SUMMARY

The microwave spectra of cyclobutanone and of three isotopically substituted cyclobutanone molecules have been measured and the rotational constants determined. From the observation of the STARK effect it could be concluded that the four-membered carbon ring must be planar. Further it was possible to calculate the structure of cyclobutanone from the moments of inertia, with only one arbitrary assumption. STARK effect measurements yielded a value of 2,98 D for the dipole moment of cyclobutanone.

Laboratorium für physikalische Chemie,
Institut für Hochfrequenztechnik,
der Eidg. Technischen Hochschule, Zürich

---

163. Thermodynamik der Färbevorgänge[1])

I. Absorptionsmodelle

Some comments on a recent publication by B. MILIĆEVIĆ and F. KERN
bearing the same title

von **R. McGregor**

(29. III. 63)

MILIĆEVIĆ & KERN[2]) have recently presented a general discussion of the thermodynamics of dyeing with particular reference to disperse dyeing. This represents a most welcome attempt to apply a rigorous approach to this problem, and in addition embodies some interesting, new ideas. I feel that the following comments on this work might however provoke a useful discussion in which some of the more interesting aspects of MILIĆEVIĆ & KERN's paper can be amplified.

(a) *General equations describing dyeing equilibria.* For equilibrium in the distribution of a dyestuff between dyebath and fibre, the authors have written[2])

$$a_F^{\Phi}/a_F^{\sigma} = \exp\left(\frac{A_F^{\circ}}{RT}\right) \tag{1}$$

which can conveniently be related to the absolute activities λ_F° for the reference states employed by writing

$$a_F^{\Phi}/a_F^{\sigma} = \exp\left(\frac{A_F^{\circ}}{RT}\right) = \frac{(\lambda_F^{\circ})^{\sigma}}{(\lambda_F^{\circ})^{\Phi}} \tag{2}$$

so that A_F° is determined by the reference state employed in defining the relative activity a_F of the dye in each phase.

Now in the absence of any explicit statement to the contrary, it is implicit in equations[2]) (16) and (23) that λ_F° refers to the same quantity. By normal convention, λ_F° in equation (16) would refer to a property of the pure solute because here a perfect solution is under discussion. Also in equation (23) the parameter h can only be

---

[1]) Veröffentlicht laut besonderem Beschluss des Redaktionskomitees.

[2]) B. MILIĆEVIĆ & F. KERN, Helv. *44*, 2049 (1961).

regarded as the conventional HENRY's Law constant, in the sense of the parameter which indicates the magnitude of the deviations from RAOULT's Law, if in fact λ_F° in equation (23) also refers to a property of the pure solute. Since it appears that we are to regard h as the conventional HENRY's Law constant in equation[2] (24), and a similar definition of h has also been implied elsewhere[3], it follows that MILIĆEVIĆ & KERN have employed for λ_F° a characteristic property of the pure solute *i.e.* of the pure dyestuff. The same reference state has apparently then been employed for both fibre and dyebath, so that equation[2] (24) may in fact contain a redundant term, A_F° being by definition zero if h is the conventional HENRY's Law constant. Equation[2] (24) should therefore read

$$x_F^\Phi / x_F^\sigma = h^\sigma / h^\Phi . \tag{3}$$

If, on the other hand, a different reference state is chosen for each phase such that

$$\lambda_F / \lambda_F^{\circ\prime} = x_F . \tag{4}$$

Then we now have

$$x_F^\Phi / x_F^\sigma = \exp\left(\frac{A_F^{\circ\prime}}{RT}\right) \tag{5}$$

since the conventional HENRY's Law constants have been included in the definition of $A_F^{\circ\prime}$. It does not seem necessary to retain both the ratio h^σ/h^Φ *and* the exponential term in equation[2] (24) if by the ratio h^σ/h^Φ we mean the ratio of the conventional HENRY's Law constants in the two phases i.e. we cannot under *these* circumstances say that a measurement of x_F^Φ/x_F^σ is unable to yield a value for A_F° unless we also know the ratio h^σ/h^Φ. Can we not in fact so select our reference state that only one of these two parameters is necessary to describe this particular equilibrium?

(b) *Application of the* FLORY-HUGGINS *equations.* Here the authors make the valid assumptions[2] that φ_L is near unity and that ϱ is large. If we apply these assumptions directly to equation (27)[2] we obtain for the dye in the fibre phase

$$\ln a_F^\Phi = \ln \varphi_F^\Phi + (\chi + 1). \tag{6}$$

MILIĆEVIĆ & KERN further assume that x_L is near unity, but this is certainly not so for the experimental results they present; in fact x_L is as low as 0.625 in the most extreme instance. We can reject this assumption and instead assume that if $\varrho = k^1 \cdot M_L^\Phi / M_F$, then

$$\varphi_F \approx \frac{m_F^\Phi \cdot M_L^\Phi}{m_F^\Phi M_L^\Phi + \varrho} \approx \frac{m_F^\Phi \cdot M_F}{k^1} \tag{7}$$

where M_F (kg. Mole^{-1}) refers to the dyestuff and k^1 is a constant which is not far from unity.

Since the reference state implicit in equation (6) above is that of the pure dye, we can use the same reference state for the dyebath and write

$$a_F^\sigma = h^\sigma x_F^\sigma \tag{8}$$

so that from (6) and (8), since at equilibrium

$$a_F^\sigma = a_F^\Phi \tag{9}$$

we have

$$\varphi_F^\Phi = h^\sigma \exp - ([\chi + 1]) \, x_F^\sigma . \tag{10}$$

---

[3] B. MILIĆEVIĆ, Chimia *16*, 29 (1962).

But $x_F^\sigma \approx m_F^\sigma M_L^\sigma$; so that from (7) and (10) we find

$$m_F^\Phi = \left[\genfrac{}{}{0pt}{}{M_L^\sigma}{M_F} h^\sigma k^1 \exp (- [\chi + 1] \right] m_F^\sigma \tag{11}$$

or

$$m_F^\Phi = K m_F^\sigma \tag{12}$$

where K is a constant.

The curvature of the theoretical isotherms given by MILIĆEVIĆ & KERN in Fig. 1[2]) presumably arises from their assumption that $x_L \rightarrow 1$ and not from the postulated mechanism of dyeing. The upward curvature of their experimental isotherms is contrary to all previous findings[4]) and requires more experimental support in view of the implications of this curvature. Such a deviation from a linear isotherm should occur only at higher concentrations than those employed by MILIĆEVIĆ & KERN[2]), if the treatment given here is valid.

It should, however, be stressed that the FLORY-HUGGINS equations apply only to linear, independent polymer chains which do not hydrogen-bond together. This is certainly not a valid picture of the disperse dyeing of nylon polymers, for example, and the FLORY-HUGGINS equations can only be applied here in an empirical sense.

It is interesting that MAJURY[5]) obtained linear isotherms for the absorption of azobenzene by cellulose acetate from the vapour phase, at temperatures from 120° to 150° C, up to molalities of azobenzene in the fibre as high as 0.825. There were no anomalous entropy effects in the mixing process even at this high molality, so that the theories of polymer solutions are certainly not applicable in this instance.

(c) *Effect of dispersed additives.* The explanation given in equation (37)[1]) for the effect of emulsification upon disperse dyeing in the presence of an immiscible solvent cannot be a complete one. In order to explain the increase of dye uptake found in practice, would it not be necessary to postulate an impossibly small radius for the particles of the dispersed phase?

SUMMARY

A brief discussion is given of the selection of the reference states for defining the relative activity of a disperse dye in the fibre phase and in the solution phase. Contrary to recent findings[2]), it is suggested that the application of the FLORY-HUGGINS equations for polymer solutions to disperse dyeing equilibria leads to the prediction that the adsorption isotherm will be linear for concentrations expressed in molalities. Furthermore, the partition coefficient should not vary with the molecular weight of the polymer or fibre phase.

Department of Polymer and Fibre Science,
Manchester College of Science and Technology,
Sackville Street, Manchester, 1, England

---

[4]) T. VICKERSTAFF, The Physical Chemistry of Dyeing, Oliver and Boyd, London 1954; H. J. WHITE, J. R., Textile Res. J. *30*, 329 (1960); C. L. BIRD & P. HARRIS, J. Soc. Dyers Colourists *73*, 199 (1957); M. J. SCHULER & W. R. REMINGTON, Discuss. Faraday Soc. *16*, 201 (1954); C. L. BIRD & F. MANCHESTER, J. Soc. Dyers Colourists *71*, 604 (1955); C. L. BIRD & P. RHYNER, *ibid.* *77*, 12 (1961).

[5]) T. G. MAJURY, J. Soc. Dyers Colourists *72*, 41 (1956).