^1H and ^2H NMR Studies of Mixtures 2,6-Lutidine/Water Near the Lower Critical Solution Point

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Deuteron spin-lattice relaxation time (T_1) measurements of binary mixtures 2,6-lutidine/D_2O have been done near the lower critical solution point ($T_{C,L}$), $\varepsilon = (T - T_{C,L})/T_{C,L} \geqq 10^{-5}$. Singularities are observed at $T_{C,L}$. The changes in the slope of T_1 (^2H) $= f(T)$ can be interpreted as due to the effect of concentration changes on T_1 and simultaneously strong overlaping of ^2H NMR signals from coexisting phases. In the two-phase region, ca. 2 °C above $T_{C,L}$ two D_2O signals with very strong temperature evolution have been detected. Similar doubling of 2,6-lutidine ^1H NMR signals has been observed already at $T - T_{C,L} \leqq 1$ °C. It is shown that the two signals arise from the nuclei in two coexisting phases; they are not due to pecularities of hydrogen bond. The difference between chemical shifts of both D_2O signals $\delta' - \delta''$ possess the property of an order parameter, i.e. $\delta' - \delta'' \sim \varepsilon^\beta$ with $\beta = 0.336 \pm 0.030$.

Key words: NMR spectra / Critical phenomena / Hydrogen bonding / Solutions.

1. Introduction

Aspects of liquid-liquid equilibria and critical phenomena are studied by means of a large variety of physical and chemical methods. The competence, shortcommings and advantages of the different methods are reviewed in literature, e.g. [1, 2]. Reported NMR studies on this field are focused on the spin-echo measurements of self diffusion and on the determination of the spin-lattice relaxation time T_1 [3]. There has been noticed a weak influence of the critical state on the NMR signals. After the chemical shifts studies reported some years ago [4, 5], recently some new features and possibilities of high resolution NMR have been demonstrated [6–9]. It has been shown [8] that in the two-phase region the difference of chemical shifts of protons involved in molecular association behaves as a function of temperature like an order parameter.

Studies of NMR relaxation T_1 (^2H) and other quadrupolar nuclei in the critical region are absent. But, as it has been shown in [10], the deuterium quadrupole coupling constant (e^2Qq/h) of D_2O is changing drastically when the composition of a binary mixture DMSO/D_2O changes from its value around ca. 0.95 mol fraction of D_2O. The critical concentrations of the majority of binary aqueous mixtures are close to this value. Thus a strong influence of local concentration fluctuations in the critical region on the quadrupolar relaxation rate of D_2O can be expected.

The purpose of this work was a precise ^1H and ^2H high resolution NMR study of aqueous (H_2O and D_2O) solutions of 2,6-lutidine in the critical region, i.e. in the vicinity of the lower critical solution point ($T_{C,L}$). This system has been chosen because precise measurements of the phase diagram and other critical data are available [11–15]. Moreover the critical anomalies of ^1H NMR chemical shifts and linewidth in 2,6-lutidine/H_2O solutions have been reported [5]. On the other hand, $T_{C,L}$ of this system is convenient, facilitating precise temperature measurements.

2. Experimental

The ^1H and ^2H NMR studies have been performed with a BRUKER CXP 200 spectrometer operating at 200 MHz (^1H) and 30.18 MHz (^2H), respectively. The ^2H relaxation times (T_1) have been measured by using the inversion-recovery pulse sequence ($\pi - \tau - \pi/2$) in the usual way. The T_1 values have been determined at 20 different τ. The delay time between two sequences was $\geqq 10\ T_1$. The reproducibility of T_1 is within 2%.

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A superconducting magnet with 130 mm bore diameter was used. The NMR signal coil was placed into an 80 (outside diameter) × 90 mm (height) two-walls brass-copper cylinder within a glass dewar. The circulating thermostating fluid (CCl_4 or n-butanol) flows first into the inner copper cylinder and then back through the spacing between the inner and outer cylinder. The fluid is pumped through a copper spiral placed in an isolated water bath (20 l volume). The temperature of the water bath was controlled by a thermostat (LAUDA). The probe temperature was measured by a thermosensor containing 5 copper-constantan contacts placed very close to the NMR signal coil. Its other contacts were placed in an isolated bath with water–ice mixture. The thermosensor was connected to a digital microvoltmeter; the achieved thermoelectric power was amplified 1:100 and recorded. This allowed a continuous control of the temperature drift during the whole period of measurements. The temperature at the sample was changed by a change of the water thermostat. A typical thermogram is presented in Figure 1. A temperature stability of $\pm 0.005\,^{\circ}C$ for the range $+10 \leqq T/^{\circ}C \leqq 50$ and $\pm 0.01\,^{\circ}C$ for $+50 \leqq T/^{\circ}C \leqq 90$ can be assumed in a period of $\geqq 24$ h.

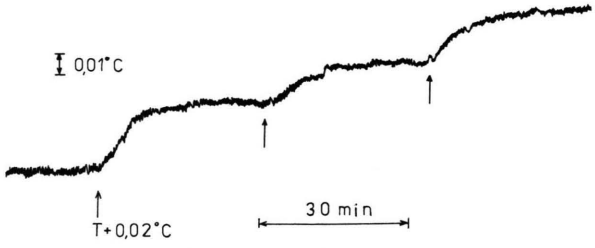

Fig. 1. A typical thermogram of temperature stability for a precise NMR measurement.

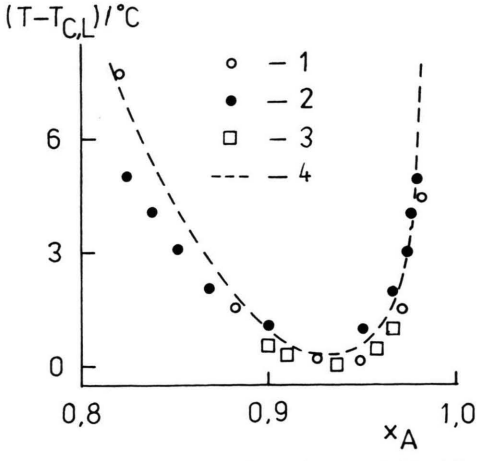

Fig. 2. Phase diagrams for mixtures 2,6-lutidine/H_2O (or D_2O) in the region near $T_{C,L}$: 1 – with D_2O, this work, $T_{C,L} = 28.35\,^{\circ}C$; 2 – with H_2O, this work from integrated doubled ^1H NMR signals; 3 – with H_2O [11], $T_{C,L} = 33.87\,^{\circ}C$; 4 – with H_2O [15]; x_A is the mol fraction of water.

Commercially available 2,6-lutidine (99 + %) and D_2O (isotopic purity 99.8% D) from Aldrich Chemical Co. were used without further purification. H_2O was bidistilled. The samples were prepared by weighting the two components. They were degassed by the freezing-pumping-thawing procedure (3–5 cycles) and sealed in glass ampoules (outside diameter: 10 mm; wall thickness: 1 mm; height: 15–20 mm). Inaccuracies in composition of the samples may be involved by the degassing and sealing procedures. However due to the fact that the phase diagram obtained for these probes is identical to that published up to now in literature (Fig. 2), the error in composition is considered to be negligible.

3. Results and Discussion

The phase diagram for 2,6-lutidine/H_2O is known [11, 14, 15]. Recently [11] a very accurate study of it, close to $T_{C,L}$ ($< 1\,^{\circ}C$), has been performed. The $T_{C,L} = 33.87\,^{\circ}C$ established here is within the values reported earlier [13–15]. The phase diagram for the system 2,6-lutidine/D_2O has not been found in literature. The lower and upper critical solution points ($T_{C,L} = 28.7\,^{\circ}C$ and $T_{C,U} = 228\,^{\circ}C$) have been reported only [16]. Therefore we determined the critical temperatures for all compositions investigated by NMR on the basis of visual observation of the onset of turbidity. $T_{C,L} = 28.35\,^{\circ}C$, following from these studies, is $\sim 0.3^{\circ}$ lower than reported in [16]. The phase diagrams for both systems, 2,6-lutidine/H_2O (D_2O) are shown in Fig. 2, where the coordinate $T - T_{C,L}$ is used for convenience to compare both curves. Except the difference in $T_{C,L}$, no other distinguishing features of the phase diagrams of solutions in H_2O or $T_{C,L}$ near $T_{C,L}$ have been detected.

The measured dependencies of the spin-lattice relaxation time T_1 of D_2O on temperature and concentration are presented in Figs. 3 and 4. Note the much stronger dependency of T_1 on concentration than for the system pyridine/D_2O [17], which is chemically similar to 2,6-lutidine/D_2O.

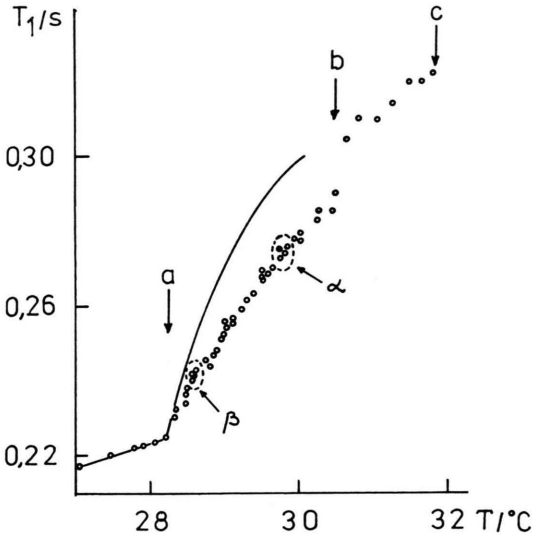

Fig. 3. Dependence of the spin-lattice relaxation time T_1 (^{2}H) of D_2O in 2,6-lutidine/D_2O solution ($x_A = 0.926$) on temperature in the region near $T_{C,L}$: a) onset of turbidity ($T = T_{C,L}$); b) onset of doubling (asymmetry) of D_2O signal; c) two resolved signals observed; solid line – result of T_1 simulation by using (1) and (2). α – points have been measured keeping the constant temperature over 36 h; β – over 10 h.

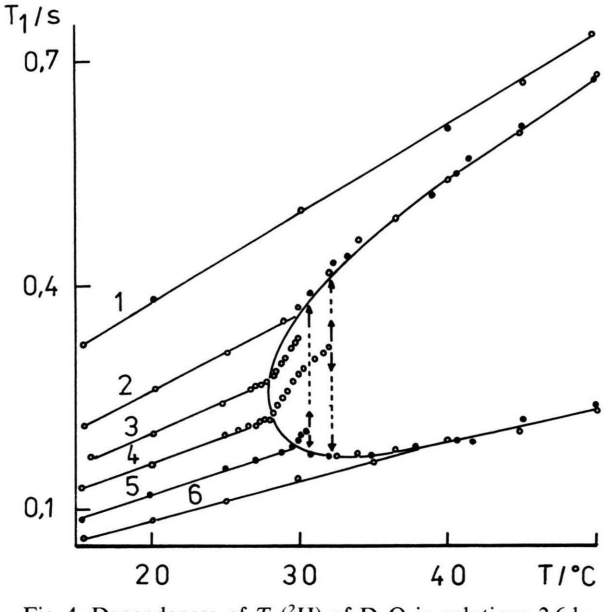

Fig. 4. Dependences of T_1 (^{2}H) of D_2O in solutions 2,6-lutidine/D_2O on temperature at different concentration x_A: 1 – $x_A = 1.0$; 2 – 0.974; 3 – 0.950; 4 – 0.926; 5 – 0.881; 6 – 0.828. The "jumps" of T_1 of the D_2O doubled signals are shown by broken lines with arrows. Comments see in text.

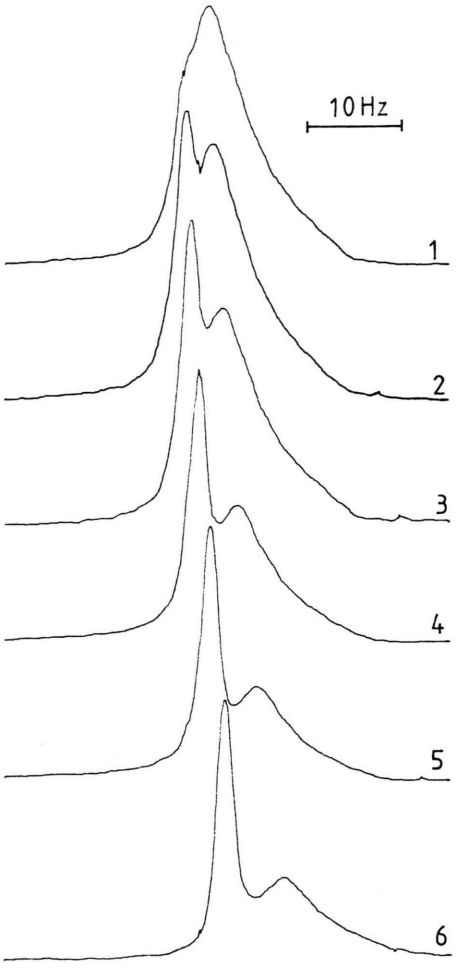

Fig. 5. The temperature evolution of ^{2}H NMR spectra of solution 2,6-lutidine/D_2O ($x_A = 0.926$) close to $T_{C,L}$ = 28.35 °C: 1 – T = 30.35 °C; 2 – 31.83; 3 – 33.15; 4 – 35.05; 5 – 37.95; 6 – 41.55.

Singularities are observed at $T_{C,L}$, i.e. changes in the slope of $T_1 = f(T)$. They are the more pronounced (Fig. 4) the closer the composition of the samples to the critical value x_c. For our system the critical mol fraction of water is $x_c = 0.93$ (Figure 2).

In the two-phase region, ca. 2 °C above $T_{C,L}$, a doubling of the D_2O ^{2}H NMR signal has been detected (Figure 5). The values of T_1 of both signals "jump" on the curve built by the T_1 values at the critical points. These "jumps" are shown on Figure 4. It is evidenced that the two signals arise from the D_2O deuterons in two coexisting phases. Hence it may by suspected that the appearance of these two signals only 2 °C away

from $T_{C,L}$ is due to nonequilibrium, i.e. to the step change of the external temperature. In order to check this possibility some measurements have been done in the range $|T-T_{C,L}|<2\,°C$, keeping the temperature constant over 10–36 h (Figure 3). No signal doubling has been detected. The question arises whether the change in slope of $T_1=f(T)$ is due to the critical fluctuations, or its origin is inhomogeneous broadening of the signals in the two-phase region. In other words, there are registered two D_2O signals even at $|T-T_{C,L}|\leqq 2\,°C$ but they are not resolved because the difference of their chemical shifts is smaller than their halfwidth. This possibility can be clarifyed by a simple simulation of the T_1 behavior with changing T.

The magnetisation $M(t)=1-2\exp(-t/T_1)$ can be written as

$$M(t)=x'M'(t)+x''M''(t), \tag{1}$$

where x', x'' are the fractions of deuterons in coexinting phases, and M', M'' are the magnetisations of those phases, relaxing with T_1' and T_1'', respectively. x' and x'' can be expressed as

$$\begin{aligned} x'&=(1/x_A-1/x_A'')/(1/x_A'-1/x_A''),\\ x''&=(1/x_A'-1/x_A)/(1/x_A'-1/x_A''), \end{aligned} \tag{2}$$

where x_A' and x_A'' are the mole fractions of D_2O in the coexisting phases. x_A being the mean mole fraction of D_2O. x_A' and x_A'' are obtained by interpolation of the data shown in the phase diagram (see Figure 2). T_1' and T_1'' are found by interpolation of the $T_1=f(x_A, T)$ data, see Figure 4. The T_1 values calculated by use of (1) and (2) are presented on Figure 3. Thus this simulation reproduces the T_1 behavior above $T_{C,L}$, i.e. the slope of $T_1=f(T)$ increases in the two-phase region. Some discrepancy, see Fig. 3, may arise because the dependence of the chemical shifts for both overlapped signals on temperature was not taken into account in this simulation.

A similar doubling of the 2,6-lutidine proton signals has been observed in the ^1H NMR spectra just ($\leqq 1\,°C$) above $T_{C,L}$ (Figure 6). It has not been detected in earlier studies of this system [5]. Most probably it could not be resolved on the spectrometer operating at lower (60 MHz) frequency but it should have influenced the measured chemical shifts and line widths.

At the first look on the ^1H and ^2H NMR spectra such changes can be mistaken as a manifestation of protonation or other pecularities of hydrogen bonding in this system. And indeed a protonation via an

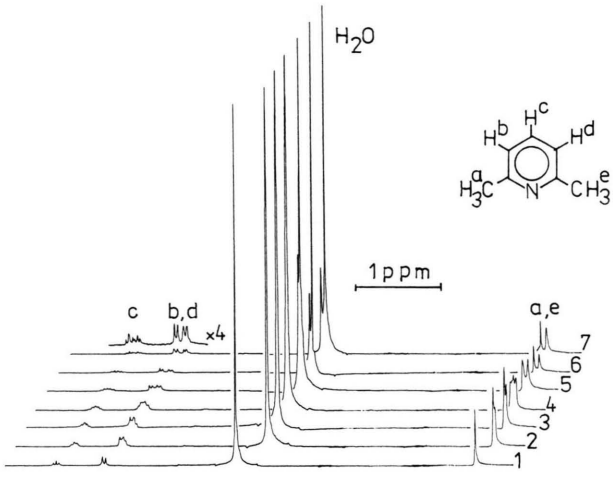

Fig. 6. The evolution of ^1H NMR spectra of a solution 2,6-lutidine/H_2O ($x_A=0.937$) close to $T_{C,L}=33.8\,°C$: 1 – $T=30.0\,°C$ (homogeneous mixture); 2–7 – $T=34.1\pm0.2\,°C$ (two-phase region) after: 2 – $t=0$; 3 – 3 min; 4 – 10 min; 5 – 20 min; 6 – 1 h; 7 – 5 h.

N ··· H–O bridge

$$N\cdots HOH \leftrightarrows NH^+ + OH^-$$

takes place in solutions of pyridine/H_2O and similar compounds [18] quite often. But the concentrations of the components calculated from the integrated split ^1H NMR signals at different temperatures close to $T_{C,L}$ lay on the phase diagram fairly precisely, see Figure 2. Thus it can be concluded that both 2,6-lutidine signals arise from the nuclei in two coexisting phases, too, and there is no reason to attribute the changes in the NMR spectra to pecularities of hydrogen bond.

For the region $|T-T_{C,L}|\geqq 2\,°C$ where both D_2O signals are resolved, dependencies of their chemical shifts (δ' and δ'') on temperature have been measured. As it has been shown in [8], for nuclei involved in equilibrium association processes the difference of chemical shifts $\delta'-\delta''$ can be considered under certain conditions as an order parameter. That means

$$\delta'-\delta''\sim|T-T_{C,L}|^{\beta}, \tag{3}$$

where β is the critical index of the order parameter. The measured $\delta'-\delta''$ as a function of the reduced temperature $\varepsilon=(T-T_{C,L})/T_{C,L}$ is shown on Figure 7. β calculated from these data ($\beta=0.336\pm0.030$) is in a good agreement with that obtained from precise phase diagram determinations close to $T_{C,L}$ [1].

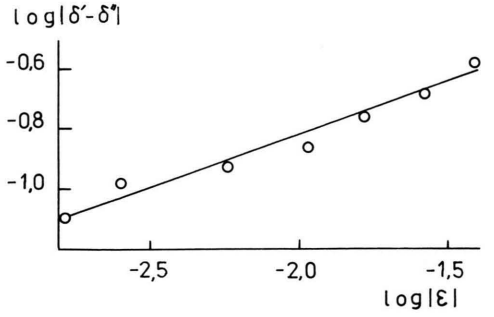

Fig. 7. Plot of $\log|\delta'-\delta''|$ vs. $\log|\varepsilon|$ for estimation of the critical index β.

The main conclusion we take from these studies, is that D_2O deuteron quadrupolar relaxation is unaffected by critical fluctuations even at $|T-T_{C,L}| \sim 0.005\,°C$, i.e. $\varepsilon \sim 10^{-5}$. The singularities of T_1 observed at $T_{C,L}$ can be interpreted as a pure concentrational effect together with inhomogeneous broadening of the D_2O signals. Several physical reasons can be supposed. (i) The diffusional motion is fast enough to average (in time scale of NMR) all local concentration fluctuations to zero. (ii) The dependency of e^2Qq/h on concentration is for 2,6-lutidine/D_2O solutions too weak (in contrast to DMSO/D_2O [10]), or it is monotonous. Thus any deviation ($-\delta x$ or $+\delta x$) from x_A gives rise to a deviations of e^2Qq/h in the opposite direction; this was undetected in T_1 measurements.

The role of inhomogeneous broadening of the NMR signals in the vicinity of the critical point should be noticed as extremely important. The anomalies observed for this and some others systems earlier [5, 19] can be caused by this phenomena but not critical fluctuations.

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