Temperature Dependence of the Proton NMR Spectra of Bitumen

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The temperature dependence of the proton NMR spectra of bitumen samples of different origin and quality has been measured between 400 K and 80 K. Whereas the linewidths of different samples are essentially identical above 340 K and below 240 K, there is a significant difference in the linewidth transition region around room temperature.

The results show that it is possible to discriminate between bitumen samples of different composition and quality by simply measuring the proton NMR linewidth at room temperature.

Bitumen [1] is the most essential part of colloidal asphalt suspensions. It determines to a large extent the quality of the asphalt covering layer of highways and other roads. It is a multi-component hydrocarbon obtained by destillation of petroleum and represents a highly structured colloidal system where micellar and lamellar liquid crystalline phases may exist [1]. The commercially available bitumens greatly vary in chemical composition and quality. If the bitumen in the asphalt surface layer is not of sufficiently high quality, it becomes rather soft in hot summer days so that sand particles in the asphalt suspension drop from higher parts into lower parts of the layer thus reducing the mechanical strength of asphalt. Because of insufficient mechanical strength, cracks and other defects are formed. Heavy traffic enhances this process considerably.

The rapid characterization of the physical properties of bitumen [1] and asphalt suspensions is one of the important problems [2] in road construction. The standard characterization techniques comprise measurements of the viscosity, the complex elastic modulus, the shear and tensile strengths and other dynamic rheological properties. NMR has so far not been used for a determination of the rheological properties of bitumen though it has been used for the determination of its composition [3].

In order to determine if NMR can be used for a rapid characterization of the physical properties of bitumen we decided to measure the temperature dependence of the 1 H NMR spectra of bitumen of different origins and different suspensions. The measurements were performed at 270 MHz. The probe temperature was kept constant to ± 0.5 K. The spectra were measured by the Fourier transform spin-echo NMR technique.

The ^{1}H NMR absorption spectra of bitumen B 1074 of Croatian origin are presented in Fig. 1 a for different temperatures between 400 K and 200 K in 10 K intervals, whereas the corresponding spectra of B 798 of Italian origin are presented in Fig. 1 b for temperature between 400 K and 80 K.

The temperature dependence of the half width at half height (HWHH) of the proton spectra between 400 K and 200 K of B 1074 is presented in Fig. 2 and compared with the results for bitumen B 798. As expected, the width of the proton NMR absorption lines greatly changes during the hardening of bitumen.

Both in B 1074 and in B 798 the spectra are liquid like above 340 K, demonstrating that we are in this temperature range in the extreme motional narrowing limit. The two different varieties of bitumen have here essentially the same widths of the NMR spectra, which are of the order of 50 Hz. Below 340 K the viscosity of the samples increases so much that the dipolar broadening is not any more completely motionally averaged out by molecular motions. The onset of an NMR line width transition is evident in both samples. Below 340 K the linewidth quickly increases with decreasing temperature and reaches 60 kHz at 200 K.

The line shapes are super-Lorentzian above 200 K (Figures 1 a – b). Below 200 K the lineshape in B 798 becomes first Gaussian and then structured, showing a three peak feature at 80 K. The width of the central peak is about 5 kHz, whereas the separation of the outer peaks is of the order of 100 kHz. The proton NMR linewidth $\Delta\nu$ thus changes by a factor of 1000 in course of the hardening of bitumen.

The shape of the linewidth transition is qualitatively different from the one expected for the freezing of a simple classical liquid. The variation of $\Delta\nu$ with tem-

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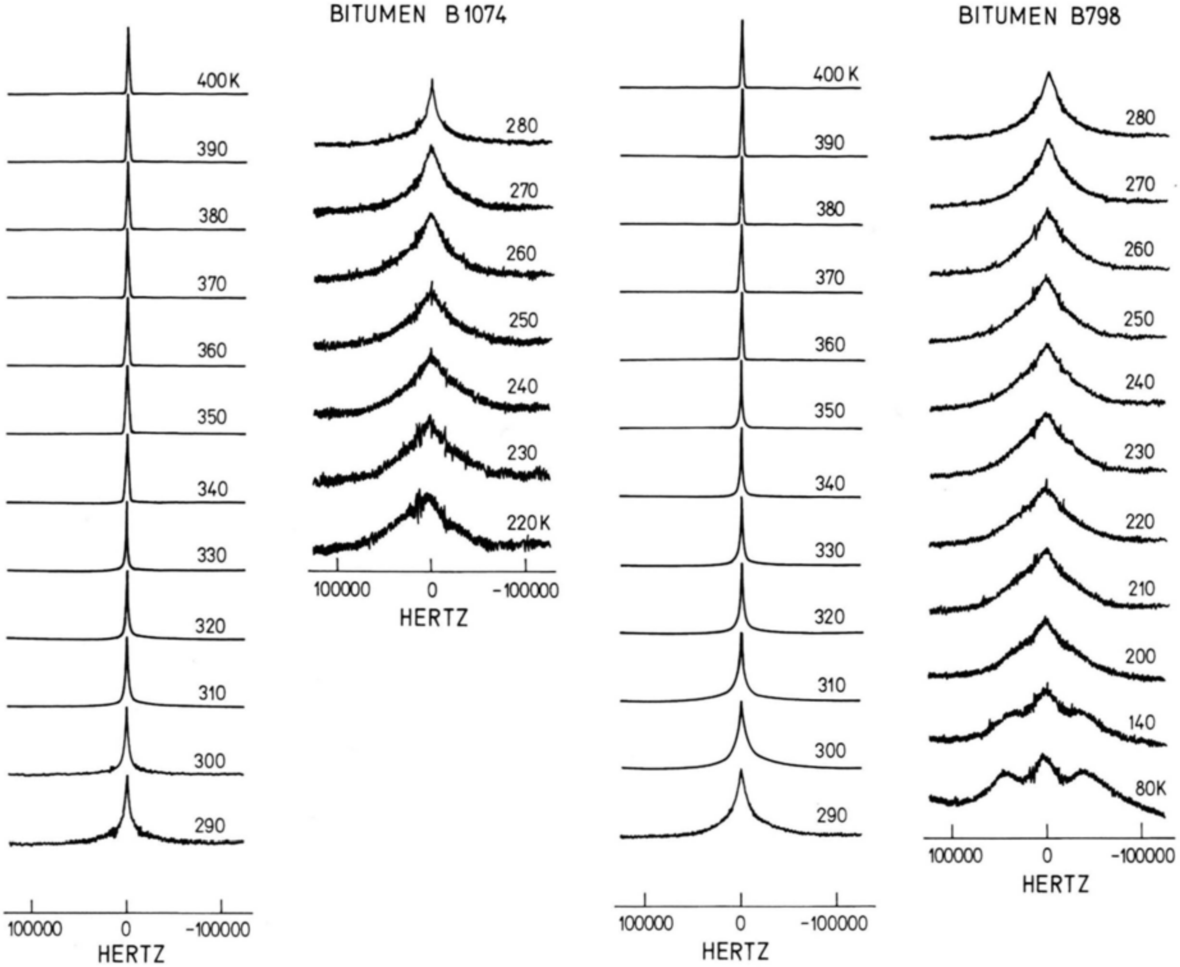

Fig. 1. Temperature dependence of the proton NMR spectra of: (a) bitumen B 1074, and (b) bitumen B 798 at a Larmor frequency of 270 MHz.

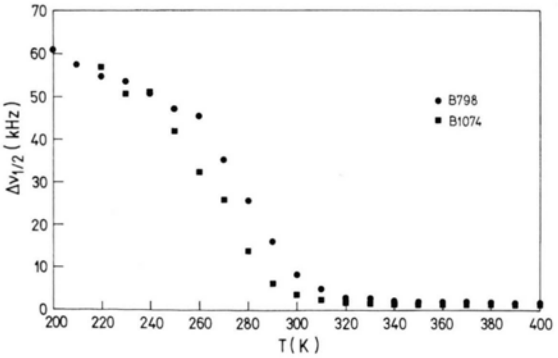

Fig. 2. Temperature dependence of halfwidth at half height of the proton NMR spectra of bitumen B 798 and B 1074.

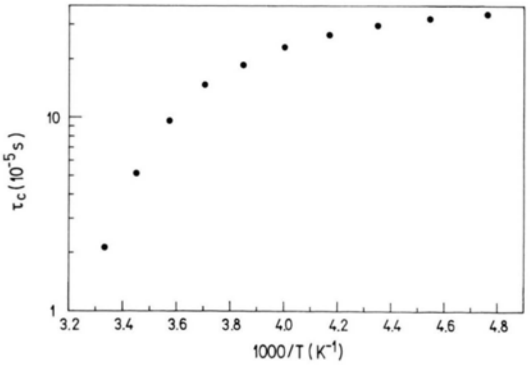

Fig. 3. Temperature dependence of the apparent rotational correlation times τ_c of the bitumen B 1074 as deduced from equation (1). The data show that we deal with a distribution of activation energies rather than with a single one.

perature is much more gradual than predicted [4] by the well known equation

$$(\Delta\nu) = (\Delta\nu_0)\, 2/\pi \tan^{-1}[2\pi\,\Delta\nu\,\tau_c] \qquad (1)$$

and can not be described by a single thermally activated molecular correlation time $\tau_c = \tau_\infty \exp(E/kT)$. Here $(\Delta\nu_0)$ is the rigid lattice linewidth.

This is not surprising for such a complex multi component system where the molecular dynamics is expected to be governed by a distribution of correlation times [5], e.g.

$$g(\ln\tau_c) = \text{const and non-zero for } \tau_{c1} < \tau_c < \tau_{c2} \text{ and zero otherwise}, \qquad (2)$$

rather than by a single τ_c. If one nevertheless tries to use (1) to describe the linewidth transition one finds for e.g. bitumen B 1074 that the effective τ_c varies with temperature as show in Fig. 3, i.e. the plot of log τ_c as a function of $1/T$ is not a straight line and we have a whole distribution of activation energies rather than a single one.

The rather low values of τ_c at relatively high temperatures further demonstrate that we do not deal here with reorientation of individual molecules but rather with colloidal clusters.

It is interesting to note that above 300 K or below 240 K there is no significant difference in the linewidth between the two different bitumen samples. There is, however, a significant difference in the linewidth in the transition region. The width of the B 798 sample at 280 K amounts to 25 kHz whereas the corresponding width of the B 1074 sample is only about 15 kHz at the same temperature. This means that it is possible to discriminate between bitumen samples differing in their rheological properties by a simple measurement of the width of the proton NMR spectrum around room temperature. Practical applications of this method are now being tested.

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[5] See, for instance, Y. Tazuke and F. Matsukura, J. Phys. Soc. Jpn. **65,** 2994 (1966) and references therein.

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