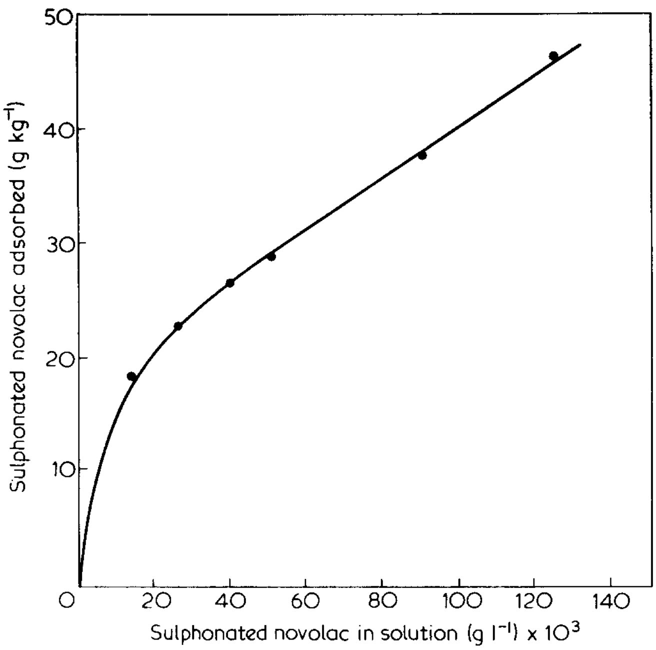


*Figure 3* Equilibrium adsorption isotherm for sulphonated novolac

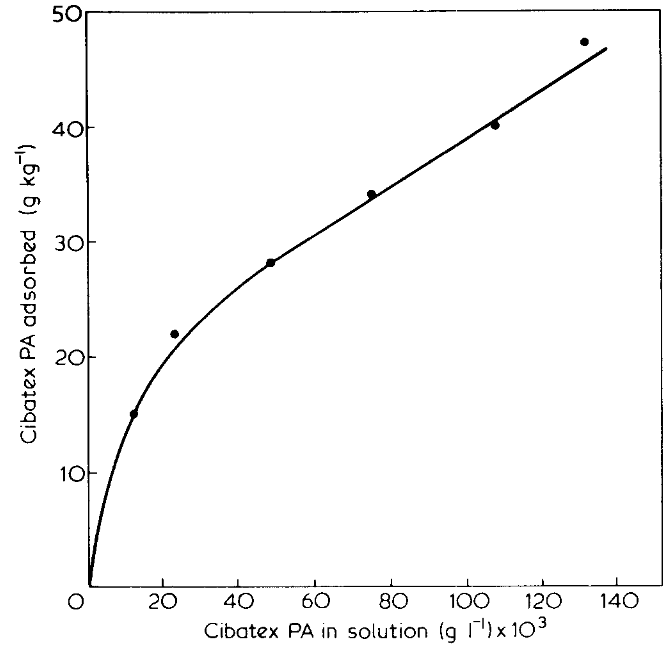


*Figure 4* Equilibrium adsorption isotherm for Cibatex PA

## CONCLUSIONS

The synthetic tanning agent, Cibatex PA, is readily adsorbed by nylon-6 polymer. It shows a type of behaviour very similar to that obtained for a sulphonated novolac. The equilibrium isotherms indicate that the compounds are taken up by a mechanism similar to that for a relatively hydrophobic anionic dye. The hydrophobicity of these materials (degree of sulphonation) is at present under investigation.

Some estimation has been made of the diffusion coefficients of these materials in nylon, although the measurement of diffusion coefficients from rate of adsorption curves can often be misleading, it would appear that the apparent diffusion coefficients are about ten times smaller than those found for anionic dyes[9].

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# The effect of hydrodynamic interaction on the intrinsic flow birefringence of a rigid rod


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A few years ago Svetlov[1] proposed a solution to the Krikwood–Riseman diffusion equation without preaveraging of the Oseen tensor of hydrodynamic interaction. Using this solution, he derived a general relation for the intrinsic flow birefringence, $[n]$. Since this expression is rather complicated, Svetlov suggested an approximative relation in a later paper[2]. In this note we try to compare expressions for $[n]$ and the ratio of intrinsic birefringence with intrinsic viscosity, $[n]/[\eta]$, of a rigid long rod obtained from the exact[1] and approximative[2] Svetlov's theory, and from the theory of Shimada and Yamakawa[3].

For the intrinsic flow birefringence, equation[1] (in ref. 1, G is inadvertently used instead of $\eta_s$)

$$[n]=\frac{\pi}{135}\cdot\frac{(n_s^2+2)^2}{\eta_s n_s}\cdot\frac{N_A}{M}\langle Tr\,\underset{\sim}{X}\;Tr\,\underset{\sim}{\gamma}-3Tr(\underset{\sim}{\gamma}\cdot\underset{\sim}{X})\rangle \quad (1)$$

is valid; $n_s$, $\eta_s$ denote the refractive index and viscosity of the solvent respectively, $M$ is the molecular mass of the particle, $\gamma$ is its polarizability tensor, $N_A$ is the Avogadro number, $\langle\ \rangle$ denotes averaging over conformations of the particle, $Tr$ is the trace of the tensor, and the tensor $\underset{\sim}{X}$ is the solution to equation[1]


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$$3(\underset{\sim}{D}.\underset{\sim}{X}+\underset{\sim}{X}.\underset{\sim}{D})-4Tr(\underset{\sim}{D}.\underset{\sim}{X})-2Tr(\underset{\sim}{X}.\underset{\sim}{D})=6Tr\ \underset{\sim}{E}-4(Tr\ \underset{\sim}{I}^{-1}).\underset{\sim}{I}-2(Tr\ \underset{\sim}{I}).\underset{\sim}{I}^{-1} \quad (2)$$

where $\underset{\sim}{E}$ is the unit tensor, $\underset{\sim}{I}^{-1}$ is the inverse tensor to $\underset{\sim}{I}$, and $\underset{\sim}{D}$ is defined by the equation

$$\underset{\sim}{D}=\underset{\sim}{I}^{-1}.\underset{\sim}{G}.\underset{\sim}{I}^{-1} \quad (3)$$

where for $\underset{\sim}{G}$ it holds that

$$\underset{\sim}{G}=\frac{kT}{\zeta}\left[\underset{\sim}{I}+\frac{\zeta}{8\pi\eta_s}(\underset{\sim}{\tilde{I}}+\underset{\sim}{\Pi})\right]; \quad (4)$$

$\zeta$ is the frictional resistance of the frictional centre, $k$ is the Boltzmann constant, $T$ is the absolute temperature and

$$\underset{\sim}{I}=\sum_i\left(R(i)^2\ \underset{\sim}{E}-\vec{R}(i)\ \vec{R}(i)\right) \quad (5)$$

$$\underset{\sim}{\tilde{I}}=\sum_i\sum_{j\neq i}\frac{\vec{R}(i).\vec{R}(j)\underset{\sim}{E}-\vec{R}(j)}{|\vec{R}(i)-\vec{R}(j)|} \quad (6)$$

$$\underset{\sim}{\Pi}=\sum_i\sum_{j\neq i}\frac{\left(\vec{R}(i)\times\vec{R}(j)\right)\left(\vec{R}(i)\times\vec{R}(j)\right)}{|\vec{R}(i)-\vec{R}(j)|^3} \quad (7)$$

where $\vec{R}(i)$ is the position vector of the $i$-th frictional centre with respect to the gravity centre of the particle, $\vec{R}(i)\vec{R}(j)$, $\vec{R}(i).\vec{R}(j)$ and $\vec{R}(i)\times\vec{R}(j)$ respectively are the dyadic, scalar and vector products of vectors $\vec{R}(i)$ and $\vec{R}(j)$, and $|\vec{R}(i)-\vec{R}(j)|$ is the magnitude of the vector $\vec{R}(i)-\vec{R}(j)$.

In his further work Svetlov[2] suggests that the tensor $\underset{\sim}{G}$ may be replaced with the tensor $\underset{\sim}{G}'$, for which it holds that

$$\underset{\sim}{G}'=\frac{kT}{\zeta}\underset{\sim}{I}\left[1+\frac{\zeta}{8\pi\eta_s}\frac{\langle Tr(\underset{\sim}{\tilde{I}}+\underset{\sim}{\Pi})\rangle}{\langle Tr\ \underset{\sim}{I}\rangle}\right] \quad (8)$$

For a rigid rod, the average values over conformations directly equal the quantities. Equations (5)–(7) give for the rod:

$$\underset{\sim}{\tilde{I}}=K\ \underset{\sim}{I} \quad (9)$$

$$\underset{\sim}{\Pi}=\underset{\sim}{0} \quad (10)$$

where $K$ is a scalar quantity and $\underset{\sim}{0}$ is a zero tensor. Substitution from equations (9) and (10) into equations (4) and (8) provides evidence that the equality

$$\underset{\sim}{G}=\underset{\sim}{G}' \quad (11)$$

is valid for a rigid rod. We can see that in this case Svetlov's approximation[2] coincides with the exact solution[1]. Owing to the symmetry, the same conclusion is reached for a rigid assembly of frictional centres possessing spherical symmetry.

Hence, $[n]$ of the rod may be calculated using Svetlov's approximative relation[2]

$$[n]=\frac{4\pi}{9}\cdot\frac{(n_s^2+2)^2}{n_s\eta_s}\cdot\frac{N_A}{M}\cdot\frac{1}{20D_r}\cdot\frac{\langle Tr\ \underset{\sim}{I}\ Tr\ \gamma-3Tr(\underset{\sim}{\gamma}.\underset{\sim}{I})\rangle}{\langle Tr\ \underset{\sim}{I}\rangle} \quad (12)$$

According to Tsuda's theory[2,4], we have for $D_r$

$$Dr=\frac{3kT}{2\zeta\langle\sum_i R^2(i)\rangle}\left\{1+\frac{\zeta}{8\pi\eta_s\langle\sum_i R^2(i)\rangle}\sum_i\sum_{j\neq i}\left\langle\frac{\vec{R}(i).\vec{R}(j)}{|\vec{R}(i)-\vec{R}(j)|}+\frac{1}{2}\cdot\frac{[\vec{R}(i)\times\vec{R}(j)]^2}{|\vec{R}(i)-\vec{R}(j)|^3}\right\rangle\right\} \quad (13)$$

For a rigid rod consisting of $N$ contiguous spheres having the diameter $l$, we obtain[2]

$$\frac{\langle Tr\ \underset{\sim}{I}\ Tr\ \underset{\sim}{\gamma}-3Tr(\underset{\sim}{I}.\underset{\sim}{\gamma})\rangle}{\langle Tr\ \underset{\sim}{I}\rangle}=\Delta\gamma \quad (14)$$

$$Dr=\frac{3kT}{2\zeta\sigma l^2}\left[1+\frac{\zeta}{8\pi\eta_s\sigma l}\sum_{i=-N/2}^{N/2}\sum_{j=-N/2}^{N/2}\frac{i.j}{|i-j|}\right] \quad (15)$$

where $\Delta\gamma$ is the anisotropy of polarizability of the rod, $l$ is the diameter of the frictional centre and $\sigma=\sum_{i=-N/2}^{N/2}u^2$. By calculating $\sigma$ and the double sum in equation (15), we obtain for a long rod (if the summation is replaced with integration) for $\zeta=3\pi\eta_s l$

$$D_r=\frac{9kT(\ln N-1)}{2\pi\eta_s l^3N^3} \quad (16)$$

It should be noted that for $\ln N\gg1$ the relation for $D_r$ is independent of the magnitude of $\zeta$.

After substitution from equations (14) and (16) into equation (12), we obtain

$$[n]=\frac{2\pi^2}{405}\cdot\frac{(n_s^2+2)^2}{n_s}\cdot\frac{N_A}{MkT}\cdot\frac{l^3N^3}{\ln N-1}\Delta\gamma=\frac{2\pi^2}{405}\cdot\frac{(n_s^2+2)^2}{n_s}\cdot\frac{N_A}{MkT}\cdot\frac{L^4}{\ln(L/l)-1}\Delta\alpha \quad (17)$$

where $L=Nl$ is the length of the rod and $\Delta\alpha$ is the anisotropy of optical polarizability of the unit of length of the rod. In comparison with the expression obtained by Shimada and Yamakawa for a long rigid cylinder[3]

$$[\eta]=\frac{2\pi^2}{405}\cdot\frac{(n_s^2+2)^2}{n_s}\cdot\frac{N_A}{MkT}\cdot\frac{L^4}{\ln(L/l)+2\ln2-11/6}\Delta\alpha \quad (18)$$

we can see that for $\ln(L/l)\gg1$ the intrinsic viscosity is independent both of a detailed hydrodynamic model of the rod and of the procedure used, i.e., Svetlov's procedure with $D_r$ taken from Tsuda's theory or Shimada–Yamakawa's procedure using the orientational distribution function obtained by Yamakawa[5] on the basis of Kirkwood–Auer's[6] procedure.

In his calculations of $[n]/[\eta]$, Svetlov uses Kirkwood–Auer's[6] relation between $D_r$ and $[\eta]$. We believe that with respect to the utilization of Tsuda's relation for $D_r$ in deriving Svetlov's theory, it would be more consistent to use Tsuda's theory[4] also for $[\eta]$.

For a rigid rod we obtain from equation (27) in ref. 4 for $[\eta]$

$$[\eta]=\frac{N_A\zeta l^2\sigma}{6M\eta_s}\left[1+\frac{7\zeta}{40\pi\eta_s\sigma l}\sum_i\sum_{j\neq i}\frac{i.j}{|i-j|}\right]^{-1} \qquad (19)$$

By comparing equations (15) and (19) (and substitution), it is easy to demonstrate that for $\ln N \gg 1$, $D_r$ and $[\eta]$ are related by

$$\frac{kT}{D_r}=k_1\frac{M}{N_A}\eta_s[\eta] \qquad (20)$$

where $k_1=28/5$.

It can be seen that the coefficient $k_1$ differs somewhat from $k_1=5$, which is obtained by using Kirkwood–Auer's theory[6]. In the case of pre-averaging of the hydrodynamic interaction[4,7], $k_1=4$.

After substitution from equation (20) into equation (12) we obtain

$$\frac{[n]}{[\eta]}=\frac{4\pi}{45kT}\cdot\frac{(n_s^2+2)^2}{n_s}k_2\,\Delta\gamma \qquad (21)$$

where $k_2=7/5$. If the Shimada–Yamakawa theory is used, equation (21) with $k_2=5/4$ is valid. By preaveraging the Oseen tensor, generally, we obtain $k_2=1$. We can see that in the case of a rigid rod and with the unpreaveraged Oseen tensor we obtain, unlike the Gaussian coil[8], $[n]/[\eta]$, which is higher than for the free draining case.

If it does not hold that $1 \ll \ln N$, $k_1$ and $k_2$ are generally functions of $N$ (or $L$) and depend on the hydrodynamic model of the rod (assembly of frictional centres or a cylinder).

## ACKNOWLEDGEMENT

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# Errata

*Charge transfer complex between maleic anhydride and pyridine* 1981, Vol. 22, pages 129–131.
**J. A. Chamizo, G. Mendoza-Diaz and J. L. Gázquez**
Page 129, line 9, column 2 reads 'These results together with the values of the LEMO and HOMO predict that Pyacts like an acceptor and MAH acts acts like a donor of charge (see *Table 1*):

But should infact read: 'These results together with the values of the LEMO and HOMO predict that Py acts like a donor and MAH acts like an acceptor of charge (see *Table 1*):

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*Observation of disclinations and optical anisotropy in a mesomorphic copolyester* 1981, Vol. 22, pages 437–446
**M. R. Mackley, F. Pinaud and G. Siekmann**
*Figures* 19, 20, 21 and 22, the correct dimensions for the length markers should be in nanometers (nm) and not in micrometers ($\mu$m).

*Polarized infra-red studies of sulphochlorinated polyethylene and products of its hydrolysis* 1981, Vol. 22, pages 640–646
**B. Bikson, J. Jagur-Grodzinski and D. Vofsi**
Page 640, column 2, paragraph 2, line 4 is incorrect. Paragraph should therefore read: *Sulphochlorination and chlorination procedures*

'Various polyethylene films were sulphochlorinated by bringing them in contact with carbon tetrachloride solution saturated with a gaseous mixture of sulpher dioxde–chlorine as described elsewhere[12]. The chlorination was performed under analogous conditions in carbon tetrachloride solution saturated with chlorine gas at 15°C. Methyl ethyl ketone hydroperoxide was used as initiator, and was added continuously at a rate of 0.24 g/h perl $CCl_4$.'