Nickel (II) Complexes as Possible Indicators for Structure in Alcohol–Water Mixtures

By R. D. GILLARD* and H. M. SUTTON
(*Chemical Laboratories, University of Kent at Canterbury*)

Summary Changes in the equilibrium between magnetic isomers of a nickel(II) complex are used to comment on the nature of water–alcohol mixtures.

THE behaviour of alcohol–water mixtures, and in particular the effects observed in water-rich mixtures, have recently been the subject of much investigation. Hitherto, the techniques used have been confined to measurement of thermodynamic and spectroscopic properties of the mixtures themselves,[1,2] or to the observation of kinetic effects.[3]

We report preliminary investigations on the use of bis-*meso*-stilbenediaminenickel(II) acetate, Ni(*m*-stien)$_2$Ac$_2$, as a probe for solvent structure in mixtures of water with t-butyl alcohol, isopropyl alcohol, n-propyl alcohol, ethanol, or methanol.

Certain diamines co-ordinate to nickel(II) to give complexes which exist in either blue (octahedral, paramagnetic) or yellow (square-planar, diamagnetic) forms.[4] The best known examples are probably the nickel(II) complexes of stilbenediamine, which are known as Lifschitz salts.[5] When the *meso*-isomer of the diamine is used along with an anion such as acetate, or mono-, di-, or tri-chloroacetate, then the yellow–blue transformation can be brought about with particular ease.[6] A solution of Ni(*m*-stien)$_2$Ac$_2$ in an alcohol is blue. Mixing with water at room temperature turns the solution green, and, on the addition of more water, yellow.

A solvent-controlled equilibrium between the yellow (Y) and blue (B) species is presumably operative.[7] The role played by the solvent may be a first solvation sphere influence; *i.e.* the number of solvent molecules co-ordinated to the nickel(II) ion changes from alcohol to water. On the other hand, the solvent might simply act as a dielectric continuum, and the changes in the electronic transition may occur only because of ion pairing between the anion and the nickel(II). The ease with which the complex changes colour with certain specific anions could be explained by either argument, since the ion pairing might involve conconcomitant changes in the ordering of the solvent around the nickel ion. The electronic state of the nickel(II) could be described as situated at the cross-over point of the relevant Orgel diagrams, so that small changes in the ligand field on the *z*-axis can produce complexes with different electronic spectra in equilibrium with each other.

For the formal equilibrium Y $\rightleftharpoons$ B an equilibrium constant, β, can be calculated from spectrophotometric measurements on the "yellow" band at 440 nm. Plots of

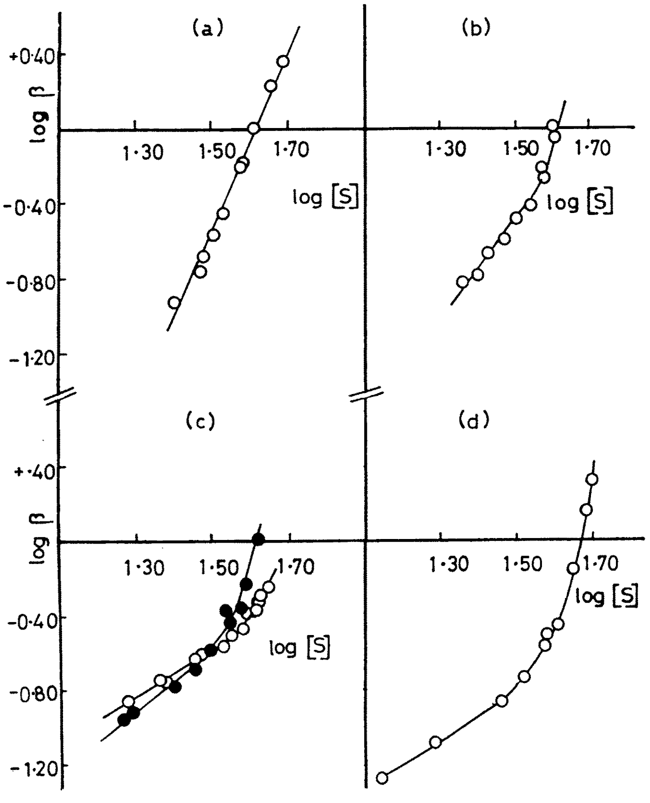

FIGURE. *Variation of* logβ *with* log[S] *for* Ni(*m*-stien)$_2$ Ac$_2$ *in alcohol–water mixtures*: (a) *in methanol–water*; (b) *in ethanol–water*; (c) *in propanol–water* (*n-propanol* ○, *isopropyl alcohol* ●); (d) *t-butyl alcohol–water.*

log β *vs.* log[S] (where $\beta = [Y]/[B]$ and [S] is the total, mixed molarity, of the solvent) at 25° are shown in the Figure. At low alcohol concentrations a deviation from linearity is frequently observed, and this is greatest for the t-butyl alcohol–water system. With methanol–water, no deviation from linearity is noticeable. With all of the systems studied where deviations occur, anomalies are found at about the same mole fractions of alcohol as those observed by previous workers using ultrasonic techniques.[1]

Thus the development of the yellow colour, and hence the value of log β, is enhanced most with those alcohols which (according to a mass of earlier evidence[1,2]) build up large clusters of water about themselves in a water-rich environment.

Work is continuing on the possible uses of Ni(*m*-stien)$_2$Ac$_2$ and similar nickel(II) complexes as indicators for solvent structure, in particular on aqueous solutions of ionic and nonionic solutes, and aqueous systems of biological importance.

(*Received, July 4th*, 1969; *Com.* 977.)

---

[1] F. Franks and D. J. G. Ives, *Quart. Rev.*, 1966, **20**, 1.

[2] M. J. Blandamer, D. E. Clarke, T. A. Claxton, M. F. Fox, N. J. Hidden, J. Oakes, M. C. R. Symons, G. S. P. Verma, and M. J. Wooten, *Chem. Comm.*, 1967, 273; M. J. Blandamer, D. E. Clarke, N. J. Hidden, and M. C. R. Symons, *ibid.*, 1966, 342.

[3] J. Burgess, *Chem. Comm.*, 1967, 1134; H. P. Bennetto and E. F. Caldin, *ibid.*, 1969, 509.

[4] B. Bosnich, J. H. Dunlop, and R. D. Gillard, *Chem. Comm.*, 1965, 274.

[5] J. G. Bos, I. Lifschitz, and K. M. Dijkema, *Z. anorg. Chem.*, 1939, **242**, 97; *Rec. Trav. chim.*, 1940, **59**, 407.

[6] W. C. E. Higginson, S. C. Nyburg, and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 468.

[7] E. Kent Barefield, D. H. Busch, and S. M. Nelson, *Quart. Rev.*, 1968, **22**, 457.