Intramolecular Thermal Motions in Liquid *n*-Propanol (+ Glycerol), A Proton Magnetic Relaxation Study. 2

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The proton magnetic relaxation times T_1 and T_2 of the four *n*-propanol species HOC₃D₇, DOCH₂CD₂CD₃, DOCD₂CH₂CD₃, and DOCD₂CD₂CH₃ have been measured at the resonance frequency $\nu = 12$ MHz as a function of the temperature in the range 80 < T/K < 330. T_1 measurements were performed at a second frequency, $\nu = 48$ MHz, as well. Further measurements of the same general kind were done on the mixtures *n*-propanol + 50 mol % glycerol (glycerol- d_5 and $-d_8$) and *n*-propanol + 70 mol % glycerol (glycerol- d_5 and $-d_8$). Isotopic dilution measurements with constant content of propanol and varying degree of deuteration were made to obtain the intramolecular relaxation rates. The proton NMR spectra of the four propanol species were recorded at T = 130 K. From all these data correlation times for the various proton-proton vectors were derived. It turned out that to each motion a slow and a fast mode contribution exists; however, the results are not compatible with the model of a molecule as a system of rigid bodies connected by axes about which rotation occurs. A formal description and interpretation is given involving the molecule concept without the presupposition of a microscopic rigid body.

1. Introduction

In the preceding paper¹ we have shown that the propionic acid molecule in the liquid and glassy state on a microscopic level is not correctly described as an atomic (point) system consisting of three rigid bodies: (1) the planar group C-COO with a hydrogen atom attached to one of the oxygens, (2) the tetrahedron $C-CH_{2}$ -C, and (3) the tetrahedron C-CH₃. In this model all the bars-representing the C-C chemical bonds-are axes of rotation of the rigid bodies relative to one another. The basic criterion for the existence of rigid bodies was whether or not exponential time correlation functions corresponding to the motion of certain intramolecular vectors were found experimentally. Such exponential correlation decays lead to nuclear magnetic relaxation rates which are linear combinations of Lorentzian functions of certain frequencies derived from the NMR resonance frequency, and this functional behavior has not been found. Rather, the Fourier transform of the time correlation function extends to fairly high frequencies which should practically not occur in the frequency distribution connected with rotational diffusive motion of a rigid body. But these frequencies are also in excess of those 3n - 6 vibrations which one normally would allow to be called intramolecular vibrations of a molecule. On the other hand, in appropriate temperature ranges certain higher correlations of intramolecular atomic motions beyond pair correlation could be detected, although it was not possible to extract quantitative information. One might be interested to know how to describe such a system of atoms, called the molecule, which conventionally is taken to be a thing in three-dimensional space. Formally, however, it should be a system in 3n - 6-dimensional space. Nevertheless, experimentally it appears to us in most cases only in one-dimensional space (radial pair correlations); in rare cases it appears in higher dimensional spaces, but it is not a microscopic rigid body or a system of these bodies in three-dimensional space. Before dealing with this problem, which will be done in the Discussion, we wish to report on further experimental results. As a brief denotation of the object we are dealing with we have introduced the name "soft molecule".1

The molecule we studied in the present work contains one methylene group more than propionic acid, but the slow motion

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We performed complete T_1 and partial T_2 measurements on suitably deuterated substances. In the following we shall refer to our propionic acid paper as part 1.1 Deuteron magnetic relaxation studies with pure propanol have already been performed by Versmold² and by Mall.³ In these works T_1 was measured as a function of the temperature down to 130 K; T_1 was measured for each of the groups OD, α -CD₂, β -CD₂, and CD₃, separately. We shall occasionally incorporate the results of Mall's work in this article. 2. Experimental Section All instrumental details were the same as described in part 1. Fully deuterated n-propanol was purchased from the Zentralinstitut für Isotopen-und Strahlungsforschung, Leipzig. It was not possible to purchase the four specifically deuterated npropanols used in this work: HOC3D7, DOCH2CD2CD3, DOCD2- CH_2CD_3 , and $DOCD_2CD_2CH_3$. So we had to prepare these compounds from commercially available propionic acid employing the reaction

part is somewhat smaller. Instead of the carboxyl group we now have a hydroxyl group, thus *n*-propanol is the object of the present

investigation. In the previous paper¹ we had to work with a

mixture of propionic acid and dimethyl sulfoxide (DMSO) in

order to make measurements in the supercooled liquid possible.

With *n*-propanol the pure liquid C_3H_7OH may be supercooled

without difficulties. Yet we wanted to see the effect of binding

the hydroxyl group of *n*-propanol to another strongly H-bond

forming substance for which we chose glycerol. So, besides the

liquid pure n-propanol we also studied the systems 50% n-propanol

+ 50% glycerol and 30% n-propanol + 70% glycerol. The general

procedure of measurement and evaluation is the same as before.1

$$R = C = OH \xrightarrow{\text{LIAID}_4} \xrightarrow{D_2O, D^*} R = CD_2 = OD$$

For the preparation of the propanol containing the α -CH₂ group LiAlD₄ has to be replaced by LiAlH₄. The primary product of the above reaction is obtained in highly diluted form in a diethyl ether solution saturated with H₂O. Drying of this ether phase by the aid of sodium sulfate yielded not more than the azeotropic

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Figure 1. (a) 300-MHz proton magnetic resonance spectra of CH₃, β -CH₂, α -CH₂, and the OH group (from left to right) of pure *n*-propanol at *T* = 130 K. (b) 300-MHz proton spectra of (left) the CH₃, β -CH₂, and α -CH₂ group (top to bottom) and of the (right) OH group of the system *n*-propanol + 70 mol % glycerol at 130 K. The inset shows the α -CH₂ and β -CH₂ spectra again, now in comparison with the CH₂ spectrum of the system propionic acid + 33 mol % DMSO at *T* = 130 K (lowest curve).¹

mixture of propanol with water. After application of a specifically developed procedure using a Soxhlet extractor we were successful in removing the water quantitatively without loss of product due to adsorption on the molecular sieve employed as a drying substance. During these operations the degree of deuteration of the hydroxyl group sank somewhat due to proton exchange with the slightly acid molecular sieve material. Repeated deuteron exchange and distillation with the aid of CH₃OD was employed until in all positions to be deuterated the degree of deuteration was >99%.

3. Results and Evaluation

3.1. Glass Temperatures. The glass temperature T_g of propanol is known to be 95 K;⁴ another source gives $T_g = 98$ K.⁵ For glycerol we find a rather wide range of values in the literature; the lowest is 183 K,⁴ and the highest is $T_g = 190.9$ K.^{6,7} The glass temperature for the propanol-glycerol mixtures we have measured by application of the differential scanning calorimetry method. The results are *n*-propanol + 50 mol % glycerol, $T_g = 164$ K; *n*-propanol + 70% glycerol, $T_g = 178$ K (see also ref 1).

3.2. Proton Magnetic Resonance Spectra. In Figure 1 we show the proton magnetic resonance spectra at $\nu = 300$ MHz of the molecules HOC₃D₇, DOCH₂CD₂CD₃, DOCD₂CH₂CD₃, and DOCD₂CD₂CH₃ in the pure liquid and in the mixture with glycerol-d₅, respectively, all recorded at a temperature T = 130 K. For pure *n*-propanol the line shapes of the alkyl protons are Lorentzian and thus allow a direct determination of T_2 . The line widths are entirely determined by the motion of the respective proton-proton vector, and $1/T_2$ is proportional to the correlation time. The dominant influence of the motion is understandable since we are far above the glass temperature. In Table 1 we

TABLE 1: Spin-Spin Proton Relaxation Rates of Pure (Partially Deuterated) *n*-Propanol As Determined from the Line Width of the NMR Spectrum at T = 130 K, Compared with $1/T_2$ Values Found as the FID of the NMR Signal ($T_2 = 2/\Delta$)

proton species	line width Δ (s ⁻¹)	$\frac{1/T_2}{(\text{spectrum}) (\text{s}^{-1})}$	$\frac{1/T_2}{(\text{FID}) (\text{s}^{-1})}$
CH ₃	2.88×10^{4}	$\begin{array}{c} 1.44 \times 10^{4} \\ 2.07 \times 10^{4} \\ 4.41 \times 10^{4} \\ 2.7 \times 10^{4} \end{array}$	1.6×10^{4}
β-CH ₂	4.14 × 10 ⁴		2.3 × 10^{4}
α-CH ₂	8.83 × 10 ⁴		4.8 × 10^{4}
OH	5.4 × 10/ ⁴		6 × 10^{4}

demonstrate that T_2 results derived from these proton resonance spectra are in good agreement with those obtained from FID measurements. Table 1 also shows that for the OH protons there is no longer such agreement; in fact the OH proton motion is effected by H-bonding and thus is comparatively slow such that the condition

$$(\Delta\omega^2)^{1/2}\tau\ll 1$$

is no longer fulfilled. The OH line shape may be understood as a superposition of Gaussian and Lorentzian curves. The line width of the alkyl protons increases in the order CH₃, β -CH₂, α -CH₂, which confirms the expectation that we get a stronger retardation of motion the closer we get to the OH group, the center of molecular interaction.

This is also clearly seen from the alkyl proton spectra in the mixture system propanol + glycerol 70% (see Figure 1b). The central line representing motional narrowing becomes increasingly more dominant, and the shoulders become weaker as we go from α -CH₂ to CH₃. 130 K is now a slightly lower temperature compared to the glass temperature than that which was found with the $C_2H_5COOH + DMSO$ system,¹ but all these spectra no longer have relative maxima at both sides of the central peak, so we are unable to determine proton-proton distances directly from these spectra as we did with the propionic acid-DMSO system in part 1. In the inset of Figure 1 we show the comparison of the propionic acid CH₂ spectrum obtained in part 1 with both the CH₂ spectra of the present mixture, and there is no doubt that the proton-proton distance obtained there, namely, r(H-H) = $1.82 \pm 0.05 \times 10^{-8}$ cm, is also valid here. So, all the alkyl proton resonance lines in the propanol mixture are narrower than in the propionic acid system, but the OH line width is broader in the former case (see Figure 1b). The line is of Gaussian shape showing no motion, and thus with a second moment $\Delta \omega^2 = 6.33 \times 10^9 \, \text{s}^{-2}$

yields a coupling constant of $C = 1.41 \times 10^{10} \text{ s}^{-2}$. The corresponding coupling constant for the C₂D₅COOH + 30% DMSO system is $2.87 \times 10^9 \text{ s}^{-2.1}$ Due to the higher number density of protons in the former system one would in fact expect $C(\text{propanol-}d_7 + \text{glycerol-}d_5) > C(\text{propionic acid-}d_5 + \text{DMSO-}d_6)$; however, as we shall see below, other effects are of importance too.

3.3. Relaxation Rates. In Figure 2 we show the proton $1/T_1$ relaxation rates of the four species of pure *n*-propanol: OHC₃D₇, ODCH₂CD₂CD₃, ODCD₂CH₂CD₃, and ODC₂D₄CH₃ at a frequency $\nu = 48$ MHz as a function of the reciprocal temperature. In Figure 3 the proton $1/T_1$ relaxation rates at 12 MHz of the same four species as given in Figure 2 are depicted, together with the deuteron relaxation rates of the four species ODC₃H₇, OHCD₂-CH₂CH₃, OHCH₂CD₂CH₃, and OHC₂H₄CD₃ in part of the temperature range. The deuteron relaxation rates were measured at almost the same frequency, i.e., $\nu = 13.8$ MHz.

In Figures 2 and 3 some typical features have to be stressed. The most important fact is that the log $1/T_1$ vs 1/T curves for the various groups are more strongly overlapping than for the system propionic acid + DMSO.¹ In other words, slow motion and fast motion are now separated to a lesser degree. The OH protons have their relaxation maximum at the highest temperature,



Figure 2. Proton $1/T_1$ at $\nu = 48$ MHz for the four groups of *n*-propanol (neat liquid) as a function of the reciprocal temperature.



Figure 3. Proton $1/T_1$ at $\nu = 12$ MHz for the four groups of *n*-propanol (neat liquid) as a function of the reciprocal temperature. For comparison some deuteron relaxation rates measured at $\nu = 13.8$ MHz are included in the lower part of the figure (data from ref 3); they are given as $(1/T_1)10^{-2}$; |-|| indicates the temperature range of multiexponential decay of CH₃ magnetization.

thus their motion is slowest. It is instructive to see this behavior in a wider context: the $\log 1/T_1$ vs 1/T curve of the methyl protons as shown in Figures 2 and 3 has a weak shoulder at $1000/T \approx 6.2$ K⁻¹ which represents the slow motion residuum due to the OH group being effective for the motion of CH₃. In pure ethanol such a residuum of the slow OH motion does not effect the movement of the CH₃ protons.⁸ Furthermore, in the system propionic acid + DMSO¹ where the fixation of the H-bonded group is stronger than in both the pure alcohols, EtOH and *n*-PrOH, the effect of this slow motion on the methyl proton relaxation has become still stronger; what was a shoulder for *n*-propanol now is a separate maximum of the curve $\log 1/T_1$ vs 1/T.

Next let us turn to the $1/T_1$ relaxation curves for the methylene protons. Before dealing with their OH slow motion residua we notice the surprising feature that at the lowest temperatures accessible in our study, 1000/T > 9, the slope of $\log 1/T_1 vs 1/T$ becomes less negative. This is indeed part of a flat shoulder on the low temperature side of the total relaxation curve,^{9,10} indicating that there is some rapid motion, the correlation time of which is of the order of ω^{-1} at these temperatures. After this outlook to the low temperature range we return to the region around the main maximum of the $\log 1/T_1 vs 1/T$ curve for the CH₂ protons. It will be seen from Figures 2 and 3 that for *n*-propanol both of them practically do not show any residuum of the slow OH motion at the high temperature side of the maximum. This is so in spite of the fact that they are closer to the hydroxylic group than CH₃.

If glycerol or $D_2O + LiCl$ is added to EtOH, so as to strengthen the bonding of the OH group, then for CH_2 only the slow motion



Figure 4. Proton $1/T_1$ at $\nu = 48$ MHz for the four groups of *n*-propanol in its mixture with 50 mol % glycerol (glycerol- d_5 for the OH protons, glycerol- d_8 for all other protons) as a function of the reciprocal temperature. |-| is as described in Figure 3.



Figure 5. Same as Figure 4, however $\nu = 12$ MHz.

residuum due to OH remains detectable, any higher mobility part is pushed away in the direction of lower temperatures; however, in the course of this process, the total correlation time is lengthened so much as compared to the relaxation time that the resulting effective dipole-dipole coupling constant is reduced.¹ As a consequence the fast motion part of CH₂ is almost no longer detectable.^{11,12} And this is, as far as we can see, also the behavior of the CH₂ proton relaxation in the "strong bonding" system propionic acid/DMSO.¹ Unfortunately we have no knowledge of the respective properties of pure propionic acid because the liquid cannot be sufficiently supercooled.

In this situation the question arises: what is the behavior of the methylene proton $1/T_1$ relaxation if a stronger interaction partner is added to *n*-propanol? Figures 4–7 give the answer. First let us consider the effect of the smaller amount of added glycerol, i.e., the mixture propanol/glycerol, 50:50 mol% (Figures 4 and 5). Indeed for α -CH₂ no shoulder is growing on the higher temperature side of the log $1/T_1$ vs 1/T curve (1000/T < 4.5)as a residuum of the slow OH motion, rather the slow motion part of $1/T_1$, i.e., the higher temperature left-hand part, with its definite maximum follows the displacement of the OH relaxation maximum to higher temperatures (slower motions) while the part representing comparatively fast motion essentially stays where it was and in this way forms a shoulder on the lower temperature side of the total log $1/T_1$ vs 1/T curve.

So far we have dealt with the behavior of the α -CH₂ protons. Now let us turn to the β -CH₂ proton relaxation, considering first the 48-MHz results, Figure 4. We see that there is a broad maximum of the log $1/T_1$ vs 1/T curve; the system has not yet followed a definite way to react on the addition of glycerol. But at a lower frequency, $\nu = 12$ MHz, we can detect that for β -CH₂ the tendency is more in the direction of the CH₃ group than of α -CH₂, so it takes a behavior which is similar to that of CH₃. There has appeared a shoulder on the left-hand side of the total



Figure 6. Filled symbols: proton $1/T_1$ at $\nu = 12$ MHz for the four groups of *n*-propanol in a mixture with 70% glycerol (glycerol- d_5 for OH protons, glycerol- d_8 for all other protons) as a function of the reciprocal temperature. For a more extended temperature range see Figure 11 of ref 9. Open symbols with the same group assignment give deuteron relaxation rates $(1/T_1)10^{-2}$ at $\nu = 13.8$ MHz. |-| is as described in Figure 3.



Figure 7. Same as proton data of Figure 7 (and Figure 11 of ref 9), however, $\nu = 48$ MHz. |--| is as described in Figure 3.

relaxation maximum. In a somewhat preliminary and anticipating way we may say that a shoulder or even a partial maximum at the high temperature side of a main maximum is the reflection of a slow motion residuum on a fast motion; a shoulder or flat maximum at the low temperature side of the main relaxation effect is a manifestation of persistance of fast motion. However, superimposed on the latter process is a gradual restriction of the range of rotational freedom due to decreasing available thermal energy.

Next, there is more glycerol added to *n*-propanol; the results are shown in Figures 6 and 7. Further $1/T_1$ results for the range 7 < 1000/T < 12 K⁻¹ at $\nu = 12$ MHz are given in Figure 11 of ref 9. The lower frequency measurements yield more detail, and so we shall only describe Figure 6. In this figure we have also included some deuteron relaxation results at 13.8 MHz from Mall's work.³ It will be seen that in the temperature range covered by both measurements the qualitative features are the same.

We are beginning with the log $1/T_1$ vs 1/T curve for the methyl protons. At $1000/T \approx 4.1 \text{ K}^{-1}$ there is a shoulder on this curve which is almost a relative maximum. The maximum of the OH relaxation is at $1000/T = 3.85 \text{ K}^{-1}$, so it is clear that the CH₃ shoulder (almost a maximum) is the slow motion residuum due to OH in the fast motion of CH₃. The OH-OH vector is an

intermolecular vector, and since it is inappropriate to base our treatment on intermolecular vectors there is a need to introduce intramolecular vectors as tools to analyze the observed relaxation effects. From all we have found in the present and in the preceding paper it is obviously legitimate to consider the OH proton-methyl carbon vector as one of the longest intramolecular vectors to be the vector with the slowest motion with a time constant equal to that of the intermolecular OH-OH vector (more details will be given in the Discussion). It follows that the shoulder (almost a maximum) at $1000/T = 4.1 \text{ K}^{-1}$ is the residuum of the OH \rightarrow C_{Me} vector motion in the fast motion of the methyl proton-proton vector, and furthermore it follows that the shoulders (almost maxima) in the CH₃ log $1/T_1$ vs 1/T curve at 1000/T = 5.1 and 5.7 K⁻¹ are the residua of the motions of the vectors $C_{\alpha-CH}$, \rightarrow C_{Me} and $C_{\beta-CH_2} \rightarrow C_{Me}$, respectively, in the fast motion of the CH₃ protons. The situation is analogous for the β -CH₃ protons; the two relaxation maxima at 1000/T = 4.0 and 5.0 K⁻¹ are the residua of the motions of the vectors $OH \rightarrow C_{\beta-CH_2}$ and $C_{\alpha-CH_2}$ $\rightarrow C_{\beta-CH_2}$ in the fast motion of the β -CH₂ proton-proton vector. However, there is one difference when compared with the behavior of the CH₃ proton motion: for the methylene protons we have a much stronger restriction of rotational space accessible to dipoledipole interaction fluctuations,¹ and thus the maximum at 1000/T= 5.5 K^{-1} is already significantly suppressed. If we follow this scheme, the maximum of the α -CH₂ relaxation at 1000/T = 4.0 K^{-1} is the residuum of the motion of the OH $\rightarrow C_{\alpha-CH}$, vector in the fast motion of the α -CH₂ H-H vector, to which the low temperature shoulder at $1000/T = 5.5 \text{ K}^{-1}$ has to be ascribed. The motion appears as a shoulder only because the rotational space is strongly restricted, a fact which is understandable because the α -CH₂ group is close to the center of the H-bond interaction. Finally, the shoulder at $1000/T = 4.9 \text{ K}^{-1}$ is the residuum of the $C_{\alpha-CH}$, $\rightarrow C_{\beta-CH}$, vector motion in the α -CH₂ proton-proton vector movement. Before leaving this description of the $1/T_1$ results it should be remarked that according to Figure 11 of ref 9 the intermolecular OH-OH proton relaxation rate at low temperatures shows a broad flat maximum which now is clearly separated from the main maximum, because the latter is strongly shifted to higher temperatures as compared with the pure propanol liquid. In pure propanol this fast motional effect formed a shoulder on the low temperature side of the main relaxation effect. Such a flat maximum in the low temperature range has also been observed for the OH-OH intermolecular relaxation rate in the system propionic acid/DMSO.1 Another remarkable feature of our results is the fact that $1/T_1$, when plotted versus 1000/T, passes entirely smoothly through the region where $T = T_g$.

In Figure 8 we show the transverse proton relaxation rates $1/T_2$ as a function of the reciprocal temperature for the four groups of *n*-propanol. For comparison some $1/T_1$ data are included. It will be seen that at temperatures below the $1/T_1$ maximum temperatures $1/T_2$ is many orders of magnitude larger than $1/T_1$. Measurements have been performed only for $1000/T < 9 K^{-1}$. We learned from our previous study¹ on the system propionic acid/DMSO that $1/T_2$ does not change for temperatures lower than the glass temperature, and thus we feel entirely justified to state that $1/T_2$ is constant for $1000/T > 9 K^{-1}$ here as well. Thus, none of the "particular structures" of the log $1/T_1$ vs 1/T curves are reflected on the log $1/T_2$ vs 1/T curves. Of course, there is a theoretical justification of this statement as will be seen below. In Figure 9 we give some further $1/T_2$ results which are needed for the evaluation to be described in section 4.

For this evaluation the raw material must be the intramolecular relaxation rate, not the total relaxation rate we have shown so far in Figures 2–9. The intramolecular relaxation rates are obtained by suitable isotopic substitution techniques:

$$\left(\frac{1}{T_1}\right)_x = \left(\frac{1}{T_1}\right)_{\text{intra}} + x \left(\frac{1}{T_1}\right)_{\text{inter}}$$
(1)



Figure 8. Proton $1/T_2$ at $\nu = 12$ MHz for the four groups of *n*-propanol (neat liquid) as a function of the reciprocal temperature.



Figure 9. Proton $1/T_2$ at $\nu = 12$ MHz for the four groups of *n*-propanol in the mixture with 50 mol % glycerol (open symbols) and with 70 mol % glycerol (filled symbols) as a function of the reciprocal temperature.

where x is the mole fraction of the proton-containing compound (propanol) in the mixture with the deuterated compound. In the case of the system propanol/glycerol 50:50 the content of glycerol is kept constant. We made measurements at x = 0.5 and x =1.0 in the systems pure *n*-propanol and propanol/glycerol 50:50. From these measurements we determined the two unknowns (1/ T_1)_{intra} and (1/ T_1)_{inter}. We define a quantity y by the relation

$$\left(\frac{1}{T_1}\right)_{\text{intra}} = y\left(\frac{1}{T_1}\right) \tag{2}$$

The results for the y values were approximated by a linear relation with respect to 1000/T:

$$y = u \, \frac{1000}{T} + v \tag{3}$$

The numerical results are collected in Table 2. In the system propanol/glycerol 30:70 the experimental proton relaxation rates are almost intramolecular relaxation rates, because the glycerol is fully deuterated. Due to a poor signal-to-noise ratio it was not possible to perform a further isotopic dilution experiment, for instance with x = 0.5 in eq 1. Straightforward interpolation with the aid of the propanol/glycerol 50:50 results was not possible

because, very surprisingly, it turned out that the y value of the 50:50 propanol/glycerol mixture is smaller than that of the pure alcohol. In view of the spin-spin interaction, one representative example is shown in Figure 10, and we had to perform an interpolation using second-degree polynomials for an appropriate set of temperatures. The numerical results of this procedure are included in Table 2. In Figures 11 and 12 we show some results for the intramolecular only relaxation rates. It will be seen that all essential features of Figures 2, 3, 6, and 7, which we described qualitatively, are preserved a fortiori by this method. The deuteron relaxation rates shown in Figures 3 and 6 are intrinsically intramolecular relaxation rates. For the system propionic acid/ DMSO the special features of the log $1/T_1$ vs 1/T curve were also appearing in the $log(1/T_1)_{inter}$ vs 1/T representation, certainly an interesting feature in itself which, however, we had no occasion yet to consider in detail. Here in particular for the system propanol/glycerol 30:70 the question whether $(1/T_1)_{inter}$ as well has certain "wave structures" must be left open.

4. Correlation Times and Correlation Functions

4.1. General. The total time correlation function of the spherical harmonic of second degree (divided by r^3) associated with a given proton-proton vector and normalized to unity at t = 0 we wish to represent as a linear combination of stretched exponentials or Kohlrausch-Williams-Watts "correlation" functions.¹

$$g(t) = \sum_{k} b_k \exp(-(t/\tau_{WK})^{\gamma_k}), \quad 0 < \gamma_k \le 1$$
 (4)

with

$$\sum b_k = 1 \tag{5}$$

As has been explained in the preceding paper¹ it is a general experience that the case $\gamma = 1$ (spectral density Lorentzian) has to be excluded; this statement is valid for the present study as well and will only briefly be discussed again. In the present paper we do not write down or use for computation the complete Woessner-Wallach-Versmold formula which now has $27 b_k$ terms (or 8 for jumpwise internal rotation).¹³ The corresponding relaxation maxima cannot be resolved, and too short relaxation times prevent the scanning of the whole correlation function which would be needed to examine the (very complicated) rigidity conditions. The only exception we make in our analysis on the following pages regards the $\sum b_k = 1$ condition for those contributions which can be resolved. The spectral density of the stretched exponential cannot be written in a closed mathematical form. Therefore, for the evaluation we use the spectral densities belonging to the Cole-Davidson (CD) distribution of correlation times¹ which gives

$$J(\omega) = \sum_{k} b_{k} \frac{\sin(\beta_{k} \arctan(\omega \tau_{\text{CD},k}))}{\omega(1 + \omega^{2} \tau_{\text{CD},k}^{2})^{\beta_{k}/2}}$$
(6)

The correlation time $\tau_{CD,k}$ is the slow motion limit of the distribution of the kth mode. β_k with $0 < \beta_k \leq 1$ is the width parameter of the distribution. Unfortunately, there is no closed analytical expression for $g_{CD}(t)$; but there are approximate relations between the parameters τ_{CD} , τ_W , β and γ , ¹ so that having an appropriate set of $\tau_{CD,k} \beta_k$, and b_k values by the application of eq 6, an approximate result for g(t) according to eq 4 can be calculated.

When the temperature decreases, $\tau_{CD,k}$ becomes longer and each of the terms in the sum in eq 6 increases, passes through a maximum, and then decreases monotonically to zero. In general, the various terms in the sum in eq 6 overlap, this the more for

TABLE 2: Parameters for Interpolation Formulas Eqs 2 and 3 To Obtain the Intramolecular Relaxation Rate

system	proton species	y = u(1000/T) + v range of validity (K ⁻¹)	u (K)	v	largest deviation (%)
n-propanol	α-CH ₂	3.00-12.0	0.0156	0.693	8
	B-CH	3.00-12.0	0.0167	0.660	10
	CH ₃	3.00-7.20	0.0383	0.604	6
		7.20-12.0	0	0.880	9
n-propanol + glycerol 50:50	α -CH ₂	3.00-12.0	0.0178	0.627	8
	β -CH ₂	3.00-12.0	0.0189	0.593	12
	CH ₃	3.00-7.20	0.00476	0.691	7
	2	7.20-12.0	0	0.725	8
n-propanol + glycerol 30:70	α -CH ₂	3.00-12.0	0.0131	0.723	
	β-CH ₂	3.00-12.0	0.0139	0.699	15
	CH	3.00-7.20	0.000381	0.781	
		7.20-12.0	0	0.783	



Figure 10. Representative plot of the fraction y of the intramolecular relaxation rate relative to the total relaxation rate for the alkyl protons of *n*-propanol as a function of the content \tilde{x} of propanol in glycerol.

the experimental quantity $1/T_1$ which contains a further summation of $J(\omega)$ and $2J(2\omega)$. Whereas in our preceding paper dealing with the system propionic acid + DMSO separation of the relevant two terms could be accomplished fairly well,¹ as already mentioned, with the present propanol system the problem of term separation will be the most important hindrance to obtaining information of localized motion in the molecule.

In this regard the measurement of the realxation rates at various frequencies is very helpful, because the ratio

$$\epsilon = \frac{\log\left[\left(\frac{1}{T_1}\right)_{\omega_1}^{\text{intra}} / \left(\frac{1}{T_1}\right)_{\omega_2}^{\text{intra}}\right]}{\log(\omega_1/\omega_2)}$$
(7)

yields approximate information about the width parameters β . In any limiting situation in which in eq 6 we have $(\omega \tau_{\text{CD},k})^2 \gg$ 1, ϵ assumes the value 1 + β_k , and of course in the extreme narrowing situation we have $\epsilon = 0$. In Figure 13 we show the ϵ values as a function of the reciprocal temperature for the three systems we studied in the present work. For a single Cole-Davidson distribution ϵ would increase monotonically from ϵ = 0 to the final ϵ value at which it stays constant for any lower temperature. At a certain temperature ϵ assumes the value 1, and this is the temperature of the $1/T_1$ relaxation maximum. As may be seen from Figure 13 the basic feature of the observed ϵ values in our systems is the tendency of the $\epsilon(1/T)$ curve to go back to small values after having passed a maximum. This return to small values of $\epsilon(1/T)$ indicates that the motion, after having passed the maximum due to progressive retardation, reveals a new fast mode of motion in a quasi extreme narrowing situation, which then in turn becomes slower when T decreases.

The numbering k in eqs 4 and 6 is the same as in part $1.^{1}$ k = 1 designates the slowest partial motion, and as was explained above, this corresponds to the motion of the longest intramolecular vector. With increasing k we go to the motional effect of the next shorter vector until finally we arrive at the respective proton-



Figure 11. $(1/T_1)_{intra}$ for the various alkyl protons of pure *n*-propanol.

proton vector, which is the direct object of observation. In the propanol molecule we have k = 1-4.

In Table 3 we have collected b_k values which were obtained using the coupling constants listed in Table 1 of part 1 and applying Lorentzian spectral densities, that is, those given by eq 6 if we set $\beta_k = 1$. It will be seen that all the sums $\sum b_k$ are markedly smaller than one, indicating that the correlation function g(t)



Figure 12. $(1/T_1)_{intra}$ for the various alkyl protons of *n*-propanol in the mixture with 70 mol % glycerol- d_8 .

cannot be a linear combination of exponentials as required by the microscopic rigid body rotational diffusion theory. Moreover, as with the system propionic acid/DMSO the low temperature portion of the log $1/T_1$ vs 1/T curve is not compatible with log $1/T_2(T)$ when Lorentzian spectral densities are used. Therefore, here as well as for the further approach to get correlation times satisfying the requirement $\sum b_k = 1$ we apply the Cole-Davidson distribution formalism. These facts are the justification that on the following pages we consider the object of our analysis to be the soft molecule.

4.2. *n*-**Propanol, the Neat Liquid.** In Figure 14 the Cole-Davidson limiting long correlation time $\tau_{CD,1}$ of the OH-OH vector in pure *n*-propanol is shown. It was obtained from the proton relaxation results given in Figures 2, 3, and 8 according to a scheme described in part 1.¹ As outlined in section 3.2 it was not possible to determine the coupling constant from the proton NMR spectrum. The relaxation maximum is about 3 times larger in the present system than was found for the propionic acid system. This is in part due to the higher proton number density as mentioned in section 3.2. Moreover, this finding is understandable if we take into account that the H-bonding H-H distances is smaller here (≈ 2.5 Å) than for the acid (≈ 3 Å), and $(3/2.5)^6 \approx$



Figure 13. The temperature dependence of the exponent of frequency dependence in the ratio of $1/T_1$ relaxation rates at 12 and 48 MHz, see eq 7. (a) Pure propanol, (b) propanol + 50 mol % glycerol, (c) propanol + 70 mol % glycerol.

3. Thus, as for the acid system here as well we can accept $b_1 \approx$ 0.7. β_1 was found to be 0.38, and the fast motion contribution producing the low temperature shoulder of the OH relaxation curve, which was not evaluated in detail here, should be expected to be similar to the one we have found in the propionic acid system. This fast motion part of the correlation function usually is called the β process (see, e.g., refs 14 and 15); we shall not use this denotation because our interest concerns the molecule as such, not the glassy state, and we already have two quantities called β : the β -CH₂ group and the width parameter β . The reason for our presenting the $\tau_{CD,1}$ data of the OH-HO vector in Figure 14 is the fact that $\tau_{CD,1}(T)$ is almost a constant quantity for all three intramolecular vectors we are studying, where it appears as the Cole-Davidson limiting time constant of the slow motion residuum. To show this clearly we have drawn a horizontal line in Figures 14–16 which crosses the curve $\tau_{CD,1} = \tau_{CD,1}(T)$ at T = 133 K (i.e., 1000/T = 7.5). For β -CH₂ and CH₃, $\tau_{CD,1}$ (133 K) is by a factor ≈ 2 shorter than for the other vectors. These results for the $\tau_{\rm CD,1}$ values give the reason for our previous statement that we must interpret the OH-OH motion as being essentially equal to the slow motion of the $OH \rightarrow C_{CH_3}$ vector.

ш сд /)									
OH		OH α-CH ₂			β-CH ₂		CH3		
k	$(1/T_1)_k^{\max}$ (s ⁻¹)	b _k	$(1/T_1)_k^{\max}$ (s ⁻¹)	bk	$(1/T_1)_k^{\max}$ (s ⁻¹)	b _k	$(1/T_1)_k^{\max}$ (s ⁻¹)	b _k	
1	3.0	0.38	14.6	0.16	11.3	0.13	8.07	0.045	
2	0.32	0.004	10.5	0.12	12.9	0.14	11.0	0.061	
3			7.8	0.09	11.0	0.12	12.1	0.067	
4							42.3	0.24	
$\sum b_k$		0.38		0.37		0.39		0.41	

TABLE 3: Maximum Proton Relaxation Rates of Partially Deuterated *n*-Propanol Mixed with 70 mol % Glycerol at a Resonance Frequency $\nu = 12$ MHz and the Weight Factors b_k Assuming Lorentzian Spectral Densities ($\beta_k = 1$ for k = 1, 2, 3, 4 in Eq. 7)



Figure 14. Limiting Cole–Davidson correlation time $\tau_{CD,1}$ of OH protons in pure *n*-propanol as a function of the reciprocal temperature. The symbols indicate the experimental sources from which results were derived.

Generally, the intermolecular relaxation rate is determined by contributions of all proton-proton vectors in the liquid; however, each vector acts with the "weight" $1/r^6$ times a correlation time $\sim r^2$. Obviously the pair correlation function g(r) and the "dynamic" propagator $P(\dot{r}_0, \dot{r}, t)$ are of such a form to separate off all contributions from partners not belonging to H-bonded "aggregates" of limited size. We shall again consider this situation from another point of view in the discussion below.

We turn to the motion of the α -CH₂ proton-proton vector. The results are given in Figure 15. We discuss first the low temperature part, $1000/T > 4 \text{ K}^{-1}$. It was not possible to find b_k and β_k values such that for both frequencies the $1/T_1$ and $1/T_2$ values could be reproduced. Therefore from the maximum of $\epsilon(T)$ as given in Figure 13 and from fitting of $\tau_{\rm CD}$ values to the $1/T_1$ results we obtained an approximate β_1 value, $\beta_1 = 0.27$ (see Table 4). This procedure yielded different τ_{CD} values resulting from $1/T_2$ and $1/T_1$ for $1000/T \gtrsim 5.5$ K⁻¹, as shown in Figure 15. The $\tau_{\rm CD}$ stemming from the $1/T_1$ evaluation is lower than the one derived from $1/T_2$ results; it probably contains some fast motion contribution. As a consequence of this uncertainty of motional mode, we have designated the latter τ_{CD} as $\tau_{CD,k=x}$. The b_1 value resulting from the $1/T_2$ evaluation is $b_1 = 0.51$; the remainder with respect to the sum 1, i.e., 0.49, must represent motion of high frequency character, i.e., fast motion. However, it will be seen that due to strong overlap of the various motional mode contributions no further detail can be obtained from the low temperature part of the relaxation curve.

We have to proceed to the room temperature part of $\log 1/T_1$ vs 1/T to get further information, which, however, can only be approximate.

One definite result we can use for the analysis of the room temperature part is $b_1 = 0.51$. One other definite result is the effective correlation time τ_{ceff} , which is given by the relation

$$\left(\frac{1}{T_1}\right)_{\text{intra}} = \frac{3}{2}C \,\tau_{\text{ceff}} \tag{8}$$

Then we can write

$$\tau_{\text{ceff}} = b_1 \, \bar{\tau}_{\text{CD},1} + (1 - b_1) \bar{\tau}_{\text{CD},2} \tag{9}$$

where $\tau_{CD,k}$ are the Cole–Davidson mean correlation times:

$$\bar{\tau}_{\text{CD},k} = \beta_k \tau_{\text{CD},k} \qquad k = 1, 2 \tag{10}$$

In comparison with eq 4, the meaning of eq 9 is that only one fast motion contribution is taken into account, i.e., $k \leq 2$. Equation 9 is one equation for two unknowns. Our approximate solution is as follows: (1) $\tau_{CD,1}$ at T = 25 °C must be close to an extrapolation value to $1000/T \rightarrow 3.35 \text{ K}^{-1}$ of $\tau_{\text{CD},1}$ as given by the "experimental points" in Figure 15. (2) With the system propionic acid/DMSO,¹ in view of the temperature dependence of the effective dipole-dipole coupling constant we had reason to consider $\tau_{CD,2} = 10^{-7}$ s at 1000/T = 12 K⁻¹ to be an acceptable value. We take the same value at $1000/T = 12 \text{ K}^{-1}$ here as well. Furthermore, we assume that at the boiling point of propanol (T_{b} = 97.4 °C) $\tau_{CD,1} = \tau_{CD,2}$. Let the temperature dependence of $\tau_{CD,2}$ be given by an Arrhenius law. These facts together give the dashed straight line for $\tau_{CD,2}$ drawn in Figure 15. We set $\beta_2 =$ $\beta_1 = 0.27$. We thus obtain the (approximate) results listed in Table 4.

It should be emphasized that the fundamental result of our investigation here and in the following is the triplet of values, $\tau_{CD,1}$, β_1 , and b_1 and the fact that $\sum b_k < 1$, i.e., that there is some spectral density missing which must be of higher frequency nature. Thus, the triplet of values $\tau_{CD,2}$, β_2 , and E_{A2} is only understood to give qualitative figures to fill the gap between $b_1 = 0.51$ and $1 = \sum b_k$.

One further remark should be given here. As we stated above, at $1000/T = 7.5 \text{ K}^{-1} \tau_{\text{CD},1}$ for the hydroxyl H–H vector and $\tau_{\text{CD},1}$ for the α -CH₂ H–H vector slow motion residuum are almost equal (see Figures 14 and 15), β_1 is slightly smaller for α -CH₂. But at room temperature $\tau_{\text{CD},1}$ (OH) is 7×10^{-11} s while $\tau_{\text{CD},1}$ -(α -CH₂) = 4.8×10^{-11} s. Thus at room temperature the slow motion residuum of the α -CH₂ proton–proton vector has a somewhat shorter time constant than the H-bonding H–H vector.

The behavior of the slow motion residuum time constant of the β -methylene proton-proton vector is very similar to that of the α -CH₂ group. Here as well, the τ_{CD} values as determined from $1/T_2$ and $1/T_1$ results differ; the latter one is smaller and should again be called $\tau_{CD,k=x}$. All time constants are roughly a factor of 2 smaller than those obtained for α -CH₂; details are given in Table 4. Correspondingly the "spectral desity defect" due to high frequency motion for β -CH₂ is only 0.35 ($b_1 = 0.65$) compared with 0.49 for α -CH₂. In order to get approximate numbers for



Figure 15. Limiting Cole–Davidson correlation time $\tau_{CD,k}$ ("experimental" symbols with source indication) and the appropriate "real" fast motion correlation time (dashed straight line) describing the motion of the methylene proton-proton vectors of pure n-propanol as a function of the reciprocal temperature. The × marks the effective correlation time according to eq 9: a, α -CH₂; b, β -CH₂. For further details see text.

 $\tau_{\rm CD,2}$, β_2 , and $E_{\rm A2}$ we have followed the same procedure as described for α -CH₂ (see Figure 15).

A still faster motion we have found for the methyl protonproton vector (Figure 16). Now it was possible to evaluate the broad relaxation maximum occurring at 1000/T = 7.8 and 8.5K⁻¹ directly (see Figures 2 and 3). The resulting $\tau_{CD,1}$ and (apparent) $\tau_{CD,2}$ results are shown in Figure 16. The $\tau_{CD,1}$ values obtained from $1/T_1$ are somewhat smaller than those derived from the log $1/T_2$ vs 1/T curve (see Figure 8). When we

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	F. kl/mol	CH ₃		12 ± 1		10 ± 1			10±1	
	25 °C	CH3	0.68; 2.3	0.1; 0.2	1.6; 8 ^b	0.11; 0.21 ^b		3.0; 10 ⁶	0.18; 0.6	
8	тср,1 (s) at	β-CH ₂	0.69; 2.5	0.30; 1.1				1.8; 6.0 ⁶	0.21; 0.70	
ol Mixtur	11 ⁻ 7CD,1; 10 ¹¹	α-CH ₂	1.3; 4.8	0.54; 2.0				2.7; 9.0%	0.22; 0.73	
l/Glycer	10	НО						3.5; 11 ^b	1.3; 3.6	
opano		CH ₃		0.55	1	0.53		0.3"	0.4	
or <i>I</i> -Pi		β-CH ₂	0.27ª					0.3ª 0.3ª	0.4	
h and f	8	α-CH ₂	0.27ª		50:50		30:70	0.3ª 0.3	0.45	
ropanc	ropano	НО	ropanol 0.38		ilycerol, 0.20		lycerol,	0.32 0.35		
for Pure n-1		CH ₃	Pure n-P	0.55 ± 0.03	Propanol + (0.1 ^b	$0.38^{\circ} \pm 0.03$	Propanol + (0.08 ± 0.01 0.09	0.07	0.59
C (72 °C) 1)k	β-CH ₂	0.65 ± 0.03		4		-11	0.31 ± 0.02 0.27	0.23 ± 0.03	0.75
imes at 25 °	ł	a-CH ₂	0.51 ± 0.01					0.25 ± 0.02 0.25	0.17	0.67
orrelation I		НО						0.70 ± 0.03 0.007		0.71
iting C		3 k	1	7	e	<i>°</i>		ہ ا 2	ж 7	$\sum b_k$
d Lim	°C (s)	² CH	0.36			0.26		0.41		
ean an	r = 25	в-СН	0.55					0.70		
C), M	r _{cefr} at 1	α-CH ₂	0.92					0.84		
(72 %	101	НО						2.84		

^a Estimated values. ^b T = 72 °C. ^c b_k values for k = 2-4 refer to apparent correlation times.



Figure 16. Limiting Cole–Davidson correlation times $\tau_{CD,1}$ and $\tau_{CD,2}$ (apparent), for CH₃ protons of pure *n*-propanol. The "experimental" symbols give source indication. The approximate "real" fast motion correlation time is shown by the dashed straight line. The × marks the effective correlation time at T = 25 °C.

extrapolate the "experimental" $\tau_{CD,2}$ values from low temperature to room temperature we come close to the (extrapolated) slow motion residuum $\tau_{CD,1}$. On the other hand, extrapolation of $\tau_{CD,1}$ to low temperatures around the glass temperatures yields $\tau_{CD,1}$ ≈ 1 s, but in this region T_1 is less than 1 s, and it follows that the remaining motion of the methyl proton-proton vector can only scan part of the rotational space during the process of observation. Thus, as has been described in detail in part 1, we must have an effective decrease of the dipole-dipole coupling constant as the temperature approaches the glass transition point. Yet, as has already been stressed above and in part 1, it is very striking that $1/T_1$ does not show any peculiarity at the glass temperature and that in the range from $1000/T = 7.5 \text{ K}^{-1}$ to $1000/T = 12 \text{ K}^{-1} \tau_{\text{CD},2}$ can be represented as an Arrhenius plot. Taking into account these two requirements—noncrossing of $\tau_{CD,2}$ and $au_{\rm CD,1}$ and $au_{\rm CD,2} \ll T_1$ —and using an approximation of invariance of activation energy (see part 1) we arrive at the $\tau_{CD,2}(T)$ behavior as shown by the dashed straight line in Figure 16 and at time constants at T = 25 °C as given in Table 4. It will be seen that all time constants are shorter than those for the β -CH₂ group, in particular those for the fast motion $\tau_{CD,2}$ and $\tau_{\rm CD,2}$ are markedly shorter.

4.3. *n*-**Propanol in the Mixture with 50% Glycerol.** In Figure 17 we show the primary effect of the admixture of the strongly interacting component glycerol to *n*-propanol. The OH relaxation rate now is the mean value of three kinds of H-H vectors: propanol-propanol, glycerol-glycerol, and propanol-glycerol. There has been no indication of a nonexponential approach to equilibrium of the magnetization, i.e., T_1 is a well-defined quantity at all temperatures. However, at a given temperature, $\tau_{CD,1}$ for OH has become longer by 1 order of magnitude compared to pure propanol. Thus at room temperature (T = 25 °C) we are already in the dispersion range ($\epsilon \neq 0$, see Figure 13); to achieve extreme narrowing conditions we have to consider data at a higher temperature. We choose 1000/T = 2.9 K⁻¹ (T = 71.7 °C). But the shift of $\tau_{CD,1}$ to longer values is not entirely perfect, the width



Figure 17. Limiting Cole–Davidson correlation times $\tau_{CD,1}$ for the OH group and $\tau_{CD,2}$ (apparent) for the CH₃ protons in the mixture *n*-propanol + 50 mol % glycerol. The × gives the effective correlation time at T = 72 °C, and the dashed straight line approximates the fast motion "real" correlation time $\tau_{CD,2}$. Other details as in Figures 14–16.

parameter which in pure propanol was $\beta_1 = 0.38$ now has the value 0.20, i.e., there is now a wider extension to shorter times relative to τ_{CD} . In contrast to the retardation of the OH---HO vector, the experimental quantity $\tau_{CD,2}$ at $1000/T = 12 \text{ K}^{-1}$ is unchanged compared to the value of pure propanol (see Figure 16), but the activation energy of the apparent $\tau_{CD,2}$ is smaller in the mixture than in the neat liquid so that the effective correlation time, e.g., at $1000/T = 2.9 \text{ K}^{-1}$ is slightly longer in the present system. The dashed line representing $\tau_{CD,2}$ is constructed according to eq 9 and the scheme described for pure propanol.

4.4. n-Propanol in the Mixture with 70% Glycerol. When more glycerol is added to the propanol, the OH relaxation maximum shifts to higher temperatures as may be seen from Figures 4–7. The shift of the maximum to higher temperatures is due to an increase of $\tau_{CD,1}$ for the OH···HO vector. At T =222 K $\tau_{CD,1}$ is found to be 10⁻⁵ s; see Figure 18 (5 × 10⁻⁶ s in the 50:50 mixture). At 72 °C the extreme narrowing condition $\epsilon =$ 0 is fulfilled $(1000/T = 2.9 \text{ K}^{-1}$, see Figure 13). There is a broad flat maximum on the low temperature side of the log $1/T_1$ vs 1/Tcurve (see Figure 11 of ref 9) which indicates that here as well the motion of the OH ... HO vector is modulated by a fast fluctuation process of the variables ϑ , φ , and r (β process). The pertinent parameters characterizing the OH...HO motion are shown in Figure 18 and are included in Table 4. The dashed line giving the real $\tau_{CD,2}$ was constructed as described in the previous paragraphs.

The dynamical parameters of the α -CH₂ H···H vector are presented in Figure 19. To understand this picture we go back for a moment to pure propanol, Figure 15. There the dashed straight line represents the fast motion in the most simple way, as if no detailed contributions to this movement could be detected. Yet there was a slow motion curve $\tau_{CD,k=x}$ introduced which was supposed to indicate the presence of some fast motion contribution, however, without any localization being feasible. This becomes different when 70 mol % glycerol is added. Indeed, the log $1/T_1$ vs 1/T curve shows two shoulders on the low temperature side



Figure 18. Limiting Cole–Davidson correlation times $\tau_{CD,1}$ and $\tau_{CD,2}$ (apparent) of OH motion in the mixture *n*-propanol + 70 mol % glycerold₅. Approximate "real" fast motion is given by the dashed line.



Figure 19. Limiting Cole-Davidson correlation times $\tau_{CD,1}$, $\tau_{CD,2}$, and $\tau_{CD,3}$ of the H \rightarrow H vector in the α -CH₂ group of *n*-propanol in the mixture with 70 mol % glycerol-d₈. The × marks the effective correlation time at T = 72 °C. The dotted curves indicate that at higher temperatures $\tau_{CD,2}$ and $\tau_{CD,3}$ merge into the dashed line which at low temperatures approximately represents the fastest contribution to the H \rightarrow H vector motion.

of the main maximum (see Figures 6, 7, and 12). With an estimated width parameter $\beta_2 = \beta_3 = 0.3$, appropriate fitting to this "structure" of the log $1/T_1 - 1/T$ curve gives the $\tau_{CD,2} = \tau_{CD,2}(T)$ and $\tau_{CD,3} = \tau_{CD,3}(T)$ results shown in Figure 19. $\tau_{CD,1}$



Figure 20. Same as Figure 19, however referring to the $H \rightarrow H$ vector of the β -CH₂ group.

is the slow motion residuum in the α -CH₂ proton-proton vector due to the vector OH \rightarrow C_{CH₃}. At 1000/T = 4.5 K⁻¹ here we find $\tau_{CD,1} = 0.7 \times 10^{-5}$ s. This is almost equal to the $\tau_{CD,1}$ value of the OH···HO vector (1 \times 10⁻⁵ s), as mentioned above. $\tau_{CD,2}$ is interpreted to be the time constant of the $C_{\alpha-CH_2} \rightarrow C_{CH_3}$ vector motion residuum in the α -CH₂ movement. τ _{CD,3} then would be the Cole–Davidson parameter of the α -methylene proton–proton vector itself. But before drawing any further conclusion the extreme narrowing data have to be considered. τ_{ceff} according to eq 8 is marked as a \times in Figure 19. b_1 has been found to be equal to 0.25 and thus, as obtained from $1/T_2$ and $1/T_1$ curves without overlap problems, is considered to be a safe number. The same holds true for $\tau_{CD,1} = 9 \times 10^{-11}$ s. The fitting procedure yielding $\tau_{CD,2}$ and $\tau_{CD,3}$ had given $b_2 = 0.25$ and $b_3 = 0.17$. With $b_1 + b_2 + b_3 = 0.67$ it is impossible to get an effective correlation time $\tau_{\text{ceff}} = 0.84 \times 10^{-11}$ s at T = 72 °C if we perform a straight line extrapolation of the experimental $\tau_{\rm CD,2}$ and $\tau_{\rm CD,3}$ to 1000/T= 2.9 K⁻¹. Moreover, in the temperature range where $\tau_{CD,2}$ and $\tau_{\rm CD,3}$ were determined, we have already $\tau_{\rm CD} \lesssim T_1$, not $\tau_{\rm CD} \ll T_1$; thus the observed T_1 values at least partly refer to a restricted or partial rotational space. The effective dipole-dipole coupling constant will be reduced at temperatures around and below the glass temperature. Finally we have to fill the gap between $\sum b_k$ = 0.67 and $\sum b_k = 1$. As before, this is accomplished by assuming that there is a further mode of movement, the fastest movement, having a time constant $\tau_{CD,4} \approx 10^{-7}$ s at 1000/T = 12 K⁻¹ where we take the latter value as a universal quantity being more or less valid for all our systems.¹ This would then mean that $\tau_{CD,3}$ can be considered as being another slow part of the H-H vector motion, perhaps the residuum of the $C_{\alpha-CH_2} \rightarrow C_{\beta-CH_2}$ vector motion. The dashed straight line in Figure 19 gives a $\tau_{CD,2}$ which satisfies the requirement of the observed effective correlation time at 1000/T= 2.9 K^{-1} and, at lower temperature, represents the fastest thermal modulation of the orientation and magnitude of the α -CH₂ H–H vector. All pertinent numerical values are collected in Table 4.

In Figures 20 and 21 we show the Cole–Davidson correlation times for the β -CH₂ and CH₃ proton–proton vectors. From Figure 20 it will be seen that the behavior of the β -CH₂ proton–proton motion is very much the same as that of the α -CH₂ group, a



Figure 21. Limiting Cole-Davidson correlation times $\tau_{CD,1}$, $\tau_{CD,2}$, $\tau_{CD,3}$, and $\tau_{CD,4}$ (apparent) of the H \rightarrow H vectors in the CH₃ group of *n*-propanol in the mixture with 70% glycerol- d_8 . All other details are as described for Figure 19.

finding which is surprising because the β -CH₂ group should be more loosely coupled to the center of interaction, the OH–OH hydrogen bonding.

At $1000/T = 4.5 \text{ K}^{-1}$ in Figures 20 and 21 $\tau_{CD,1}$ is almost exactly 1×10^{-5} s; thus, both these proton-proton vectors are affected by the slow motion in the same way as regards the magnitude of the time constant, but the weight of the slow motion residuum is much larger for the β -CH₂ group than for CH₃. We find $b_1 = 0.31$ and $b_1 = 0.08$ for the former and latter case, respectively (see Table 4). The relaxation curve with its broad and high maximum at $1000/T \approx 7.8-8.8 \text{ K}^{-1}$ shown in Figures 6 and 7 could be evaluated directly to yield the dynamic parameters of what one might call the methyl rotation. But since again we have $\tau_{CD,4} \approx T_1$, certainly we are dealing with motion in restricted rotational space. Although as clearly seen from the absolute value of the relaxation rate $1/T_1$, the restriction is less than that of the methylene proton motion. All relevant dynamical parameters are listed in Table 4. For the methyl protons we find in Table 4 $\sum b_k = 0.59$ instead of $\sum b_k = 1$. The distribution with respect to the various $\tau_{CD,i}$ with $i \ge 2$ shown in Figure 20 must cover a total weight of 0.92 instead of 0.51 = 0.59 - 0.08. Probably it is most reasonable to imagine the real weights b_k , k = 2-4, to have the same relative magnitude as those given in Table 4, i.e., $b_2:b_3:b_4 = 0.09:0.07:0.35$; this means that the contributions of the

terms with $\tau_{CD,2}$ and $\tau_{CD,3}$ are in any case small. In Figures 20 and 21, respectively, again one finds a × which gives the effective correlation time at T = 72 °C according to eqs 9 and 10. As remarked previously, $\tau_{CD,2}$ in eq 9 comprises all contributions which are not $\tau_{CD,1}$. These are partly those which appear as the lower temperature values of $\tau_{CD,2}$, $\tau_{CD,3}$, and $\tau_{CD,4}$ in Figure 21, respectively. Furthermore, in both figures the dashed straight lines represent a time constant which gives the correct effective correlation time at 1000/T = 2.9 K⁻¹ and which at 1000/T =12 K⁻¹ yields $\tau_{CD,2} = 10^{-7}$ s (Figure 20) or shows the same activation energy as $\tau_{CD,4}$ (Figure 21). Thus at low temperatures the dashed line represents the fast motion only. All relevant dynamical parameters are listed in Table 4.

5. Discussion

With all our measurements we found $\sum b_k < 1$; thus at least one of the rigidity conditions is not fulfilled. Moreover, rigidity conditions between time constants are not fulfilled either because with the Cole-Davidson distribution we have an infinite number of partial time constants. This behavior was summarized by the denotation soft molecule. On the other hand the frequency dependence plots $\epsilon(1/T)$ show that the total spectral density cannot be described by one single Cole-Davidson distribution because in such an event $\epsilon(1/T)$ must be a monotonic function of 1/T. Thus as the simplest form we now describe the correlation function g(t) of a given vector by eq 4 with two terms and with coefficients b_1 as given in Table 4 and $b_2 = 1-b_1$. Table 5 gives the results of the conversion from the Cole-Davidson parameters $\tau_{CD,k}$ (Figures 14-21) and β_k (Table 4) to Kohlrausch-Watts-Williams parameters τ_{Wk} and γ_k , where eq 30 of part 1 was used. For the γ_k of propanol + 70% glycerol mean values of the β_k , k = 2-4were taken.

Summarizing, as a consequence of the wide spread frequency distribution of the relevant dynamical components we can state that the molecule *n*-propanol does not behave like a microscopic rigid body or like a system of rigid body links. Yet, we see from Figures 14–16 (pure propanol) and Figures 18–21 (mixture with 70 mol % glycerol) that the slow motion residuum, which might be understood to give the motion of the whole molecule, in a remarkable manner is the same as probed from all the various groups. Also fast motion, although not uniquely determinable, is recovered in a consistent way as we proceed from the vector motion of one group to the other.

In Figures 22 and 23 the various g(t) values according to the data given in Tables 4 and 5 for *n*-propanol + 70% glycerol are shown. It follows from the entries of these tables that in the -50.9 °C diagram for α -CH₂ and β -CH₂ the fast motion contribution refers to the fastest modulation of the repective vector (the dashed lines in Figures 19 and 20). But we recall from Figures 19 and 20 that apart from the k = 1 slow motion residuum there are other slow motion effects. Hence the real course of g(t) for α -CH₂ and β -CH₂ is somewhere in the hatched area in Figure 23.

We have seen that from the point of view of its dynamics, our molecule in the liquid phase cannot be considered to be a rigid

TABLE 5:	Kohlrausch-William	s–Watts Para	meters τ_w and	γ for	Correlation 1	Functions g(t	t) of <i>n</i> -Propai	101 and
Propanol-G	lycerol Mixtures (b ₂	$= 1 - b_1$)					· •	

••••••••••••••••••••••••••••••••••••••				γ					
system temperature (°C)	k	ОН	α-CH ₂	β-CH ₂	CH ₃	ОН	α-CH ₂	β-CH ₂	CH3
<i>n</i> -propanol T = 25 <i>n</i> -propanol + glycerol 50:50 T = 72 <i>n</i> -propanol + glycerol 30:70	1 2 1 2		0.53 0.22	0.275 0.121	1.04 0.029 0.19 0.09		0.38 0.38	0.38 0.38	0.65 0.411 0.30 0.63
$ \begin{array}{l} T = 72 \\ T = -51 \\ T = -51 \\ T = -51 \end{array} $	1 1 2 2	1.9 1.7 × 10 ⁵ 0.75 4.55	1.3 1.02 × 10 ⁵ 0.17 0.95	0.88 1.3 × 10 ⁵ 0.14 0.85	1.46 1.6 × 10 ⁵ 0.16 1.2	0.44 0.44 0.47 0.46	0.41 0.41 0.41 0.49	0.41 0.41 0.41 0.46	0.41 0.41 0.41 0.51



Figure 22. Second degree spherical harmonics time correlation functions g(t) for the four proton-proton vectors of *n*-propanol in the mixture with 70 mol % glycerol- d_5 (OH group) and 70 mol % glycerol- d_8 (alkyl group) at T = 72 °C (parameters are listed in Tables 4 and 5).



Figure 23. Second degree spherical harmonics time correlation functions g(t) for the four proton-proton vectors of *n*-propanol in the mixture with 70 mol % glycerol- d_8 (alkyl groups) at T = -50.9 °C (parameters are listed in Tables 4 and 5). The curves shown for the two methylene groups represent the fastest contributions; due to the admixture of slower motion, the real g(t) runs somewhere in the hatched area.

body or a system of coupled rigid bodies.¹⁶ The question arises if this statement is valid, how can the molecule properly be described?

What follows is a mathematical formulation of the concept soft molecule. The total liquid is a heap of N mass points in an envelope. To answer our question we arbitrarily choose one reference mass point (nucleus or atom), we give the number 1 to this reference atom. Then we define a set of N - 1 vector correlation functions $f_{1i}(t)$ as

$$f_{1i}(t) = \langle \vec{r}_{1i}(0) \vec{r}_{1i}(t) \rangle \qquad j = 2, 3, ..., N \tag{11}$$

where $r_{1j}(t)$ is the vector pointing from atom 1 to atom j at time t, i.e., the vector $r_j(t) - r_1(t)$. The brackets $\langle \rangle$ indicate the ensemble average. At room temperature we find two classes of $f_{1j}(t)$'s. In the first class with $j = 2, 3, ..., n, f_{1j}(t) \rightarrow [f_{1j}(t)]_{fast}$, that is $f_{1j}(t)$ decays rapidly to zero, the time constant

$$\tau = \tau_{\text{fast}} = \frac{1}{(\overline{r_{1j}}^2)}_{\text{intra}} \int_0^\infty [f_{1j}(t)]_{\text{fast}} \, \mathrm{dt} \tag{12}$$

is of the order of 10^{-11} s. $(\overline{r_{1j}^2})_{intra}$ is the mean square value of r_{1j} for $1 \le j \le n$. In the other class $f_{1j}(t) \rightarrow [f_{1j}(t)]_{slow}$, the corresponding time constant

$$\tau = \tau_{\rm slow} = \frac{1}{(\overline{r_{1j}}^2)_{\rm inter}} \int_0^\infty [f_{1j}(t)]_{\rm slow} \, \mathrm{d}t \tag{13}$$

is very long; it is determined by the size of the envelope.

Then we define the molecule as the set of atoms for which

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$$f_{1j}(t) \rightarrow [f_{1j}(t)]_{\text{fast}} \qquad j = 2, 3, ..., n$$
 (I)

Next we choose a pair of vectors within the set of n = 1intramolecular atom-atom vectors, \vec{r}_{12} and $\vec{t}r_{13}$, say. Then the vector product $\vec{r}_{12} \times \vec{r}_{13}$ defines a vector being orthogonal to the plane spanned by \vec{r}_{12} and \vec{r}_{13} ; thus $\vec{r}_{12} \times \vec{r}_{13}$ defines one particular intramolecular coordinate system. As \vec{r}_{12} and \vec{r}_{13} fluctuate with time, the coordinate system fluctuates as well. Next we choose any other pair of vectors within the set of n atoms, \vec{r}_{34} and \vec{r}_{35} , say, and form the vector product $\vec{r}_{34} \times \vec{r}_{35}$ which again defines a coordinate system. If the fluctuation with time of these two coordinate systems, expressed by some proper correlation functions, is equal or at least connected by some special mathematical relations (rigidity conditions), then the molecule is a rigid body. Although in IR and Raman spectroscopy the existence of one three-dimensional coordinate system belonging to the total molecule is taken to be self-evident, in the framework of the pertinent rigidity conditions for nonperiodic motions we could not verify rigidity. If there is no three-dimensional coordinate system for the total molecule, then the dynamics of the molecule in principle has to be described by the 3n - 3 dimensional vector correlation function

$$f_{\text{total}}(t) = \langle \vec{R}(0)\vec{R}(t)\rangle \tag{14}$$

where $\vec{R}(t)$ is the generalized 3n - 3 dimensional orientational plus (intramolecular) position vector, $f_{\text{total}}(t)$ is given by the integral

$$f_{\text{total}}(t) = \int p(\vec{R}(0)) \, \vec{R}(0) \vec{R}(t) \, P(\vec{R}(0), \vec{R}(t), t) \, \mathrm{d}\vec{R}(0) \, \mathrm{d}\vec{R}(t)$$

involving the 3n-3 dimensional propagator $P(\bar{R}(0),\bar{R}(t),t)$. $[f_{1j}(t)]$ then according to the eq 11 is the reduced total vector correlation function obtained by integration over 3n - 6 coordinates of all atoms with number $\neq j$. From these arguments it follows that due to the lack of a coordinate system for the total molecule the description I is the valid definition of the molecule.

In the *n*-propanol molecule there are 66 atom-atom distances, and 30 of these distances are independent. So we would have $30[f_{ij}(t)]_{\text{fast}}$'s for the *n*-propanol molecule, part being equal due to symmetry. The present investigation yields information about 7 of these vector correlation functions. They refer to the vectors α -methylene H \rightarrow H and C \rightarrow D, β -methylene H \rightarrow H and C \rightarrow D, methyl group H \rightarrow H and C \rightarrow D, and hydroxyl group D \rightarrow O. The H \rightarrow H vector of the OH-OH belongs to the class $[f_{ij}(t)]_{\text{slow}}$. Our liquid is a system which is macroscopically and microscopically isotropic. Therefore, without loss of generality we can give $r_{ij}(0)$ the direction of the z axis of a laboratory coordinate system. Thus our vector correlation function reads, e.g.,

$$f_{1i} = \langle r_{1i}(0)r_{1i}(t)\cos\vartheta(t)\rangle \tag{15}$$

where $\vartheta(t)$ is the angle between $\dot{r}_{1j}(0)$ and $\dot{r}_{1j}(t)$. $r_{1j} = |\dot{r}_{1j}|$. It follows that τ_{fast} according to eq 12 is approximately given by the time after which the vector $\dot{r}_{1j}(t)$ passes through the plane $\vartheta = \pi/2$.

The NMR relaxation experiment does not yet yield the Fourier transform of $f_{ij}(t)$ directly; rather we merely obtain the Fourier transform of the time correlation function of a function of $\tilde{r}_{ij} = \{r_{ij}, y_{ij}, z_{ij}\}$ namely

$$\psi(\vec{r}_{1j}) = (r_{1j})^{-3} (3(z_{1j}/r_{1j})^2 - 1)$$

= $(r_{1j})^{-3} (3\cos^2 \vartheta - 1)$ $j = 2, 3, ..., N_{\text{proton}}$ (16)

Equation 15 describes the dynamics of the liquid free of any

features of the experimental method, whereas eq 16 is based on the magnetic dipole-dipole (or electric quadrupole) interaction. Our aim is the knowledge of $f_{1i}(t)$, however, information is available only via eq 16. What are the differences between 15 and 16? (1) The correlation time with respect to the function $\psi(\vec{r}_{1i})$ essentially is the time after which the vector \vec{r}_{ii} passes through a cone defined by the magic angle $\vartheta = 54.4^{\circ}$. This difference is not very important. (2) Due to the factor $(r_{1i})^{-3}$ of the two quantities to which the correlation functions refer the long lasting part of $[f_{1i}(t)]_{slow}$ is essentially cut off. In the correlation function of 16 the range of effectiveness of the intermolecular motion is about equal to the spatial extension of the molecule. This feature is of great importance for us as we took the $OH \rightarrow OH$ relaxation rate to be a measure of the movement of the longest intramolecular vector. However, according to our experience this is not a general feature of

$$\langle \psi(\vec{r}_{ij}(0))\psi(\vec{r}_{ij}(t))\rangle$$

for intermolecular motion.¹⁶ It should be noted that at low temperatures the situation regarding the "observable" function $\psi(\vec{r}_{ii})$ is slightly more complicated, as was outlined in part 1, section 4.1

Thus we now arrive at the result: all correlation times given in Figures 15–17 and 20–21 for the intramolecular vectors α -CH₂ $H \rightarrow H$, β -CH₂ $H \rightarrow H$, and CH₃ $H \rightarrow H$ qualitatively are properties of the vector correlation function $[f_{ij}(t)]_{\text{fast}}$. In contrast to this, we obtained the result that the OH-OH data given in Figures 14 and 18 represent the features of a truncated (i.e., divided by r_{ii}^{-8} vector correlation function $[f_{ii}(t)]_{slow}$; however, we claim that the division by r_{ii}^{8} should not influence the temperature dependence so that we postulated that the temperature dependence of $\tau_{CD}(OH)$ is virtually the same as the temperature dependence of τ_{slow} according to eq 13.

In the light of these statements we now consider the correlation functions g(t) (the correlation functions of $\psi(\vec{r}_{ij}(t))$ shown in Figures 22 and 23. We recall that all our correlation functions were given in a two-term representation. For intramolecular vectors, the first term represents the residuum of some long vector slow motion, the second term is assigned to the vector motion itself. For the OH-proton the situation is reversed; the main motion is the slow one, and there is a certain fast motion residuum. It will be seen from Figure 22 that at T = 72 °C the effect of the residuum on the main motion is not resolved. Only g(t) of OH, the correlation function of the truncated slow class of the vector correlation functions, decays somewhat slower than the g(t)'s of the three other kinds of proton-proton vectors.

Now, as we go to lower temperatures τ_{slow} according to eq 13 increases very strongly. This means that the self-diffusion coefficient decreases very strongly. We did not measure the respective quantity, but we draw this conclusion from our Figures 14-21 and the statement that $\tau_{slow}(T) \sim \text{constant } \tau_{OH}(T)$. But Figure 18 tells us that there is still a fast motion residuum in the slow motion of OH and thus in $[f_{ij}(t)]_{slow}$. It will be seen from Figure 23 that now in g(t) of the OH proton the separation in a fast decaying part and a slowly decaying part is detectable. Furthermore, and this perhaps is the most important result of our investigation, at low temperature the influence of the very slowly decaying intermolecular vector correlation function crosses the boundary of the molecule and produces a very effective residuum of slow motion of the α -CH₂ and β -CH₂ proton-proton vector (such as to prevent the recording of the whole correlation function by T_1). This effect will clearly be seen from Figure 23, where the course of g(t) is somewhere in the hatched area, but in any case a slow motion part and a fast motion part of g(t) are resolved in the upper left-hand region. Finally, when we turn to the CH₃ group we see from Figure 23 that here the effect of $[f_{ii}(t)]_{slow}$ is merely very small, so the methyl group behaves as if it were a molecule in the matrix glycerol + HO-CH2-CH2; this should be seen in contrast to the possibility of comparatively fast motion of the total C_3H_7OH molecule in the matrix glycerol which is not realized. It must be remarked that for CH₃, multiexponential relaxation was observed, so that in principle vector cross correlation functions $\langle \tilde{r}_{12}(0) \tilde{r}_{13}(t) \rangle$ could be modeled to yield local anisotropy of motion, that is, rotation of CH₃ about an axis. Finally, we state that all arguments of the present section mutatis mutandis can also be applied to the propionic acid results presented in part 1.

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