An Equilibrium Model of the Self-Association of 1- and 3-Pentanols in Heptane

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The near-IR spectra in the first overtone of the OH stretching vibrational range have been measured over all the alcohol concentrations from 0.002 mol dm^{-3} to neat pentanol at 25 and 35 °C. The spectra were best fitted by a monomer-dimer model at concentrations below 0.025 mol dm^{-3}, by a monomer-dimer-tetramer model in the concentration range of 0.025—0.35 mol dm^{-3}, and by a monomer-dimer-tetramer-octamer model at concentrations above 0.35 mol dm^{-3}. The dielectric constants and losses of pure 1- and 3-pentanols and heptane solutions of 1-decanol have been measured at frequencies from 1.35 to 4500 MHz at 15, 25, and 35 °C. The dielectric absorption could be resolved into three Debye-like dispersion regions. The concentrations of a free monomer, a chain dimer and trimer, a linear chain polymer, and a nonpolar cyclic polymer have been obtained by applying a modified Kirkwood-Fröhlich equation. From a comparison of the near-IR results with the dielectric results, we can recognize at least the coexistence of a free monomer, a chain dimer, a nonpolar cyclic tetramer, and a linear chain octamer at higher concentrations of 1- and 3-pentanols in heptane at room temperature.

Wide-frequency measurements of complex dielectric constants have reported the coexistence of two or three dielectric dispersion regions.[1-3] The three dispersion regions observed for primary, secondary, and tertiary alcohols have been assigned to a free monomer, a chain dimer and trimer, and a linear hydrogen-bonded chain polymer respectively. The concentrations of these three species and a nonpolar cyclic polymer were evaluated by applying a modified Kirkwood-Fröhlich equation to each dispersion region.[4-6] The existence of a nonpolar cyclic polymer was indicated experimentally in more sterically hindered alcohols. The transformation of a nonpolar cyclic polymer into a linear chain polymer was observed in binary mixtures of 1-butanol in sterically hindered octanol isomers.[7] From the dielectric investigation, however, it was difficult to obtain a number of molecules in the hydrogen-bonded species.

On the other hand, many studies of the intermolecular association of alkanol in nonpolar solvents have been carried out by the use of various methods, such as vapor pressure, near-IR, IR, and NMR techniques. There is a general agreement that an alcohol molecule may associate into some hydrogen-bonded species. Various assignments, however, have been reported on the self-association of alkanol in nonpolar solvents. Fletcher and Heller[8-10] have reported near-IR absorptions in the first overtone of the OH stretching vibrations for solutions of 1-octanol and 1-butanol in decane. They have explained the absorptions in terms of a monomer-linear tetramer-cyclic tetramer model. Van Ness et al.[11] indicated a monomer-cyclic dimer-linear polymer model for solutions of ethanol in heptane and in toluene. They indicated that there exists at least the possibility of seven types of OH stretching vibrations contributing to the IR spectra. A monomer-dimer-tetramer model has been reported for 1-octanol and 1-dodecanol in octane by Aveyard et al.,[12] for ethanol in nonpolar solvents by Brink and Glasser,[13] for 1-alkanol in carbontetrachloride by Kunst et al.,[14] and for 1-butanol in heptane by Verrall et al.[15] Moreover, a monomer-chain trimer-cyclic polymer model[16] and a monomer-cyclic trimer-linear hexamer model[17] have been reported for 2-methyl-2-propanol in a nonpolar solvent.

We have extended the investigation of the self-association by performing near-IR measurements for heptane solutions of 1- and 3-pentanols over all the alcohol concentrations. By comparing the results obtained by two different methods of dielectric relaxation and near-IR techniques, it is desirable to clarify an equilibrium model of the self-association of alkanol in a nonpolar solvent at room temperature.

Experimental

Purification of Materials. The alkanols (1- and 3-pentanols) and heptane were purified by the method described in previous papers.[4,5]

Dielectric Measurements. The dielectric constants and losses were measured using three apparatuses: a Boonton Radio RX meter (Type 250A), a Hewlett-Packard VHF Bridge (Model 803A), and a General Radio Precision Slotted Line (Type 900-LB), over the frequency range of 1.35—4500 MHz.[4]

Near-IR Measurements. Twenty-eight heptane solutions of 1- and 3-pentanols were prepared over concentrations from 0.002 mol dm^{-3} to neat pentanol. The weights of the solute and solvent were measured by a direct reading balance before measurements. The volumes of the solute and the solvent were calculated by assuming a zero volume change upon mixing and by using density data as a function of the experimental temperature for alkanol and heptane. The near-IR spectra were observed with a UV-340 spectro-

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photometer (Hitachi Co.) over the wavelength range of 1350—1650 nm at 25 and 35 °C. Two cells of the sample and a reference were placed in a cell holder, whose temperature was kept constant within ±0.2 °C of the specified values by circulating water from a thermostat. The reference beam always passed through a 1-cm cell filled with pure heptane.

Results and Discussion

The absorptions for heptane solutions of 1-pentanol in the first overtone of the hydroxyl stretching vibrational range are shown in Fig. 1 at five higher concentrations. In the spectra at higher concentrations, three major peaks could be observed at about 1403, 1490, and 1580 nm, and two small peaks at 1455 and 1532 nm. Two peaks could be observed at 1403 and 1532 nm at lower concentrations. On the assumption that the end O-H of a linear chain polymer does not contribute any significant absorbance at the monomer peak, the monomer absorbance (A_1) was decided as the difference between the absorbance at 1403 nm (1406 nm for 3-pentanol) and that at a standard wavelength for 1-pentanol. This standard wavelength was expressed as the "near isosbestic point" by Fletcher and Heller[8] and selected to be at 1390 nm for 1-pentanol (1392 nm for 3-pentanol) in the present work. It is assumed, for the analysis of the data, that all heptane solutions are ideal solutions. In these heptane solutions, alkanol has absorbances of both CH_2 and OH groups in the wavelength range of 1350—1650 nm. The heptane used as the solvent and as the reference has the absorbance of only the CH_2 group. When the concentration of the CH_2 group between the sample (heptane solution of alkanol) and the reference (heptane) is different, it is necessary to correct the absorbance by making use of that of pure heptane.

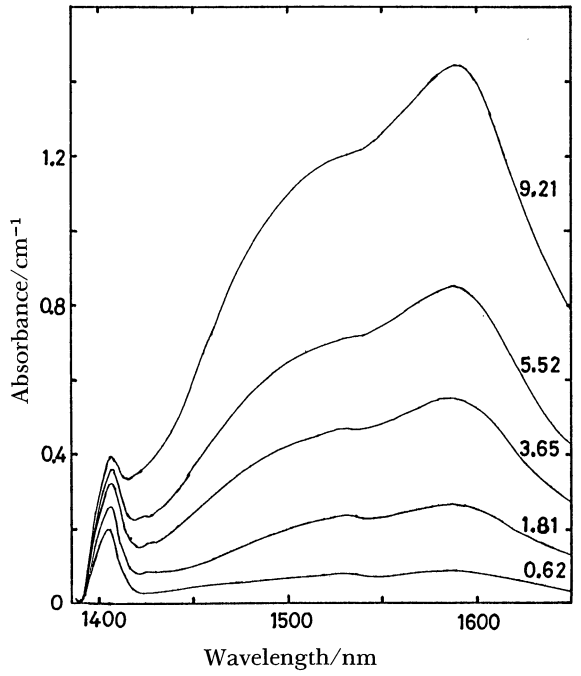

Fig. 1. Near-IR spectra in the first overtone of the hydroxyl stretching vibrational range for heptane solutions of 1-pentanol. Number is the concentration in mol dm^{-3} of 1-pentanol.

The gross stoichiometric concentration (C_0) of alkanol can be expressed by:

$$C_0 = C_1 + 2C_2 + \cdots\cdots + nC_n. \quad (1)$$

Here, C_n is the n-mer concentration. By substituting $C_n = K_{1,n} \times C_1^n$ and $C_1 = A_1/E_1$ into Eq. 1, we obtain:

$$C_0 = C_1 + 2K_{1,2}C_1^2 + \cdots + nK_{1,n}C_1^n$$
$$= (A_1)/E_1 + 2K_{1,2}(A_1)^2/E_1^2 + \cdots + nK_{1,n}(A_1)^n/E_1^n. \quad (2)$$

Here, $K_{1,n}$ ($n=2 \cdots n$) is the equilibrium constant between the monomer and n-mer, while E_1 is the molar absorptivity of the monomer. The E_1, $K_{1,n}$, and C_n values could be calculated from Eq. 2 by making use of C_0 and A_1 for all heptane solutions, using a least squares method. The standard deviation (ρ) in the calculation of Eq. 2 was obtained by the summation of the square of the relative difference between the observed and calculated values of the A_1 as follows:

$$\rho = [\sum_1^K \left\{ \frac{A_1(\text{obs}) - A_1(\text{cal})}{A_1(\text{obs})} \right\}^2 / (K-N)]^{1/2}.$$

Here, K is the number of heptane solutions, and N the number of species including a monomer. For the main combinations in which N is 3, 4, or 5, we searched for the mathematical best fit of Eq. 2 using the criteria that the ρ is the smaller value and that the E_1 calculated is constant with the temperature. Typical combinations in which $N=4$, for example, are shown in Table 1 for heptane solutions of 3-pentanol, together with ρ and E_1 at 25 and 35 °C. If the absorbances of the monomer and polymer species were overlapped at higher concentrations, the $K_{1,2}$ were determined from the data at lower concentrations (up to 0.02 mol dm^{-3}). The E_1, $K_{1,n}$, and C_n values were again calculated from Eq. 2 by making use of C_0, A_1, and $K_{1,2}$. Moreover, the absorbance (A_m) at a certain wavelength (m) can be written as follows:

Table 1. Standard Deviations and Molar Absorptivities for Some Typical Combinations ($N=4$) of 3-Pentanol at 25 and 35 °C

Combination	Standard deviation ρ		Molar absorptivity E_1/(mol^{-1} dm^3 cm^{-1})	
	25 °C	35 °C	25 °C	35 °C
1-2-4-8	0.0170	0.0206	1.68	1.69
1-2-4-11	0.0136	0.0427	1.65	1.79
1-3-4-7	0.0182	0.0454	1.67	1.75
1-3-4-10	0.0174	0.0175	1.64	1.70
1-3-5-7	0.0203	0.0256	1.69	1.70
1-3-5-8	0.0184	0.0340	1.62	1.72

Table 2. Molar Absorptivities at 10 Wavelengths of a Monomer-Dimer-Tetramer-Octamer Model for 3-Pentanol

m / nm	E_1		$E'_{2,m}$		$E'_{4,m}$		$E'_{8,m}$	
	$mol^{-1}\,dm^3\,cm^{-1}$		$mol^{-1}\,dm^3\,cm^{-1}$		$mol^{-1}\,dm^3\,cm^{-1}$		$mol^{-1}\,dm^3\,cm^{-1}$	
	25 °C	35 °C	25 °C	35 °C	25 °C	35 °C	25 °C	35 °C
1406	1.68	1.69						
1432	0.0425	0.0468	—	0.0218	0.0518	0.0628	0.0119	0.0181
1472			0.104	0.131	0.0931	0.0940	0.0992	0.112
1498			0.147	0.166	0.0951	0.0864	0.139	0.145
1516			0.194	0.209	0.0906	0.0780	0.141	0.145
1540			0.249	0.229	0.0899	0.0774	0.130	0.132
1566			0.143	0.158	0.113	0.0984	0.131	0.132
1578			0.147	0.175	0.117	0.0954	0.137	0.143
1590			0.139	0.174	0.114	0.0885	0.134	0.141
1602			0.133	0.168	0.105	0.0800	0.115	0.119

Table 3. Equilibrium Constants and Thermodynamic Parameters for 1- and 3-Pentanols

Compound	$K_{1,2}$	$K_{1,4}$	$K_{1,8}$
	$(mol\,dm^{-3})^{-1}$	$(mol\,dm^{-3})^{-3}$	$(mol\,dm^{-3})^{-7}$
		25 °C	
1-Pentanol	1.25	6.55×10^2	7.21×10^5
3-Pentanol	1.91	9.37×10	2.72×10^3
		35 °C	
1-Pentanol	0.804	2.27×10^2	7.71×10^4
3-Pentanol	1.24	2.41×10	1.79×10^2

	$-\Delta H$ / $kJ\,mol^{-1}$ of 1-pentanol	$-\Delta H$ / $kJ\,mol^{-1}$ of 3-pentanol
Dimer	34.0	33.2
Tetramer	80.8	103.8
Octamer	170.7	207.9

$$A_m = A_{1,m} + A_{2,m} + \cdots\cdots + A_{n,m}$$
$$= E_{1,m}C_1 + E_{2,m}C_2 + \cdots\cdots + E_{n,m}C_n$$
$$= E_{1,m}C_1 + 2E'_{2,m}C_2 + \cdots\cdots + nE'_{n,m}C_n. \quad (3)$$

In this equation, $A_{n,m}$ and $E_{n,m}$ are the absorbance and the molar absorptivity of the n-mer at a certain wavelength, m, respectively. The $E'_{n,m}(E'_{n,m}=E_{n,m}/n)$ was calculated from Eq. 3 by making use of A_m and C_n at about 10 wavelengths, using a least squares method. Some proper combinations were examined to see whether the $E'_{n,m}$-m curve exhibits a smooth and reasonable behavior at temperatures of both 25 and 35 °C. From the above considerations, a monomer-dimer-tetramer-octamer model was selected as the most proper combination. The $E'_{n,m}$ values of the model for 3-pentanol are shown in Table 2 as functions of 10 wavelengths. The E_1 values evaluated from Eq. 2 become 1.76 and 1.68 $mol^{-1}\,dm^3\,cm^{-1}$ for the heptane solutions of 1- and 3-pentanols respectively. By assuming the following equation:[8]

$$-\Delta H = R\,\mathrm{d}\ln(K_{1,n})/\mathrm{d}(T^{-1}),$$

$-\Delta H$ was calculated from $K_{1,n}$ and T^{-1}, where R is the gas constant, and T the absolute temperature. The

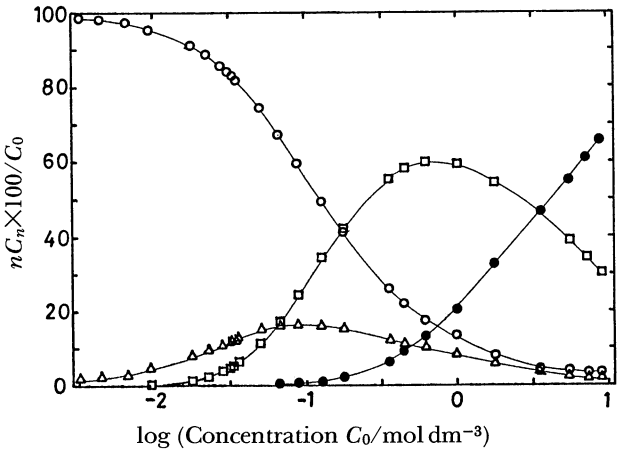

Fig. 2. Concentrations ($nC_n\times100/C_0$) calculated by a monomer-dimer-tetramer-octamer model for heptane solutions of 1-pentanol.
○: a monomer, △: a dimer, □: a tetramer, ●: an octamer.

$K_{1,n}$, and $-\Delta H$ values are given in Table 3.

A monomer-dimer-tetramer-octamer model was determined as the best-fit model. The concentrations ($nC_n\times100/C_0$) calculated by this model are plotted in

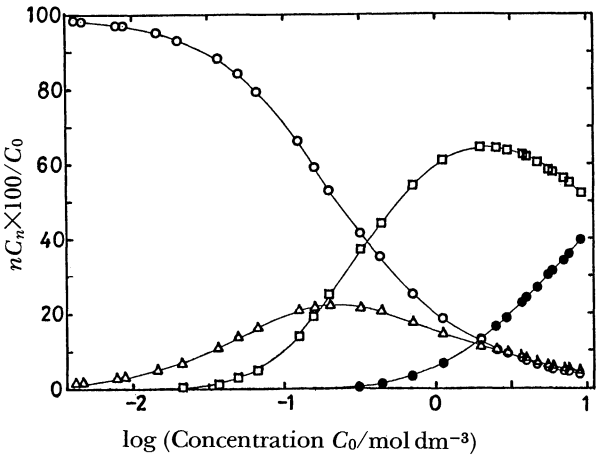

Fig. 3. Concentrations ($nC_n \times 100/C_0$) calculated by a monomer-dimer-tetramer-octamer model for heptane solutions of 3-pentanol.
○: a monomer, △: a dimer, □: a tetramer, ●: an octamer.

Fig. 2 for heptane solutions of 1- pentanol and in Fig. 3 for heptane solutions of 3-pentanol as functions of the logarithm of the alcohol concentration at 25 °C. Figure 2 shows that both monomer and dimer exist over all the alcohol concentrations from 0.0023 mol dm^{-3} to neat 1-pentanol. A monomer is predominant at lower concentrations and then decreases with an increase in the alcohol concentration. A dimer increases gradually with an increase in the alcohol concentration, reaches its maximum value of 16% at about 0.1 mol dm^{-3}, and thereafter decreases with an increase in the alcohol concentration. A tetramer, which appears at about 0.01 mol dm^{-3}, increases with an increase in the alcohol concentration and reaches its maximum value of 60% at about 0.8 mol dm^{-3} (log 0.80=−0.097). An octamer appears in the vicinity of 0.1 mol dm^{-3} and increases with an increase in the alcohol concentration. It can, therefore, be considered that the absorption of the heptane solution of 1-pentanol can be best fitted by a monomer-dimer model at concentrations below 0.02 mol dm^{-3} (log 0.02=−1.7), by a monomer-dimer-tetramer model in the concentration range of 0.02—0.2 mol dm^{-3}, and by a monomer-dimer-tetramer-octamer model at concentrations above 0.2 mol dm^{-3}.

For heptane solutions of 3-pentanol, Fig. 3 shows that the absorption can be best explained by a monomer-dimer model at concentrations below 0.03 mol dm^{-3}, by a monomer-dimer-tetramer model in the concentration range of 0.03—0.5 mol dm^{-3}, and by a monomer-dimer-tetramer-octamer model at concentrations above 0.5 mol dm^{-3}. Figure 3 shows that the maximum values are 22% at 0.18 mol dm^{-3} (log 0.18 =−0.74) for a dimer and 65% at 2.2 mol dm^{-3} (log 2.2=0.34) for a tetramer. These maximum values are larger than those in the respective heptane solutions of 1-pentanol. The concentration of an octamer is less than that at the same alcohol concentration in the heptane solutions of 1-pentanol. Figures 2 and 3 show that the concentrations of an octamer, a tetramer, a dimer, and a monomer are 65, 30, 3, and 2% for pure 1-pentanol, and 39, 52, 5, and 4% for pure 3-pentanol, respectively.

In dielectric relaxation studies,[4,5] on the other hand, the dielectric absorptions for 1- and 3-pentanols have been resolved into three Debye-like dispersion regions. The limiting low- and high-frequency dielectric constants, ε_0, ε_1, ε_2, and ε_3, of the three dispersion regions at 25 °C are 15.10, 3.37, 2.85, and 2.23 for 1-pentanol, and 13.38, 3.20, 2.75, and 2.23 for 3-pentanol, respectively. The three dispersion regions have been assigned to a linear chain polymer, a chain dimer and trimer, and a free monomer. The concentrations of a linear chain polymer(C_1), a nonpolar cyclic polymer(C_R), a chain dimer and trimer(C_2), and a free monomer(C_3) have been obtained by applying a modified Kirkwood-Fröhlich equation to each dispersion region.[4] The percentages of C_1, C_R, C_2, and C_3 against the gross concentration are 72, 5, 6, and 17% for 1-pentanol, and 66, 14, 5, and 15% for 3-pentanol, respectively, at 25 °C. From a comparison of the dielectric results with the near-IR results, therefore, it may be considered that the linear chain polymer, nonpolar cyclic polymer, chain dimer and trimer, and free monomer assigned in the dielectric study correspond to the octamer, tetramer, dimer, and monomer respectively obtained in the near-IR study. The comparison also indicates that a linear chain octamer decreases from 65(72)% for 1-pentanol to 39(66)% for 3-pentanol because of the steric hindrance of the alkyl groups on both sides of the hydroxyl group.[4] The number in parentheses is the concentration obtained in the dielectric study. A nonpolar cyclic tetramer increases from 30(7)% for 1-pentanol to 52(15)% for 3-pentanol. The concentration of a nonpolar cyclic tetramer in the near-IR results is much larger than that in the dielectric results. As a possible cause of the difference of the concentration, it is considered that, in the dielectric study, the concentrations of a free monomer and a linear dimer may contain experimental errors because of the lack of higher-frequency data in the absorption. Therefore, the concentration of a nonpolar cyclic tetramer also contains experimental errors. However, it is noticeable that the coexistence of a monomer and three hydrogen-bonded species were recognized in two different methods. For pure 1- and 3-pentanols, the concentrations of a free monomer and three hydrogen-bonded species, as calculated by means of a monomer-dimer-tetramer-octamer model in the near-IR measurements, agree roughly with the dielectric relaxation results. Moreover, the concentrations of these four species have also been obtained for heptane and cyclohexane solutions of 1-decanol in a dielectric relaxation study.[5] Unfortunately, the measurements of the same alcohol could

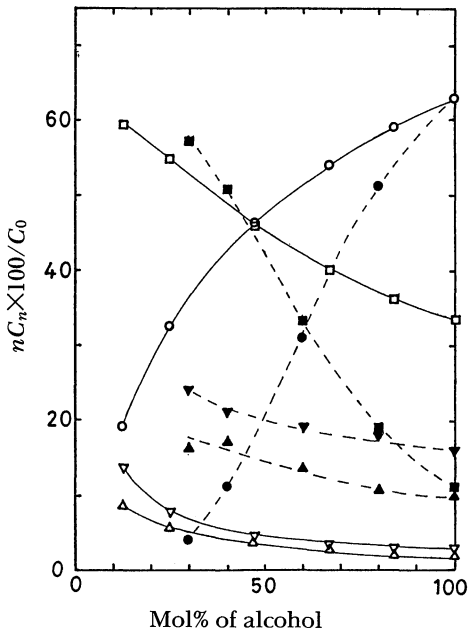

Fig. 4. Concentrations ($nC_n \times 100/C_0$) obtained in near-IR results and dielectric results. Near-IR results are shown by solid lines for heptane solutions of 1-pentanol.
▽: a monomer, △: a dimer, □: a tetramer, ○: an octamer
Dielectric results are shown by dotted lines for heptane solutions of 1-decanol.
▼: a free monomer, ▲: a dimer and trimer, ■: a nonpolar cyclic polymer, ●: a linear chain polymer.

not be carried out for heptane solutions in the two different methods. To compare both results obtained by the two methods, the concentrations of a free monomer and three hydrogen-bonded species in the heptane solutions are shown in Fig. 4 as a function of the mol% of 1-pentanol or 1-decanol. The concentrations of these four species indicate qualitatively similar tendencies regarding the concentration-dependence of 1-pentanol or 1-decanol respectively. The concentration of a linear chain octamer decreases from 63(63)% for pure 1-pentanol(1-decanol) to 36(4)% for a 30 mol% heptane solution. This observation indicates that the depolymerization of a linear chain octamer for 1-decanol occurs more easily than that for 1-pentanol. Therefore, the concentration of a nonpolar cyclic tetramer increases from 33(11)% for pure 1-pentanol(1-decanol) to 52(57)% for a 30 mol% heptane solution. Both the free monomer and the linear dimer increase gradually as 1-pentanol or 1-decanol is diluted with heptane.

It may be concluded that, from a comparison of the near-IR results with the dielectric results, we can recognize at least the coexistence of a free monomer, a chain dimer, a nonpolar cyclic tetramer, and a linear chain octamer at higher concentrations of 1- and 3-pentanols in heptane at 25 and 35 °C.

Some authors have reported a monomer-dimer-tetramer model for solutions of normal alcohol in a nonpolar solvent.[12-15] However, their measurements were made at a low alcohol concentration range (up to 0.15 mol dm^{-3}). In a low concentration range below 0.15 mol dm^{-3}, it is shown in Fig. 2 that the absorbance data can be satisfactorily fitted by a monomer-dimer-tetramer model. Moreover, Brink and Glasser[13] reported a monomer-linear dimer-cyclic tetramer model for solutions of ethanol in heptane in a low concentration range (up to 0.078 mol dm^{-3}). Ibbitson and Moore[18] also reported a monomer-linear dimer and trimer-cyclic polymer model for normal alcohol in cyclohexane in a low concentration range. Our analysis of the experimental data is in agreement with their model and, additionally, proposes the existence of a linear chain octamer at concentrations above 0.35 mol dm^{-3}.

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