137. ^{23}Na-NMR. Linewidths in Binary Mixtures of Oxygenated Solvents

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Summary. The inference of single bicyclic intermediates in the competition of diglyme (or triglyme)[1] with tetrahydrofurfuryl alcohol is confirmed by analysis of the linewidths. The dissymetric bicyclic species are characterized by linewidths increased markedly with respect to the pure solvents, without an accompanying change in the ^{23}Na chemical shift. Conversely, the competition of glyme with the same alcohol involves three equi-probable intermediates; that of tetrahydrofuran (or tetrahydropyran) is of greater conceptual complexity.

1. Introduction. – A crucial assumption in the preceding article [1] lies in the estimate of the chemical shift for the intermediate as the arithmetic mean of the chemical shifts in the pure solvents. We provide now a critical examination of this hypothesis, using as an independent observable ^{23}Na-NMR. linewidths in the same binary mixtures. These experimental parameters are indicated in the table 1, together with the measured viscosities.

2. Experimental Part. – The spectra are recorded as in the preceding article [1] (see also references [2] and [3]). Viscosity measurements were performed at 27.0 ± 0.1°, with 0.1 M solutions of sodium perchlorate in the glymes and 0.05 M solution in tetrahydrofuran. The glyme solutions contained a constant amount of benzene-d_6 (9%), to serve as an internal lock for the NMR. spectrometer. In the case of the THF/THFu binary mixture, shift measurements were performed with an external lock, and it was not necessary to add benzene-d_6 in the solutions whose viscosity was measured. Thus, in all cases, the linewidths and the viscosities quoted in the table are determined on the same solutions.

^{23}Na linewidth and bulk viscosities for the various solvent mixtures

Solvent A	Solvent B	M.F. of solvent B	$\nu_{1/2}$(Hz)	η (mP)
THF	THFu	0.0	14 ± 1	4.91
		0.019	28 ± 1	5.10
		0.039	35 ± 1	5.25
		0.078	42 ± 2	5.75
		0.177	57 ± 2	6.90
		0.317	71 ± 2	9.80
		0.428	89 ± 3	13.0
		0.584	109 ± 3	19.2
		0.705	127 ± 3	26.1
		0.796	138 ± 3	33.2
		0.920	166 ± 4	46.4
		1.0	176 ± 4	57.2
DME	THFu	0.0	22 ± 1	4.71
		0.067	36 ± 1	5.55
		0.095	41 ± 2	5.38
		0.333	74 ± 2	8.10
		0.871	129 ± 4	28.0
		1.0	166 ± 4	43.8

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[1] For abbreviations see the table of [1].

(Continued)

Solvent A	Solvent B	M.F. of solvent B	$\nu_{1/2}$(Hz)	η (mP)
DG	THFu	0.0	46 ± 1	9.96
		0.175	68 ± 2	11.5
		0.318	82 ± 2	12.9
		0.504	101 ± 3	16.1
		0.796	128 ± 4	26.4
TG	THFu	0.0	88 ± 2	18.0
		0.147	99 ± 3	19.1
		0.336	113 ± 3	20.5
		0.634	140 ± 4	24.5
		0.853	165 ± 4	32.2

The discrepancy between the two values quoted in pure THFu originates in the use in the second experiment (DME) of 9% of C_6D_6 co-dissolved, as an internal lock for the spectrometer.

2. Results and discussion. – As illustrated in Fig. 1, large positive deviations occur with respect to the expected *Debye-Stokes-Einstein* proportionality to viscosity [3–5]. We define a reduced linewidth $\nu^*_{1/2} = (\nu_{1/2})_{\text{exp}} \cdot \eta_{\text{MG}}/\eta$, in order to discuss viscosity-independent linewidths, and we select arbitrarily monoglyme as the reference solvent. Then, assuming that fast chemical exchange prevails, the observed linewidth is the weighted average [6]:

$$\nu^*_{1/2} = p_{\text{A}}(\nu^*_{1/2})_{\text{A}} + p_{\text{AB}} \cdot (\nu^*_{1/2})_{\text{AB}} + p_{\text{B}}(\nu^*_{1/2})_{\text{B}} \qquad (1)$$

where subscripts A et B refer to species symmetrically solvated by solvents A and B, and AB refers to the intermediate structure. The molar fractions p_{A}, p_{AB} and p_{B} are calculated from the equilibrium constants established from the chemical shift measurements [1].

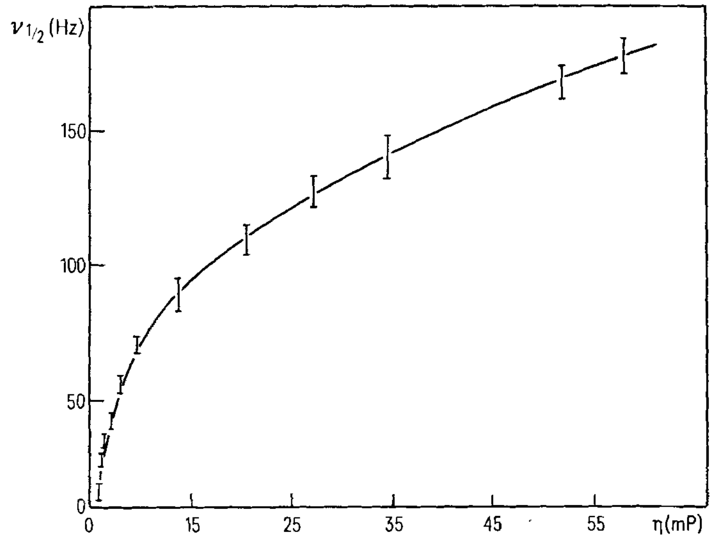


Fig. 1. *Linewidth $\nu_{1/2}$ versus viscosity η for $Na^+ClO_4^-$ dissolved in binary mixtures of THF and THFu*

A graph of $\Delta\nu^*_{1/2} = \nu^*_{1/2} - [p_A \cdot (\nu^*_{1/2})_A + p_B(\nu^*_{1/2})_B]$ against p_{AB} ought to be linear if: (1) the postulated intermediate exists; (2) it is a single species; (3) the mol fractions p_A, p_B, p_{AB} – and therefore the equilibrium constants K_1 and K_2 of [1] – are indeed correct. Condition (2) appeared to be fulfilled in the DG/THFu and TG/THFu experiments, where the observed chemical shifts indicate a single bicyclic intermediate [1]. A gratifying confirmation arises from the experimental linewidths, as shown in Fig. 2. Linear plots passing through the origin satisfy handsomely equation

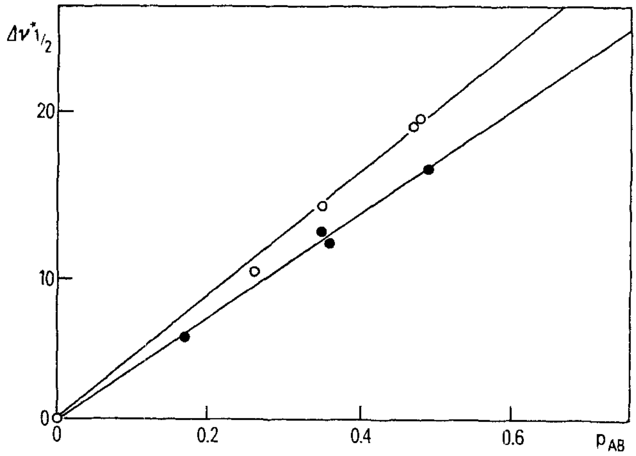


Fig. 2. *Residual line broadening* $\Delta\nu^*_{1/2}$ (Hz) *against the mol fraction* p_{AB} *of the intermediate, for diglyme* (open circles) *and triglymes* (filled circles), *in competition with tetrahydrofurfuryl alcohol*

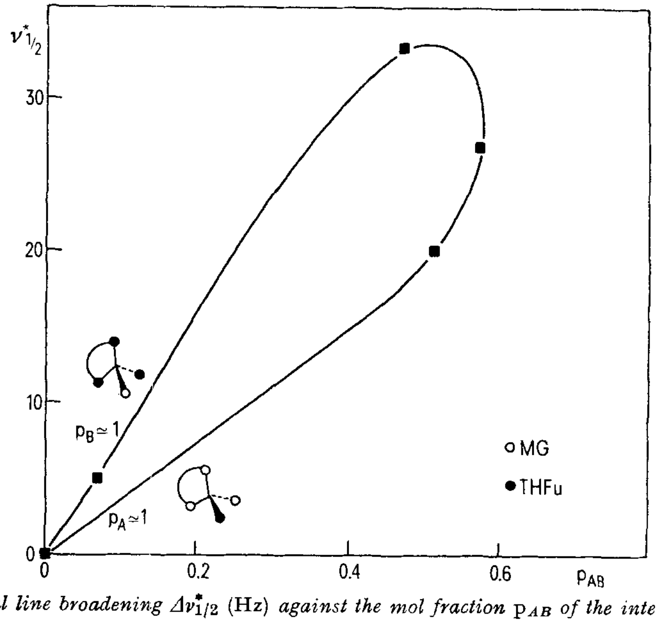


Fig. 3. *Residual line broadening* $\Delta\nu^*_{1/2}$ (Hz) *against the mol fraction* p_{AB} *of the intermediate, in the MG/THFu competition experiment* (the structure of the dominant intermediate, when either p_A or $p_B \rightarrow 1$, is also indicated)

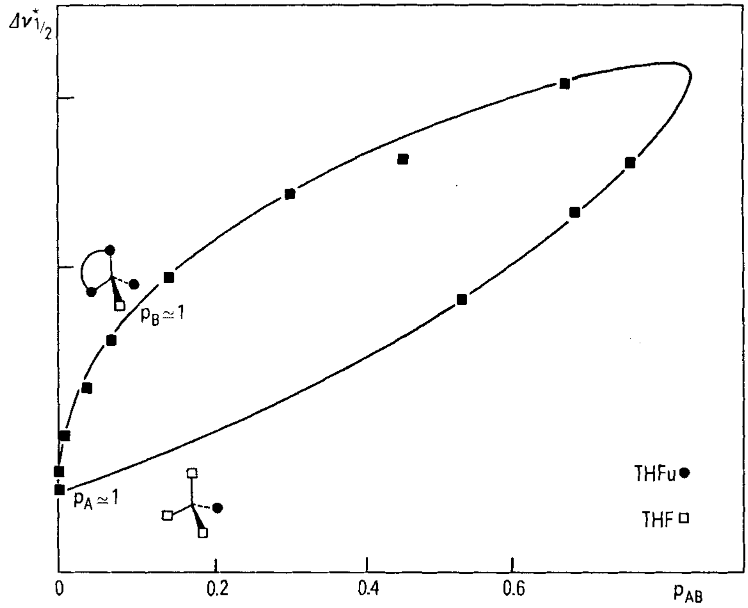


Fig. 4. *Residual line broadening* $\Delta\nu^*_{1/2}$ (Hz) *against the mol fraction* p_{AB} *of the intermediate, in the THF/THFu competition experiment* (the structure of the dominant intermediate, when either p_A or $p_B \to 1$, is also indicated)

1. Their slopes are the characteristic linewidths $(\nu_{1/2})_{AB}$ for the intermediate, 41 Hz and 33.5 Hz respectively for diglyme and triglyme.

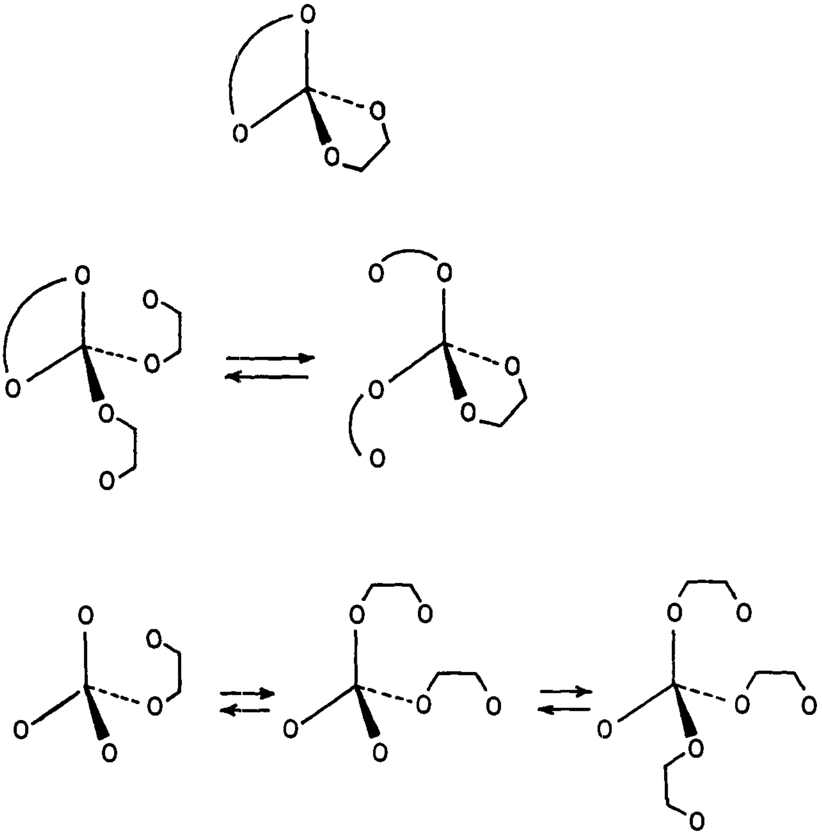
As a complementary check, the coexistence of several intermediates, for instance the coexistence of acyclic and cyclic intermediates [1], should rule out linearity of $\Delta\nu_{1/2}$ with p_{AB}: this other possibility prevails in the competition experiments between THF or MG, and THFu (or THPu) as represented in Fig. 3 and 4. We can distinguish three experimental situations, as illustrated in *Scheme 1*:

In case c, neither the linewidths nor the chemical shifts can be adequately analysed in termes of a three-states (A, AB and B) description (Fig. 4, and the discrepancy in Table 5 of reference [1]). In case b, the chemical shifts but not the linewidths (Fig. 2), are adequately analysed, and it is legitimate to discuss the K_1/K_2 ratio [1]. In case a, both the chemical shifts and the linewidths are satisfactorily explained.

From the experimental data, we are led to the conclusion that significant increases in the sodium linewidth result from incorporation of the sodium cation in dissymetric structures (*Scheme 2*).

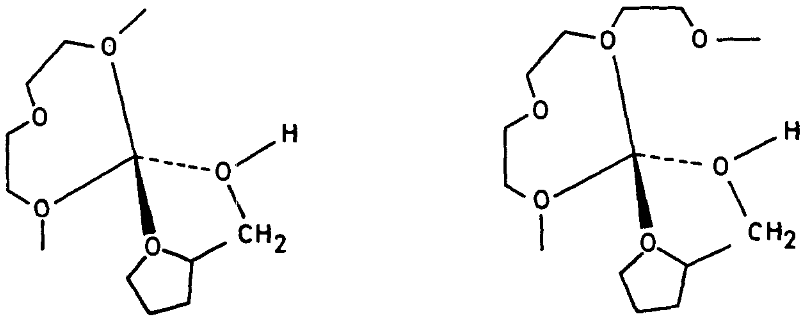
A similar finding has been reported earlier by *Van Geet* [7] for THF/H_2O binary mixtures, and by *Smid* et al. [5] for complexation of sodium by polyethers by THF. As stated above, the chemical shift in the AB intermediate is taken as the mean of those for the A and B species: there does not appear to be any extra contribution originating from the greater quadrupolar coupling constant in the AB intermediate. Yet, *Kintzinger & Lehn* [8] find a correlation between linewidths and chemical shifts for sodium cryptates: we believe that both these parameters are extremely sensitive

Scheme 1



a) A single intermediate (DG and TG).
b) Coexistence of virtually equi-probable intermediates (MG).
c) Coexistence of a number of distinct intermediates (THF).

Scheme 2



$\nu^*_{1/2} \simeq 41$ Hz

$\nu^*_{1/2} \simeq 33.5$ Hz

to the sodium-oxygen distances, which cover quite a range in the sodium cryptates, but would not vary greatly in the cases studied here.

Likewise, when $NaClO_4$ is dissolved in pyridine, the ^{23}Na linewidth increases considerably upon addition of sugar molecules known to complex the sodium cation [9] [10]; yet the ^{23}Na chemical shift remains virtually unchanged, even though the linewidth characteristic of the pure complex is in the range of 800–3000 Hz [11].

The sodium linewidths obtained in the present study for the unsymmetrical THFu/DG and THFu/TG sodium complex, *viz.* 41 and 33.5 Hz respectively, may arise both from rotation of the sodium cation together with its fixed solvation shell [12] and from vibrations within the complex [13], together with translational motions of solvent molecules outside the first solvation shell [14].

To sum up: ^{23}Na chemical shifts [1] and linewidths fit a symmetrical solvation model with *four* oxygen ligands at the corners of a tetrahedron, in conformity with theoretical calculations on $Na^+(H_2O)_n$ clusters [15], experimental determination of the corresponding thermodynamic parameters in the gas phase [16], and experimental evidence on the arrangement of water or methanol solvent molecules around the sodium cation [17].

The sodium cation itself exchanges fast between the three states in mutual equilibrium, referred to above as A, AB, and B. Since the line broadenings originate purely from modulation of the quadrupolar coupling constant by reorientation of the dissymetric AB intermediate, an upper limit of *ca.* 13 kcal.mol^{-1} can be placed on the energy barriers for chemical exchange interconverting these three species. This is consistent with an *associative* mechanism for ligand substitution. Fast exchange was to be expected: even with strongly complexing ionophores such as valinomycin or monensin, the Na^+ cation exchanges fast between a methanol environment and the central cavity of the antibiotic carrier [12].

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