The Temperature Dependence of Some Solute Proton Chemical Shifts in Aromatic Solvents

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Résumé.

On a étudié les déplacements chimiques de cyclohexane, l'iodure de méthyle et l'iodoforme en solution dans le toluène en fonction de la température de — 60° C à + 100° C. Pour cyclohexane le déplacement restait constant, mais pour l'iodure de méthyle et l'iodoforme on constate un déplacement important. On suggère la formation d'agrégats soluté-solvant et on obtient pour l'énergie et l'entropie de complexation les valeurs suivantes.

iodoforme-toluène $\Delta H = 1.6 \pm 0.2$ kcals/mole

$\Delta S = 6.4 \pm 0.2$ e.u.

iodure de méthyle-toluène $\Delta H = 1.3 \pm 0.5$ kcals/mole.

$\Delta S = 4.9 \pm 0.4$ e.u.

The formation of a solute solvent complex in the system chloroform benzene is well established both by Proton Magnetic Resonance and other techniques [1]. Recently similar complexes have been postulated to occur for other solutes in aromatic systems [2]. To test these postulates, the effect of temperature on the proton chemical shifts of the solutes methyl iodide and iodoform in toluene has been investigated. From the variation of the shifts with temperature, both the energy and entropy of formation of the complexes can be found.

The proton chemical shifts of the solutes cyclohexane, methyl iodide and iodoform in toluene were studied as a function of temperature over the range — 60° C to 100° C using a Varian 60 Mc/s Dual Purpose Spectrometer. The chemical shifts were measured from the solvent phenyl proton peak.

The cyclohexane proton chemical shift was completely independent of temperature over the entire temperature range (except for a broadening of the peak at low temperatures due to the freezing out of the different conformers [3]). This temperature independence is strong support for the theory that the cyclohexane chemical shift in aromatic solvents is due to the average effect of the magnetic field of the aromatic ring current [4].

However the proton chemical shifts of methyl iodide and iodoform change considerably over the temperature range studied, that of iodoform changing by about one p.p.m.

These results are shown in figures 1 and 2, in which the methyl iodide and iodoform shifts are given relative to that of the cyclohexane internal reference.
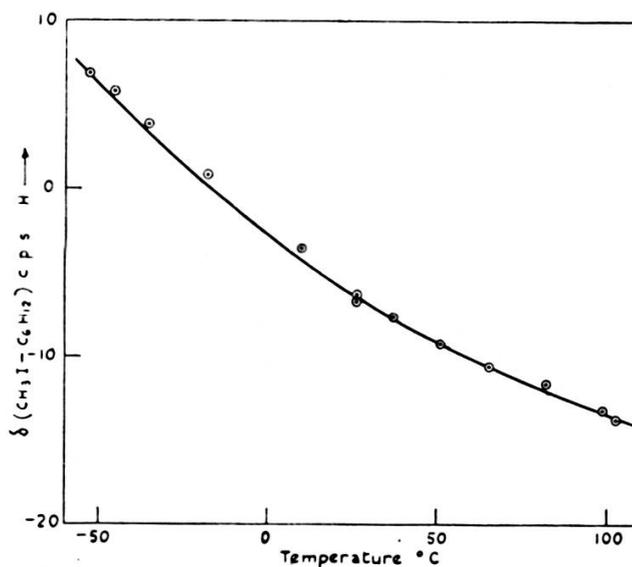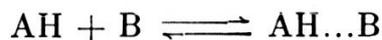

Fig. 1.

Plot of the proton resonance shift of methyl iodide in toluene (in c.p.s. at 60 Mc/s from a cyclohexane internal reference) against temperature.

The formation of the solute solvent complex may be represented as an equilibrium of the form

$$AH + B \rightleftharpoons AH...B$$

where AH represents the solute and B the solvent.

Thus the temperature dependence of the measured solute proton chemical shift, which is the weighted mean of the shift of the unassociated solute (δ_a) and that in the complex (δ_c) will be a function of the fraction of complex present at any temperature, and thus of the parameters δ_a, δ_c and the entropy and energy of formation of the complex.

The observed results are best fitted by the following values of the four parameters. For the iodoform toluene complex $\Delta H = 1.6 \pm 0.2$ kcals, $\Delta S = 6.4 \pm 0.2$ e.u. and $\delta_c - \delta_a$, the high field shift in the complex 2.3 ± 0.3 p.p.m. For the methyl iodide toluene complex $\Delta H = 1.3 \pm 0.5$

kcals, $\Delta S = 4.9 \pm 0.4$ e.u. and $\delta_c - \delta_a = 1.2 \pm 0.3$ p.p.m. The calcul-
ated curves are shown in figures 1 and 2.

These results have not specified the type of complex formed. The
complexes envisaged here are ones in which the axis of symmetry of the
solute (the dipole axis) lies along the six fold axis of symmetry of the
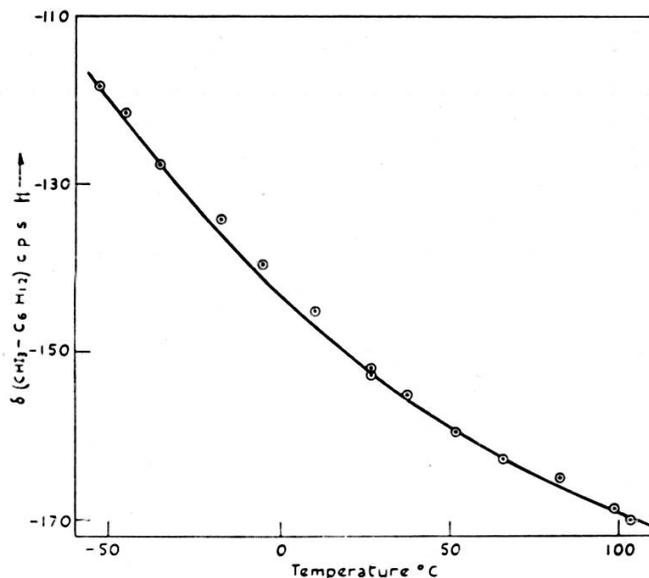

Fig. 2.

Plot of the proton resonance shift of iodoform in toluene (in c.p.s. at 60 Mc/s
from a cyclohexane internal reference) against temperature.

benzene ring with the protons (i.e. the positive end of the solute dipole)
nearest to the benzene ring. In this position the solute protons experience
a high field shift due to the aromatic ring current. By assuming that the
high field shift in the complex is solely due to the ring current, the distance
of the solute protons from the benzene ring can be calculated. This
distance was found to be 2.5 ± 0.1Å for the iodoform and 2.8 ± 0.3Å
for the methyl iodide complex.

A more detailed paper is in preparation.

REFERENCES

1. REEVES, L. W. and SCHNEIDER, W. G., *Can J. Chem.*, *35*, 251 (1957).
2. HATTON, J. V. and RICHARDS, R. E., *Trans. Far. Soc.*, *57*, 28 (1957).
3. JENSEN, F. R., NOYCE, D. S., SEDERHOLM, C. H. and BERLIN, A. J., *J.A.C.S.*,
   82, 1256 (1960).
4. BOTHNER by A. A. and GLICK, R. E., *J.C.P.*, *26*, 1651 (1957).