NMR STUDY OF ASSOCIATION PROCESSES IN SOME ALIPHATIC ALCOHOLS SOLUTED IN CARBON TETRACHLORIDE

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Measured data on the chemical shift of hydroxyl protons as a function of concentration in CCl_4 solutions of CH_3OH, CH_3CH_2OH, $CH_3(CH_2)_2OH$, $CH_3(CH_2)_3OH$ and $(CH_3)_3COH$ are used for finding the association equilibrium constants. Temperature measurements for the latter three compounds also provide values of the hydrogen bond enthalpy. Models of association in solutions of hydroxyl compounds devised by Mecke and Kempter, and Saunders and Hyne were modified by the authors for use in this work. It is found that for solutions of concentrations below 0.2 mol fraction the Saunders-Hyne model gives somewhat more realistic results, whereas over 0.4 mol fraction neither of the models in mention applies. It is also shown that the conformity of experimental and model values of changes in chemical shift for concentrations exceeding 0.3 mol fraction was obtained by Saunders and Hyne entirely by chance.

1. Introduction

The NMR technique is one of the best methods of studying the associative processes in solutions of compounds forming hydrogen bonds. It had first been applied for this purpose by Becker, Liddel and Shoolery (1958) and later by Saunders and Hyne (1958), Feeney and Walker (1966), Dixon (1970), and other. Since the infrared technique was the dominant research method in this field before NMR was introduced, the interpretation of the results of NMR studies had been based on the models of association used for the interpretation of infrared data. The basic idea of the latter, on the other hand, was given By Mecke and Kempter (1950) who assumed that the hydrogen bond can be treated like an ordinary chemical bond, thus allowing the phenomenological theory of chemical reactions to be applied. When studying association in alcohols these authors assumed that the polymers composed of alcohol molecules are open and may contain a large number of these molecules (in theory, infinitely many), and also, that the enthalpy of the hydrogen bond is independent of the polymer length. Since their studies, many different modifica-

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tions of the Mecke-Kempter model may be found in the literature, the idea being to postulate a model of association as a chemical reaction appropriate for the given situation (*e. g.*, see Becker 1961). One of these versions is the model used by Saunders and Hyne for analyzing the results of NMR measurements for methanol, ethanol, *t*-butanol and phenol, in which they assumed that in solutions of these substances only monomers and one type of cyclic polymer (closed) containing a definite number of molecules occur. This model could be fitted to the NMR results in the entire practical range of concentrations. However, it is not compatible with the infrared data because in the range from 1.0 to 0.2 mol fraction it gives several to a dozen-odd per cent of monomers, whereas in the infrared studies the monomer band appears in alcohols below 0.3 mol fraction (*cf.* Konopka 1972). Similar discrepancies, as pointed out by Buchowski (1969), appear for concentrations over 0.1 mol fraction when compared with data obtained by thermodynamic measurements.

In our laboratory Frankiewicz (1970) repeated the measurements of Saunders and Hyne for methanol and phenol soluted in CCl_4 and, using their model, so fitted the reaction equilibrium constants that the difference between the fit and experimental data did not exceed 0.025 ppm. Hence, the situation is rather enigmatic and indicates the large flexibility of the model assumed, all the more so that Saunders and Hyne and Frankiewicz alike used concentrations expressed in mols per liter in their computations, which for large concentrations of alcohol in solutions is erroneous from the viewpoint of thermodynamics of ideal solutions. In this respect Dixon (1970) correctly applied the Saunders-Hyne model for interpreting his results for solutions of methanol in cyclohexane and cyclopentane, and he found good agreement with experimental data in a wide range of concentrations (up to 0.4 mol fraction).

These facts urged us to use both the Saunders-Hyne and the Mecke-Kempter models for interpreting results, but with some innovations. Firstly, all computations will be carried out according to the requirements of the thermodanymics of ideal solutions (of course, the solutions being considered may diverge from ideal ones, but any assumption otherwise would make a quantitative interpretation of measurements practically impossible); hence, all concentrations of the various polymers are defined in mol fractions. Secondly, the accepted criterion of compatibility between model and experiment will now be the constancy of reaction equilibrium constants with respect to concentration, and not, as done hitherto, the fitting of changes in the chemical shifts of the hydroxyl protons. Apart of this, in the Mecke-Kempter model the length of any possible multimers will be cut off.

2. *Mathematical form of Mecke-Kempter and Saunders-Hyne models*

If we number by $p = 1, 2, 3, \ldots$ the kinds of associations A_p containing p molecules of alcohol and denote by n_p their number in mols and by n_0 the number of mols of solvent, then the mol fractions f_p of A_p are given by the relations

$$f_p = \frac{n_p}{n_0 + \sum_{q=1} n_q} \tag{1}$$

and, hence, the equilibrium constant for the reaction $A_p \rightleftarrows A_{p-k} + A_k$ must be defined as follows:

$$K_{p,k} = \frac{f_p}{f_{p-k} f_k}. \tag{2}$$

Gutowsky and Saika (1953) were the first to find a pronounced change in the chemical shift of hydroxyl protons in solution of substances forming hydrogen bonds. They postulated that the average shift (at a rapid exchange), with the shift of protons in polymers being δ_p and in monomers δ_M, is expressed by the formula

$$\delta = \frac{\delta_M f_1 + \delta_p \sum\limits_{s=2} s f_s}{\sum\limits_{s=1} s f_s}. \tag{3}$$

The assumption of equality of chemical shifts of all hydroxyl protons in an open polymer is not at all obvious. But experimental data show that the change in chemical shift for various alcohols in the region of concentrations of 1.0 to 0.4 mol fraction is minute, and becomes very intense below 0.3 mol fraction, that is, in the region where infrared data show monomers to appear in higher concentration. This justifies the assumption just expressed. As a consequence of Eqs (3) and (1) we have

$$\frac{\delta_p - \delta}{\delta_p - \delta_M} = \frac{f_1}{\sum\limits_{s=1} s f_s} = \frac{n_1}{n_A}, \tag{4}$$

where n_A is the mol fraction of alcohol in the solution. Along similar lines we may get for the case of infrared measurements

$$\frac{\varepsilon_{10}}{\varepsilon_{11}} = \frac{n_1}{n_A}, \tag{5}$$

where ε_{10} is molar extinction — a function of concentration for solutions of alcohols — and ε_{11} is its limit for infinite dilution. In order to be able to treat NMR and IR data together in subsequent calculations, we assume that $n_1/n_A = \eta(f_A)$, with $\eta(f_A)$ defined by formula (4) or (5), and

$$f_A = \frac{n_A}{n_0 + n_A}. \tag{6}$$

Hence,

$$\frac{f_1}{\sum\limits_{s=1} s f_s} = \eta(f_A), \tag{7}$$

which trough formula (2) relates the experimental results contained in $\eta(f_A)$ with the reaction equilibrium constants describing the association process. This relation may be used

in practice, however, only when one or at most two of the reaction equilibrium constants $K_{p,k}$ constitute the independent variable.

If we introduce the aforementioned Mecke-Kempter model (1950), but with the additional assumption that the largest permissible polymers contain N alcohol molecules, we get

$$K_{p,1} = [K_N]^{p-1} \quad \text{and} \quad f_p = [K_N]^{p-1} f_1^p \tag{8}$$

where the first of these expressions is at the same time a definition of K_N when we put $p = 2$. Now, Eq. (7) becomes an equation of degree $(N-1)$ for $K_N f_1 = F(f_A)$, and for $n \neq 2$ and $\neq \infty$ it has to be solved numerically. On the other hand, from Eq. (1) we have

$$\sum_{s=1}^{N} s f_s = \frac{n_A}{n_0} \{1 - \sum_{s=1}^{N} f_s\}, \tag{9}$$

and this equality taken together with Eqs (2) and (8) yields

$$K_N = \frac{1-f_A}{f_A} \eta^{-1}(f_A) F(f_A) + \sum_{s=1}^{N} [F(f_A)]^s. \tag{10}$$

In particular, for $N = \infty$ we have $F(f_A) = 1 - \eta^{\frac{1}{2}}(f_A)$ and

$$K_\infty = \frac{1}{f_A} \frac{1-\eta^{\frac{1}{2}}}{\eta} - \left(\frac{1-\eta^{\frac{1}{2}}}{\eta^{\frac{1}{2}}}\right)^2. \tag{11}$$

This formula becomes formally identical with that of Mecke and Kempter (1950) if f_A is replaced by concentration C_A in mols per liter and the last member is neglected. Such operations are passable, however, only when concentrations are low enough.

For the Saunders-Hane model formula (7) takes on the very simple form

$$1 + mK(m) f_1^{m-1} = \eta^{-1}(f_A), \tag{12}$$

because here only monomers and cyclic polymers containing m alcohol molecules appear, where $K(m)$ is the equilibrium constant of the reaction $A_m \rightleftarrows m(A_1)$. Whence it is easily obtained that

$$K(m) = \frac{\eta^{-1}-1}{m} \left[\frac{\eta^{-1}}{f_A} + \frac{m-1}{m}(1-\eta^{-1})\right]^{m-1}. \tag{13}$$

Once again, if f_A is replaced by C_A and the second term under the brackets is discarded the result is the same as obtained by Saunders and Hyne. But simple calculations with the use of experimental data show that for $f_A = 0.3$ mol fraction the second term under the brackets constitutes about 30% of the total value of the brackets; hence, it should not be neglected.

3. Experimental

The spectra of the examined alcohol solutions were recorded by means of a Tesla (NMR-BS 487–80 MHz) spectrometer with fully automatic frequency measurement based on the technique of side bands with proton stabilization. The external etalon was HMDS for all alcohols except methanol, for which C_6H_6 was used in the form of an

internal standard. For methanol and ethanol temperature stabilization was $\pm 2°C$ whereas for the other alcohols it was $\pm 1°C$. The origin of the reagents was:

1. CH_3OH — Chemical Works in Oświęcim,
2. CH_3CH_2OH — Łódź Factory of the Spirits Industry,
3. $CH_3(CH_2)_2OH$ — Łódź Factory of the Spirits Industry,
4. $CH_3(CH_2)_3OH$ — "Isopharm" Pharmaceutical and Chemical Cooperative, Warsaw
5. $(CH_3)_3COH$ — "Reanal" Budapest (Hungary)
6. CCl_4 — Polish Chemical Reagents Gliwice.

All of the agents were re-distilled but this is not essential importance in these measurements.

4. Analysis of results and conclusions

All numerical computations were performed with the use of the formulae derived in Section 2. The value accepted for δ_M was taken from the measurement at the lowest alcohol concentration for which it was still possible to separate the hydroxyl proton line from the noise. In the case of the Mecke-Kempter model the shift for pure alcohol was accepted as δ_P (increasing δ_P does not produce any essential changes for this model) whereas for the Saunders-Hyne model δ_P was fitted by starting from the shift in pure alcohol to higher values, because increasing this shift as compared with that of pure alcohol was found to improve results (Table I).

TABLE I

Alcohol	Temp. [°C]	δm [Hz]	Mecke-Kempter model			Saunders-Hyne model			
			δ_p [Hz]	$\langle K_{10}\rangle$ (mol fraction)$^{-1}$ $\pm 10\%$	enthalpy of bond [kcal/mol] $\pm 20\%$	δ_p [Hz]	$\langle K(n)\rangle 10^{-2}$ (mol fraction)$^{-n+1}$ $\pm 10\%$	enthalpy of bond [kcal/mol] $\pm 20\%$	n
CH_3OH	26	-343[1]	-4	14.2		24[1]	4.6		3
						14[1]	148		4
CH_3CH_2OH	26	86	418	18.2		438	6.8		3
$CH_3(CH_2)_2OH$	26	67	427	26.5		447	19.3	3.9	3
	36	67	427	17.4	5.6	447	10.0		3
	46	67	427	12.2	7.1	447	5.7	3.6	3
$CH_3(CH_2)_3OH$	36	102	407	18.5		427	8.1		3
	46	102	407	10.9	9.0	427	3.1	3.1	3
$(CH_3)_3OH$	36	103	369	11.8		389	3.0		3
	46	103	369	7.2	9.7	389	1.3	4.0	3

For the Mecke-Kempter model the versions with $N = 2, 3, 4, 6, 10$ and ∞ were investigated. The best constancy of K_N was achieved for $N = 10$ and, very characteristically, the results for $N = 10$ and $N = \infty$ are practically identical. The run of $K_{10}/\langle K_{10}\rangle$

(where $\langle K_{10} \rangle$ is the mean value of K_{10} over the domain of f_A considered here) against f_A is shown in Fig. 1; the value of K_{10} is seen to generally increase but slightly with increasing f_A. Beyond the region included in the graphs K_{10} changes considerably. Mean values of $\langle K_{10} \rangle$ are given in Table I. Apart from this, in events when measurements were carried
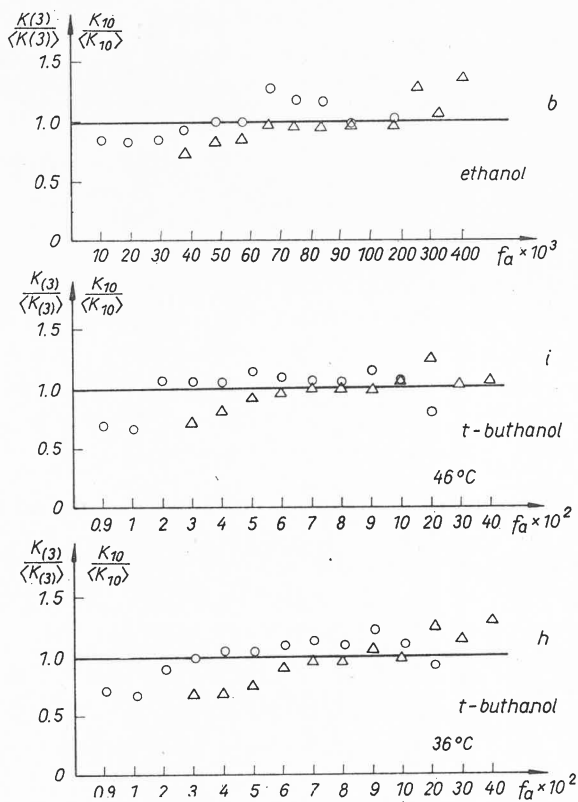

Fig. 1. Mean value of $K_{10}/\langle K_{10} \rangle$ *versus* of f_A $\triangle$ — Mecke-Kempter model, $\bigcirc$ — Saunders-Hyne model

out at least two temperatures the enthalpies of hydrogen bonds have been estimated by means of vant'Hoff's formula (Table I). As is evident, these enthalpies are much greater than should be expected following the results of Becker (1961) obtained for complexes of aliphatic alcohols with such molecules as acetone or dioxane.

The Saunders-Hyne model was checked for $m = 3, 4, 5, 6$ (for $m = 2$ it coincides with the Mecke-Kempter model with $N = 2$). The best results were obtained for $K(3)$. This is seen in the curves of $K(3)/\langle K(3) \rangle$, where the regions of stability and the stability itself is better than for the Mecke-Kempter model in the range of low concentrations (below 0.2 mol fraction). In the case of methanol good stability was found also for $K(4)$. Hence, these results for low alcohol concentrations are in principle in agreement with those of Saunders and Hyne (1958). But, as both $K(3)$ and $K(4)$ are found to rise abruptly for higher concentrations, the agreement between experimental and model runs of changes in chemical shift as a function of f_A is fortuitous. This fortuity stems from the fact that

the main change in chemical shift occurs in the region below 0.3 mol fraction, where the models under consideration work well at least formally, whereas from 0.3 to 1.0 mol fraction the experimental δ changes very little, but the formulae arrived at on the basis of these models ensure a monotonic increase of the calculated δ. Thus, Saunders and Hyne incorrectly and unnecessarily extended their model to high concentrations. All arguments put forward hitherto do not speak in favour of either of these models, however. But the values of hydrogen bond enthalpies calculated for the Saunders-Hyne model do, as they are very close to the values obtained by Becker (1961) mentioned earlier. In general, however, neither of the models gives satisfactory results. The reason for this is presumably because these models oversimplify the description of the actual process of association (Dixon 1970).

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