

Solvent Effects in NMR Spectroscopy

II. Toluene-Induced Shifts in the Spectra of Non-Aromatic Heterocycles. Self-Association of Toluene. Solvation Clusters as the Most Probable Explanation for the Solvent Shifts

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The temperature-dependent variations of the chemical shifts of 2,2-dimethyl-1,3-oxathiane and 2,2-dimethyl-1,3-oxathiolane in toluene solution have been determined. Also the methyl proton resonance of toluene itself has been found to vary appreciably with temperature. According to the collision complex theory, this means that toluene molecules are self-associated. Accordingly, the formation of solute complexes in dilute solutions of polar solutes in toluene may well be excluded, but the dimerization, trimerization, *etc.*, of toluene itself cannot. Consequently, the frequently postulated existence of one-to-one complexes between polar solute and toluene must be an over-simplification. A time-averaged solvation cluster is proposed instead of some definite collision complex structure.

An error in the general treatment of the so-called collision complex equilibria was pointed out in the first paper of this series.¹ Apparent thermodynamic quantities were calculated for numerous polar solutes and they were found to be only slightly dependent on the nature of the solute. This observation led us to conclude that the observed temperature-dependent chemical shifts cannot be due to the formation of one-to-one solute-solvent complex but preferably to solvation. In other words, all of the studied solutes are nearly equally solvated by toluene molecules unless the steric requirements make the solvation very loose.

In order to avoid further confusing publications in the field of aromatic solvent induced shifts, it is necessary to collect further data and, moreover, to check whether toluene is complexed or solvated by other toluene molecules. After our work was completed, an independent investigation dealing with the origin of solvent effects was published by Engler and Laszlo.² Their results are supported by the following discussion.

EXPERIMENTAL

2,2-Dimethyl-1,3-oxathiane ^a and 2,2-dimethyl-1,3-oxathiolane ^a had been prepared previously. Toluene was a product of Merck.

The NMR spectra were recorded on a 60 MHz Perkin-Elmer R 10 NMR spectrometer equipped with a variable temperature probe. Carbon tetrachloride was used as the

Table 1. Chemical shifts of the 4- and 5-protons of 2,2-dimethyl-1,3-oxathiolane in carbon tetrachloride at 33.2°C and in toluene at different temperatures. Also the correlation coefficients and parameters of the equation $\Delta_i = mT + \Delta_c$ are shown.

°C	4-H		5-H	
	Δ_{obs}	Δ_t	Δ_{obs}	Δ_t
33.2 (CCl ₄)	243.0		180.0	
91.5	227.0	16.0	162.5	17.5
81.5	226.0	17.0	161.5	18.5
71.6	225.5	17.5	161.0	19.0
61.7	225.0	18.0	161.0	19.0
51.8	224.0	19.0	160.5	19.5
33.2	223.0	20.0	158.0	22.0
0.3	220.0	23.0	155.0	25.0
-19.5	216.5	26.5	153.0	27.0
-39.5	214.5	28.5	151.5	28.5
-59.2	214.0	29.0	151.0	29.0
<i>m</i>	0.09164	± 0.00433	0.08290	± 0.00372
Δ_c	-48.99	± 1.32	-47.41	± 1.14
<i>r</i>	0.986		0.988	

Table 2. Chemical shift of the 4- and 6-protons of 2,2-dimethyl-1,3-oxathiane in carbon tetrachloride at 33.2°C and in toluene at different temperatures. Also the correlation coefficients and the parameters of the equation $\Delta_i = mT + \Delta_c$ are shown.

°C	4-H		6-H	
	Δ_{obs}	Δ_t	Δ_{obs}	Δ_t
33.2 (CCl ₄)	168.5		228.5	
91.5	155.0	13.5	220.0	8.5
81.5	153.5	15.0	218.5	10.0
71.6	153.0	15.5	218.0	10.5
61.7	153.0	15.5	217.0	11.5
51.8	151.5	17.0	216.0	12.5
33.2	150.0	18.5	215.5	13.0
10.1	149.0	19.5	214.0	14.5
-9.5	147.0	21.5	212.0	16.5
-29.5	145.0	23.5	210.5	18.0
-49.5	143.0	25.5	207.5	21.0
-59.2	142.0	26.5	207.0	21.5
-68.8	141.5	27.0	205.0	23.5
<i>m</i>	0.08317	± 0.00228	0.08594	± 0.00349
Δ_c	-43.86	± 0.67	-39.92	± 1.03
<i>r</i>	0.981		0.983	

Table 3. Chemical shifts of the toluene methyl protons in carbon tetrachloride at 33.2°C and in toluene at different temperatures. At the bottom of the table are given the parameters of the equation $\Delta_i = mT + \Delta_c$ and the correlation coefficient.

°C	Δ_{Me}	Δ_i
33.2 (CCl ₄)	141.0	
101.5	130.8	10.2
91.5	130.5	10.5
81.5	130.0	11.0
71.6	129.5	11.5
61.7	129.2	11.8
51.8	129.0	12.0
33.2	128.5	12.5
19.9	128.0	13.0
0.3	127.5	13.5
-9.5	127.3	13.7
-29.0	127.0	14.0
-39.5	126.0	15.0
-49.5	126.0	15.0
-59.2	125.0	16.0
-78.4	124.2	16.8
-88.1	123.5	17.5
-97.9	122.5	18.5
m	0.03693	± 0.00175
Δ_c	-23.898	± 0.497
r	0.977	

Table 4. The dependence of the chemical shift of toluene methyl protons on the mol fraction of toluene in toluene-CCl₄ mixtures.

x_{tol}	Δ_{Me}	Δ_x
0	141.0 ^a	0
0.25	137.9	3.1
0.5	135.5	5.5
0.75	130.9	10.1
1	128.5	12.5
	$\Delta_{Me} = mx_{tol} + b$	
	m -13.12 \pm 1.24	
	b 141.4 \pm 0.85	
	r 0.913	

^a This value was not included in the calculation owing to the small proportion (2 % w/v) of toluene present (cf. the value of b).

“inert” solvent.¹ Toluene was used as the “active” solvent to permit comparison with our earlier results.¹ The solute concentrations were 4 % (w/v) and the resonance positions (Hz) were measured from the signal of internally added tetramethylsilane (Tables 1-4 and Fig. 1). The NMR shifts in CCl₄ were measured only at the normal probe temperature of 306.35 K. The chemical shifts of the methyl protons of toluene were measured also in a number of toluene-CCl₄ mixtures (Table 4 and Fig. 2).

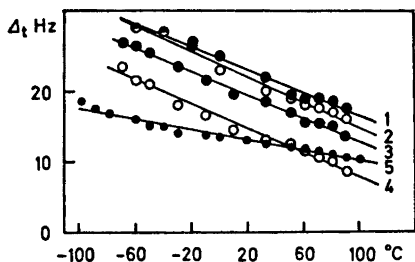


Fig. 1. Temperature-dependent solvent shifts of protons of 2,2-dimethyl-1,3-oxathiolane (1 4-H; 2 5-H), 2,2-dimethyl-1,3-oxathiane (3 4-H; 4 6-H), and methyl protons of toluene (5).

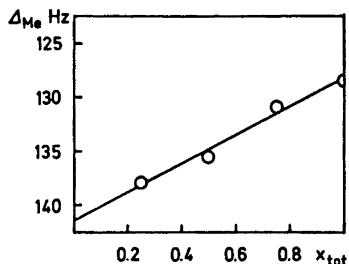


Fig. 2. Dependence of the chemical shifts of toluene methyl protons on the mol fraction of toluene in toluene-carbon tetrachloride mixtures.

RESULTS AND DISCUSSION

The toluene-induced solvent shifts of the 4- and 5-protons of 2,2-dimethyl-1,3-oxathiolane, the 4- and 6-protons of 2,2-dimethyl-1,3-oxathiane, and the toluene methyl protons are plotted against temperature in Fig. 1. A good linear correlation prevails in each case (Tables 1–3). In other words, the equations derived in the first part of this study are again applicable. Thus the apparent equilibrium constant can be represented by the equation where

$$K = (B/T) - 1 \quad (1)$$

B is the “critical” temperature for the formation of the postulated collision complex.

Table 5. Values of the “critical” temperature and thermodynamic quantities at the reference temperature 306.35 K.

Compound	B , K	$-\Delta H$, kcal/mol	$-\Delta S$, cal/mol degree	$-\Delta C_p$, cal/mol degree	Ref.
Toluene CH_3	647 ± 18	1.16 ± 0.03	3.6 ± 0.2	7.2 ± 0.4	This work
2,2-Dimethyl-1,3-oxathiane:					
4-H	527 ± 17	1.45 ± 0.06	5.4 ± 0.4	11.3 ± 1.0	This work
6-H	465 ± 31	1.79 ± 0.23	7.1 ± 1.1	17.1 ± 4.4	This work
2,2-Dimethyl-1,3-oxathiolane:					
4-H	572 ± 39	1.31 ± 0.08	4.6 ± 0.5	10.9 ± 1.6	This work
5-H	535 ± 29	1.43 ± 0.10	5.2 ± 0.6	9.2 ± 1.1	This work
1,3-Dioxane:					
4,6-H	590 ± 10	1.27 ± 0.02	4.3 ± 0.1	8.6 ± 0.3	1
2,2-Dimethyl-1,3-dioxane:					
4,6-H	501 ± 16	1.56 ± 0.08	6.0 ± 0.4	13.1 ± 1.3	1

On the basis of eqn. (1) we estimated changes in thermodynamic quantities for the solvation phenomena in toluene (Table 5).¹ The results show that the self-association of toluene is more extensive than its association with the studied polar solutes.

Consequently, our results confirm that it is not permissible to speak of only one-to-one complexes between polar solutes and toluene since self-association of toluene is at least as likely.

The above discussion leads to the conclusion that the observed toluene-induced solvent shifts are due to the influence of some time-averaged complex model, *e.g.* one-to-one, one-to-two, one-to-three, *etc.* Of course, the one-to-one complex model may in some cases be the most probable configuration of the solute-solvent system and therefore it has been possible to construct some generally applicable stereochemical models to explain the observed solvent shifts.^{1,2}

If we return to the results in Table 5, it is again possible to observe that steric requirements in the solute molecules clearly affect the extent of solvation.^{1,2} For instance, the much longer length of the C-S bond (1.8 Å) as compared to the length of the C-O bond (1.4 Å) is clearly shown by the different parameters for the 4- and 5-protons of 2,2-dimethyl-1,3-oxathiolane on the one hand and those for the 4- and 6-protons of 2,2-dimethyl-1,3-oxathiane on the other hand.

In our opinion, the most probable explanations for the observed aromatic solvent induced shifts in NMR spectroscopy are the following:

(1) Polar solute molecules are solvated by a more or less variable number of aromatic solvent molecules.

(2) There is simultaneous self-association of the solvent molecules and solute-solvent association.

(3) Steric requirements around the solute molecules that influence the solvation are responsible for the fact that it is possible to detect changes in the resonance positions of the different solute protons by NMR.

For a further discussion, we refer to the excellent paper of Engler and Laszlo.² We plan to collect additional data on the effects of structural factors and solvents on the solvation phenomena.

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