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

Vytautas Balevicius, Norbert Weiden, and Alarich Weiss

Institut für Physikalische Chemie, Physikalische Chemie III, Technische Hochschule Darmstadt, Petersenstraße 20, 6100 Darmstadt, Germany

Z. Naturforsch. 47a, 583–587 (1992); received December 28, 1991

Deuteron spin-lattice relaxation time \( T_1 \) measurements of binary mixtures 2,6-lutidine/D\(_2\)O have been done near the lower critical solution point \( T_{c, L} \). \( \tau = (T - T_{c, L}) / T_{c, L} \geq 10^{-5} \). 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 overlapping 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 \( T - T_{c, L} \leq 1°C \). It is shown that the two signals arise from the nuclei in two coexisting phases; they are not due to peculiarities of hydrogen bond. The difference between chemical shifts of both \( D_2O \) signals \( \delta^d - \delta^s \) possess the property of an order parameter, i.e. \( \delta^d - \delta^s \sim e^{\beta} \) 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, shortcomings 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 \( T_1 \). 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 \( (e^2 Q q / h) \) 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 \((H_2O \text{ and } D_2O)\) 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 CXP200 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 \( \tau \). The delay time between two sequences was \( \geq 10 T_1 \). The reproducibility of \( T_1 \) is within 2%.

Reprint requests and permanent address: Dr. V. Balevicius, Department of Physics, Vilnius University, 2734 Vilnius, Lithuania.

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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) x 90 mm (height) two-walls brass-copper cylinder within a glass dewar. The circulating thermostating fluid (CCl₄ 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 ±0.005 °C for the range +10 ≤ T/°C ≤ 50 and ±0.01 °C for +50 ≤ T/°C ≤ 90 can be assumed in a period of ≥ 24 h.

Commercially available 2,6-lutidine (99+% and D₂O (isotopic purity 99.8% D) from Aldrich Chemical Co. were used without further purification. H₂O 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/H₂O is known [11, 14, 15]. Recently [11] a very accurate study of it, close to \( T_{c,L} \) (<1°C), has been performed. The \( T_{c,L} = 33.87°C \) established here is within the values reported earlier [13–15]. The phase diagram for the system 2,6-lutidine/D₂O has not been found in literature. The lower and upper critical solution points (\( T_{c,L} = 28.7°C \) and \( T_{c,U} = 228°C \)) 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. \( T_{c,L} = 28.35°C \), following from these studies, is ~0.3°C lower than reported in [16]. The phase diagrams for both systems, 2,6-lutidine/H₂O (D₂O) 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 H₂O or \( T_{c,L} \) near \( T_{c,L} \) have been detected.

The measured dependencies of the spin-lattice relaxation time \( T_1 \) of D₂O 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/D₂O [17], which is chemically similar to 2,6-lutidine/D₂O.
Fig. 3. Dependence of the spin-lattice relaxation time $T_1$ ($^2$H) of D$_2$O in 2,6-lutidine/D$_2$O 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$_2$O signal; c) two resolved signals observed; solid line – result of $T_1$ simulation by using (1) and (2). $\alpha$ – points have been measured keeping the constant temperature over 36 h; $\beta$ – over 10 h.

Fig. 4. Dependences of $T_1$ ($^2$H) of D$_2$O in solutions 2,6-lutidine/D$_2$O 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$_2$O 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$_2$O ($x_A = 0.926$) close to $T_{c,L} = 28.35^\circ$C: 1 – $T = 30.35^\circ$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$_2$O $^2$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$_2$O 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 \( T_l = f(T) \) 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 \( |T - T_{c_L}| \leq 2°C \) but they are not resolved because the difference of their chemical shifts is smaller than their halfwidth. This possibility can be clarified by a simple simulation of the \( T_l \) behavior with changing \( T \).

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

\[
M(t) = x'M'(t) + x''M''(t),
\]

where \( x', x'' \) are the fractions of deuterons in coexisting phases, and \( M', M'' \) are the magnetisations of those phases, relaxing with \( T_i' \) and \( T_i'' \), respectively. \( x' \) and \( x'' \) can be expressed as

\[
x' = (1/x_A - 1/x_A')/(1/x_A - 1/x_A''),
\]

\[
x'' = (1/x_A' - 1/x_A)/(1/x_A - 1/x_A''),
\]

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). \( T_i' \) and \( T_i'' \) are found by interpolation of the \( T_i = f(x_A, T) \) data, see Figure 4. The \( T_i \) values calculated by use of (1) and (2) are presented on Figure 3. This simulation reproduces the \( T_i \) behavior above \( T_{c_L} \), i.e. the slope of \( T_i = f(T) \) 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 (\( \leq 1°C \)) 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 peculiarities of hydrogen bonding in this system. And indeed a protonation via an

\[
N \cdots H-O \text{ bridge}
\]

\[
N \cdots HOH \Leftrightarrow \text{NH}^+ + OH^-
\]

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 peculiarities of hydrogen bond.

For the region \( |T - T_{c,L}| \geq 2°C \) where both \( D_2O \) signals are resolved, dependencies of their chemical shifts (\( \delta' \) and \( \delta'' \)) 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

\[
\delta' - \delta'' \sim |T - T_{c,L}|^{\beta},
\]

where \( \beta \) 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. \( \beta \) calculated from these data (\( \beta = 0.336 \pm 0.030 \)) is in a good agreement with that obtained from precise phase diagram determinations close to \( T_{c,L} \) [1].
The main conclusion we take from these studies, is that D₂O deuteron quadrupolar relaxation is unaffected by critical fluctuations even at |T − T_{C,L}| ~ 0.005 °C, i.e. ε ~ 10^{-5}. The singularities of T₁ observed at T_{C,L} can be interpreted as a pure concentration effect together with inhomogeneous broadening of the D₂O 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 ε²Qq/h on concentration is for 2,6-lutidine/D₂O solutions too weak (in contrast to DMSO/D₂O [10]), or it is monotonic. Thus any deviation (−δx or +δx) from x gives rise to deviations of ε²Qq/h in the opposite direction; this was undetected in T₁ 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.

We are grateful to the Alexander von Humboldt Foundation for a fellowship to V. B. and to Prof. Dr. D. Woermann for his valuable suggestions.