PRESSURE-INDUCED CHANGES IN SOLVENT SORTING BY SOLUTE MOLECULES

Elzbieta Gebicka and W. J. le Noble*

Department of Chemistry, State University of New York,

Stony Brook, New York 11794, U.S.A.

Summary: The ultraviolet spectra of 4-amino-5-methylacridine in acidified aqueous organic
media show that the solvent sorting characteristic of the conjugate acid is most extensive
with dimethylsulfoxide, and that it is diminished by pressure.

The extensive and fascinating literature[1] on pressure effects in solution absorption
spectroscopy is by necessity often based on the use of mixed solvents, these having the advan-
tage of reduced freezing points under pressure and improved solubility characteristics. The
drawback in the use of such solvents at any pressure, of course, is the possibility that the
microscopic environment of the species being examined is not simply the stoichiometric compo-
sition. While this caveat is generally conceded,[2] the apparent difficulty in learning some-
thing about this question has tempted most authors to ignore it; yet, the polemical questions,
for example, about whether it makes sense to assign values to solvent polarity parameters for
mixed solvents continue to appear in the literature.[3]

Menger[4] recently reported that 4-amino-5-methylacridine is a remarkably effective probe
in demonstrating inhomogeneity in an environment of water-ethanol mixtures. This finding was
inspired by an earlier one by Craig[5] to the effect that protonation occurs at the primary
amino group in ethanol and at the ring nitrogen atom in water. The spectra of the ions are
quite different; the difference is readily interpretable in terms of this shift in protonation
site. Menger used the acridine as a reporter of its micro-environment and showed convincingly
that the largely hydrophobic cation is remarkably able to sort the ethanol out of aqueous
alcohol mixtures; thus, solutions which consist of about 90-95 mole percent water behave as
though they were equimolar in the solvation shell of the ion.

We have used the same species to compare several solvents that are often used in conjunc-
tion with water by both spectroscopists and kineticists, and to examine the questions whether
the sorting phenomena have measurable temperature and pressure dependences. The results, ob-
tained with the freshly prepared[5] probe, are shown in part in the Figure; they were obtained
in the manner described below.[6] The solvent effect may be described by the series
methanol < ethanol < dimethylformamide < dimethylsulfoxide (DMSO); in the latter case, the mole
fraction of water needed to achieve equipartition between the nitrogen atoms is 0.98!
Clearly, one should be very cautious when explaining electronic spectral differences obtained

in this popular mixed solvent system. The thermal instability of the probe unfortunately scuttled our hopes to measure the temperature dependence of the sorting process, but we did learn that its effectiveness is diminished by pressure. Thus, at 96 mole percent water, the fraction of ring-protonated probe increased from 46 to 48, 50, 58 and 70% as the pressure was raised from 0.1 to 20.8, 48.6, 81.3 and 132.0 MPa, respectively (1MPa ≈ 10 atm).[7]

We conclude that not only does the use of mixed solvents in spectroscopy and kinetics involve the risk of solvent sorting, but there may be second order effects for a given mixed solvent when the pressure is varied. Thus, when pressure effects in such mixtures are interpreted, one cannot safely assume that whatever the microscopic environment, it is not altered by the pressure.
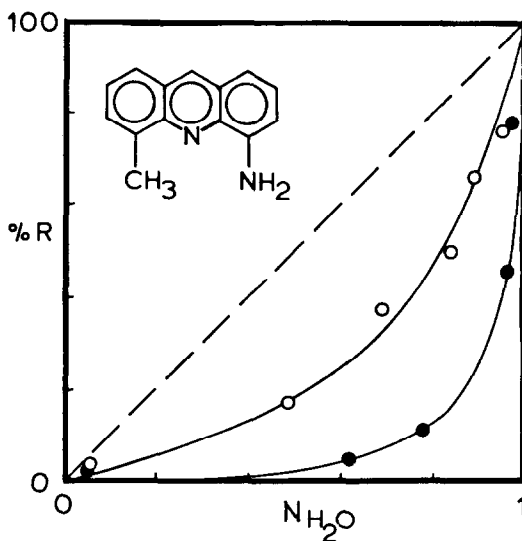

Figure. The percentage ring-protonated probe in acidified aqueous solvent as a function of composition at 25°. Open circles: methanol; filled circles: DMSO.

References and Notes

1. (a) H. Kelm, Ed., "High Pressure Chemistry," C. Reidel, Boston, MA , 1978; (b) O. E. Weigang and W. W. Robertson in "High Pressure Physics and Chemistry," R. S. Bradley, Ed., Vol. I, Academic Press, New York, NY, 1957.

2. See for instance F. Franks and D. J. G. Ives, Quart. Rev., 20, 1 (1966).

3. For a recent example, see P. Suppan, Nouv. J. Chem., 6, 285 (1982); H. Langhals, ibid., 6, 285 (1982); K. S. Nitsche and P. Suppan, Chimia, 36, 346 (1982).

4. F. M. Menger and T. D. Singh, J. Org. Chem., 45, 183 (1980).

5. D. P. Craig, J. Chem. Soc., 534 (1946).

6. All solutions were 0.05 M in the acridine and 0.22 M in HCl. The spectra exhibit a maximum between 440 and 500 nm, and a concave inflection at a higher wave length. We measured the area (a) of a right triangle along the base line, the hypotenuse beginning at the maximum and tangent to the curve near the inflection point. We could not measure a_{max} in pure water because of solubility limitations and hence this was obtained by extrapolation from several highly aqueous solutions. The %R in the Figure equals (a/a_{max}) x 100%.

7. DMSO crystallizes under pressure from more concentrated solutions at 25°, thus limiting this study.

(Received in USA 17 January 1983)