Anomalous Solvent Effect on the Optical Rotation of Tartaric Acid

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Earlier workers[1,2] who examined the solvent effect on optical rotation observed a relationship between the effect and the dipole moment of the solvent. In the present paper, the effect of the dielectric constant is sought for over a wide range. In aqueous mixtures of dioxane, the latter varying from 40 to 100% by weight, D-(+)-tartaric acid solutions of 5% by weight were prepared. Analar BDH dioxane was further purified[3] until the refractive index and the dielectric constant were 1.41411 and 2.51 respectively at 35°C.

For the mixtures of solvents used, the refractive indices were determined with a Bellingham & Stanley Pulfrich refractometer, using a Colora Ultrathermostat to control the temperature. The dielectric constants were determined at 35°C, at a frequency of 1.98 Mc/s, using a Multidekameter-type Dk06 of the Wissenchaftlich-Technische Werkstatten Gmbh, Germany, maintaining the temperature in the cell by means of the ultrathermostat.

The specific rotation, the electrical conductance, the density and the refractive index of the solutions were determined at 35°C. The optical rotation was measured using Bellingham and Stanley's Pepol 60 photoelectric polarimeter and the sodium-D-line. The electrical conductance was measured with a Leeds and Northrup Jones conductivity bridge, using a thermostat arrangement precise to ±0.05°C. The density values were obtained with a specific gravity bottle (capacity 10 *ml*) assuming the density of water at 35°C from the published values.

From curve A, Fig. 1, it is clear that the specific rotation of tartaric acid falls linearly with an increase in the content of dioxane, passes through zero, and changes sign thereafter, until the value in pure dioxane becomes −5.6. Assuming no interaction between tartaric acid and water-dioxane mixture, we sought to eliminate the effect of the solvent mixture by dividing the specific rotation by $(n^2+2)/3$, where n is the refractive index of the solvent. Even then a linear variation is obtained, with a different slope passing through almost the same region on the X-axis (curve B, Fig. 1). This remarkable behaviour of tartaric acid is difficult to explain. In Fig. 2, a plot of log(specific conductance) (proportional to the equivalent conductance in this case) *vs.* the weight per cent of dioxane shows, on detailed analysis, that the specific conductance falls off exponentially as the dioxane content increases.

A plot of log(molar refraction of the solutions) *vs.* the weight per cent of dioxane (graph not given) gives two straight lines intersecting at a point corresponding to about 70% w/w of dioxane.

Using the refractive index values of water-dioxane mixtures and the interpolated values of the densities[4] of the same, the molar refraction contribution of the mixtures was evaluated at each composition. The difference between the ternary molar refraction values and the corresponding values for water-dioxane mixtures, gave the molar refraction of tartaric acid. Figure 3 shows a plot of the molar refraction of tartaric acid thus evaluated *vs.* the weight per cent of dioxane. The plot is made up of two straight lines intersecting at a point corresponding to about 70% w/w of dioxane.

Figure 4 gives a plot of the density of the solutions *vs.* the weight per cent of dioxane. The curve shows a maximum in the region of 70% w/w of dioxane.

Considerable work on dioxane-water mixtures[5-10] indicates that, at a composition of 0.8 mol fraction of water, the heat of mixing, the X-ray structure, the viscosity, the density, the activation energy for viscous flow, and the microwave absorption show a sharp turning point. The thermodynamic properties of the water-dioxane system do not indicate the existence of a water-dioxane complex, although conductivity measurements[11] have been interpreted as indicating the existence of dioxane dihydrate. Clemett *et al.*[10] point out that the addition of dioxane to water

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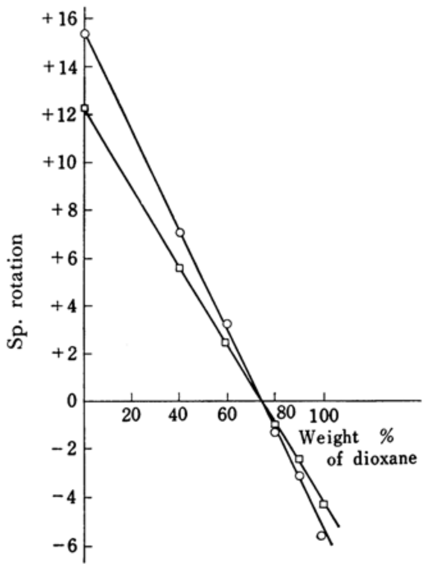

Fig. 1

—○— A —□— B

modifies the "broken-down ice" structure of water by providing bonding sites which permit a more ordered and energetically more favourable liquid structure.

The great complications in understanding the behaviour of tartaric acid in water-dioxane mixtures are that both the solvents are capable of forming four hydrogen bonds each, that the bond angles at the oxygen atoms are roughly the same for both, and that tartaric acid itself is a dihydroxy dicarboxylic acid.

Curve B, Fig. 1 shows how the correction for the solvent effect has not removed the anomaly. Therefore, if we are forced to assume the formation of a complex of tartaric acid with dioxane which gives the opposite rotation, we should then look for proof of this. An ultraviolet spectrophotometric investigation with a Beckmann DU spectrophotometer shows (results not reported) that with tartaric acid, whether in water or in dioxane, the absorption curve starts rising at about 260 mμ, increases sharply from 250 mμ, and continues to do so in the far ultraviolet region beyond 210 mμ. The sharp fall of the molar refraction of tartaric acid beyond 75% w/w of dioxane (Fig. 3) indicates, in general, a tightening of the electronic shells in the molecule of tartaric acid; it does not indicate any complexing. The exponential fall in the specific conductance and the nature of the density curve alone indicate the remote possibility of any complex formation.

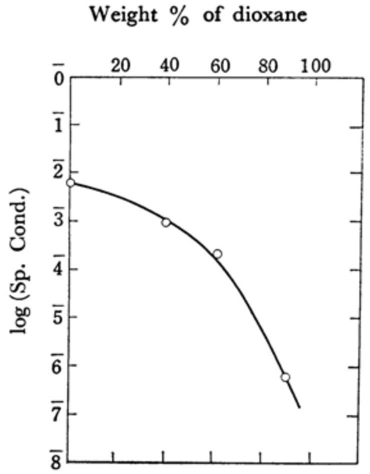

Fig. 2

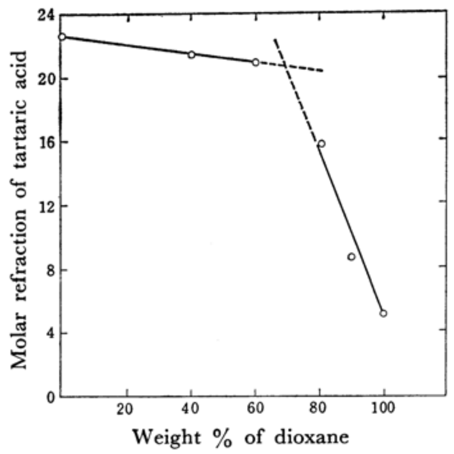

Fig. 3

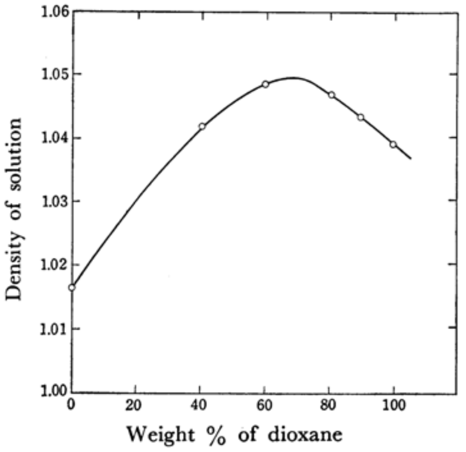

Fig. 3

Against this background, there seems to be no justification for assuming any complex formation. Basing on Fresnel's interpretation and regarding a ray of linearly-polarised light as equivalent to two circularly-polarised beams of equal amplitude, but with opposite senses of rotation, the right-hand and left-hand circular vibrations meet in a line which determines the position of the plane of polarisation. Fresnel showed that the angle of rotation per centimetre of the medium was given by:

$$\propto = \frac{\pi}{\lambda}(n_{\mathrm{L}} - n_{\mathrm{R}}) \tag{1}$$

where λ is the wavelength of light and n_{L} and n_{R} are the refractive indices for left and right circularly-polarised light respectively.

If,[12] for the right circularly-polarised light, we have:

$$\overline{E} = E(i \cos \psi - j \sin \psi) \tag{2}$$

where E is the amplitude of $\overline{E}$ and where ψ is the phase of the wave of frequency, ν, propagated with a velocity of $\nu = c/n$, it can be shown that:

$$n_{\mathrm{R}} = \varepsilon^{1/2} - 2\pi\nu g \tag{3}$$

Similarly, we may write, for the left circularly-polarised light:

$$\overline{E} = E(i \cos \psi + j \sin \psi) \tag{4}$$

and show that:

$$n_{\mathrm{L}} = \varepsilon^{1/2} + 2\pi\nu g \tag{5}$$

where g, the optical rotatory power

$$= \frac{4\pi N_1 \beta}{c}\left(\frac{\varepsilon+2}{3}\right) \tag{6}$$

ε and N_1 being the dielectric constant of the medium and the number of molecules per cc, and $\beta = \sum_a \rho_a \beta_a$, where ρ_a is the probability that the molecule will be in the state "a" and β is the rotatory parameter of the molecule.

Substituting (3) and (5) in (1), and working from (6), we obtain:

$$\alpha = \frac{16\pi^3 N_1 \beta}{\lambda^2}\left(\frac{\varepsilon + 2}{3}\right) \tag{7}$$

From Eq. (7) it is clear that the specific rotation varies linearly with the dielectric constant of the medium for a given monochromatic radiation. In the present investigation, the dielectric constant of dioxane-water mixtures varies almost linearly over the entire range, except for small deviations between 80 and 100% dioxane. Equation (7) does not, however, fully explain the variation shown in Fig. 1. To explain the zero rotation, where the straight line cuts the X-axis, and the reversal of the sign of the specific rotation thereafter, we should look at the contribution of the β factor. This necessarily involves the effect of perturbations on the rotatory strength of the tartaric acid molecule, influencing its symmetry states. Perhaps Fig. 3 is an indication of how the molar refraction variation implies a systematic effect on the symmetry states of the tartaric acid molecule. This point gets support from the fact that the specific rotation of a 5% solution of tartaric acid in formamide ($\varepsilon = 109$) gave the value of $\alpha = 14.8$ as against 15.3 in pure water ($\varepsilon = 78$). Apart from the degree of dissociation of tartaric acid itself playing an important role, a more dominant factor in deciding the rotation seems to be the symmetry states of the tartaric acid molecule in different media.

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