# Aqueous Nonelectrolyte Solutions. Water Stabilization by Nonelectrolytes

By D. N. GLEW,* H. D. MAK, and N. S. RATH

(*Exploratory Research Laboratory, Dow Chemical of Canada, Limited, Sarnia, Ontario, Canada*)

RECENTLY it has been noted[1] that small additions of the weakly interacting solute ethylene oxide to water at lower temperatures lead to unexpected solvent water stabilization and enhancement of water–water hydrogen-bonding (H-bonding). We have now measured $^1H$ n.m.r. chemical shifts at 60 MHz and 0° for dilute aqueous solutions of the weakly interacting solutes 1,4-dioxan, propylene oxide, acetone, tetrahydrofuran, and t-butyl alcohol. The Figure shows the solvent water chemical shifts relative to pure water plotted against the mole percentage for the five solutes. Positive chemical-shift values indicate solution water signals at lower magnetic field than that of pure water. The ordinate origins of the curves are separated by 5 Hz for clarity. Straight reference lines drawn through the 0 and 20% points indicate the deviations from linearity of the water chemical-shift curves. The reference line for propylene oxide is arbitrary since its immiscibility precludes measurement above 12%.

The negative slopes of the reference lines and of all curves at higher solute percentages shows the well known water chemical-shift movement from low to high magnetic field on dilution by dioxan, acetone, tetrahydrofuran, and t-butyl alcohol,[2] which movement arises from the formation of weak water–solute H-bonds with the loss of stronger water–water H-bonds. The anomalous positive deviations exhibited by all chemical-shift curves above their linear reference lines, shown for the first time, indicate enhanced solvent water–water H-bonding, similar to that first observed in dilute aqueous ethylene oxide solutions.[1] In the dilute acetone, tetrahydrofuran and t-butyl alcohol solutions at 0° the solvent water chemical shift goes to lower magnetic field than in pure water, evidence for more and/or stronger water–water H-bonds in solution than in pure water.

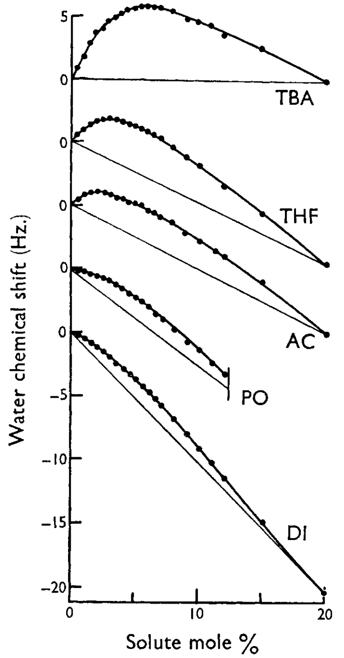

FIGURE. *Water proton magnetic resonance chemical shift composition dependence in aqueous* **1,4-*dioxan*** (DI), ***propylene oxide*** (PO), *acetone* (AC), ***tetrahydrofuran*** (THF), *and* ***t-butyl alcohol*** (TBA) *solutions at* 0°.

These $^1$H n.m.r. chemical shifts provide a striking confirmation for the strengthening of water–water H-bonding through water-shell formation around weakly interacting interstitial non-electrolytes.[3] The maximum for this water structural effect certainly obtains within the region 3—6% solute, in which solutions there is sufficient water to form completely H-bonded water shells around all solute molecules. Further, this correlates with the known Structure II clathrate gas hydrates formed by propylene oxide, acetone, and tetrahydrofuran in which 28—17 water molecules are associated with each solute molecule (3·5—5·5% solute). This oriented water-shell interstitial-solute model,[3] provides a proper explanation for many of the reported[4] anomalies of dilute aqueous nonelectrolyte solutions.

(*Received, January* 10*th*, **1968**; *Com.* **035**.)

---

[1] D. N. Glew, H. D. Mak, and N. S. Rath, *Canad. J. Chem.*, in the press.

[2] G. Mavel, *Compt. rend.*, 1959, **248**, 1505; 1960, **250**, 1477; A. Fratiello and D. C. Douglass, *J. Mol. Spectroscopy*, 1963, **11**, 465.

[3] D. N. Glew and E. A. Moelwyn-Hughes, *Discuss. Faraday Soc.*, 1953, **15**, 150; D. N. Glew and R. E. Robertson, *J. Phys. Chem.*, 1956, **60**, 332; D. N. Glew, *ibid.*, 1962, **66**, 605; *Nature*, 1962, **195**, 698.

[4] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *J. Amer. Chem. Soc.*, 1965, **87**, 1541; F. Franks and D. J. G. Ives, *Quart. Rev.*, 1966, **20**, 1; M. J. Blandamer, D. E. Clarke, N. J. Hidden, and M. C. R. Symonds, *Chem. Comm.*, 1966, **342**.