on two molecular quantities, ω_α and ω_β, the interaction energies between α units within a chain and β units in adjacent chains respectively. It is therefore necessary to determine the relationship of these quantities to the nucleation parameter σ. Consider the equation (3)

$$\frac{\tau(\ell_\beta - \ell_\alpha)}{ckT} = \ln\left[\frac{f}{1-f}\left(\frac{n_\alpha + 1 - 2f}{n_\beta - 1 + 2f}\right)^2 J_{\alpha\beta}\right] \tag{1}$$

where c represents the number of chains in a sheet, f the fractional number of units in the α form, $J_{\alpha\beta}$ the ratio of internal partition functions for the α and β forms respectively and τ, ℓ_β, ℓ_α, and T have their usual meanings.

$$n_\alpha^2 = 1 - 4f(1-f)(1-y_\alpha) \tag{2a}$$

$$n_\beta^2 = 1 - 4f(1-f)(1-y_\beta) \tag{2b}$$

where

$$y_\alpha = \exp(-\omega_\alpha/kT) \tag{3a}$$

$$y_\beta = \exp(-\omega_\beta/kT) \tag{3b}$$

In order to make a comparison with the experimental data we define:

$$\ln\rho = \ln\left[\frac{1-f}{f}\left(\frac{n_\beta - 1 + 2f}{n_\alpha + 1 - 2f}\right)^2\right] \tag{4a}$$

$$= \ln J_{\alpha\beta} - \frac{\tau(\ell_\beta - \ell_\alpha)}{ckT} \tag{4b}$$

At the midpoint of the transition region ($f = \frac{1}{2}$)

$$\ln\rho = \ln\frac{y_\beta}{y_\alpha} = \ln J_{\alpha\beta} - \frac{\tau(\ell_\beta - \ell_\alpha)}{ckT}. \tag{5}$$

Define the slope of the isotherm given by equation 4, at $f = \frac{1}{2}$, to be

$$(df/d\ln\rho)_{f=1/2} = 1/[4(y_\alpha^{-1/2} + y_\beta^{-1/2} - 1)]. \tag{6}$$

By comparing equation 6 with Applequist's (8) treatment of the Zimm-Bragg (5) theory we obtain an expression for σ in terms of Hill's parameters

$$\sigma^{1/2} = y_\alpha^{-1/2} + y_\beta^{-1/2} - 1. \tag{7a}$$

Thus,

$$(df/d\ln\rho)_{f=1/2} = \tfrac{1}{4}\sigma^{1/2}. \tag{7b}$$

Also, from equation 1,

$$(df/d\tau)_{f=1/2} = \frac{\ell_\beta - \ell_\alpha}{4ckT}(1 - y_\alpha^{-1/2} - y_\beta^{-1/2})^{-1}. \tag{8}$$

Thus,

$$(df/d\tau)_{f=1/2} = \frac{\ell_\alpha - \ell_\beta}{4ckT}\sigma^{1/2}. \tag{9}$$

In order to make a comparison with the experimental data, it was assumed that the tension acts only on the protofibrils, i.e. on 37% of the cross-sectional area of the fiber, and that there are 2.5 alpha helices per protofibril (9, 10). The resulting effective helix diameter is approximately 13 A. The yield region was expanded to 100% extension by assuming that the experimentally observed percentage elongation at the midpoint of the yield region corresponds to an extension of 50% for the extensible helical regions. Since there are two or three alpha helices per protofibril and nine (or 11) protofibrils in a microfibril, c was set equal to 25. Based on the X-ray diffraction data, $\ell_\beta - \ell_\alpha$ was taken as 1.8 A.

Using an isotherm obtained by Speakman (1) for Cotswold wool in water at 291°K we obtain $(df/d\tau)_{f=1/2} = 2.5 \times 10^5$ dynes^{-1}. The tension at the midpoint of the transition region, $f = \frac{1}{2}$, was estimated to be 1.3×10^{-5} dynes. We also assume $y_\alpha = y_\beta = y$ which considerably simplifies the analysis. Then from equation 9, $\sigma \simeq 3 \times 10^{-4}$ which gives agreement between the slope of the theoretical and experimental tension-length isotherms at the midpoint of the transition region. Substituting this value of σ into equation 7 we obtain (for $\omega_\alpha = \omega_\beta)\omega \simeq -0.78$ kcal/mole.

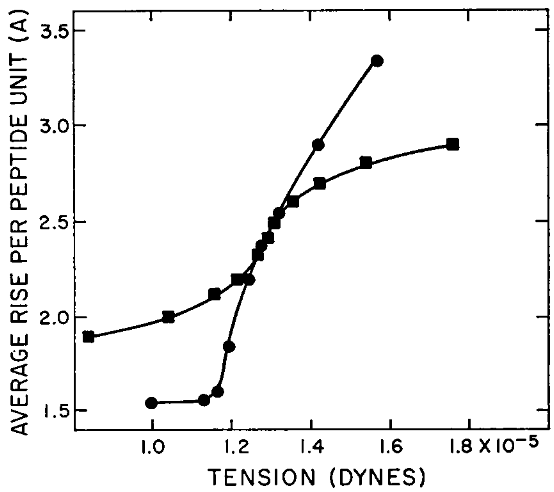

FIGURE 1 A comparison of an experimental tension-length isotherm obtained by Speakman (circles) with the one predicted by the Hill model (squares).

CONCLUSIONS

These values of σ and ω were inserted into equation 1 and the entire isotherm constructed (Fig. 1). On the basis of our assumptions the agreement between equation 1 and the experimental tension-length isotherm was found to be poor except for a small region about the midpoint of the transition region where the agreement was forced. The extent of the transition region predicted by the Hill model is much less than found experimentally. We therefore believe that it is unlikely that the Hill model (3), in this form and with our assumptions, can give detailed agreement with the experimental tension-length isotherms.

This work is being supported by Grant GB-6852 of the National Science Foundation. The computational part of this work was carried out in the Computer Center of the University of Connecticut which is supported in part by Grant GP-1819 of the National Science Foundation.

Dr. Haukaas is supported by a fellowship from the National Institutes of Health.

Received for publication 7 March 1969 and in revised form 11 June 1969.

REFERENCES

1. SPEAKMAN, J. B. 1926. *J. Text. Inst., Trans.* **17**:431.
2. ASTBURY, W. T., and A. STREET. 1933. *Phil. Trans. Roy. Soc., London, Ser. A.* **230**:75.
3. HILL, T. L., 1952. *J. Chem. Phys.* **20**:1259.
4. DAVID, C. W., and R. SCHOR. 1965. *J. Chem. Phys.* **43**:2156.
5. ZIMM, B. H., and J. K. BRAGG. 1959. *J. Chem. Phys.* **31**:526.
6. DAVID, C. W., H. B. HAUKAAS, J. G. KALNINS, and R. SCHOR. 1967. *Biophysical J.* **7**:505.
7. SCHOR, R., H. B. HAUKAAS, and C. W. DAVID. 1968. *J. Chem. Phys.* **49**:4726.
8. APPLEQUIST, J. 1963. *J. Chem. Phys.* **38**:934.
9. FILSHIE, B. K., and G. E. ROGERS. 1961. *J. Mol. Biol.* **3**:784.
10. FRASER, R. D. B., T. P. MACRAE, and G. E. ROGERS. 1962. *Nature.* **193**:1052.