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(20) Thus polydispersity becomes unimportant in this domain.

Depolarized Rayleigh Dip Spectra in the *n*-Alkanes

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ABSTRACT: The existence of the depolarized Rayleigh dip in the spectra of two *n*-alkanes is clearly demonstrated. The spectra are found to be in good quantitative agreement with the general theories of depolarized Rayleigh scattering in viscoelastic media. The coupling parameter R is found to be 0.33 ± 0.02 for *n*-hexadecane at 65 °C and 0.38 ± 0.02 for *n*-docosane at 110 °C. Thus the *n*-alkane liquids are not qualitatively different from other liquids previously studied.

General theories[2-4] of Rayleigh scattering by a viscoelastic medium predict that the depolarized (I_{HV}) spectrum will exhibit a central dip when the quantity $q^2\eta/\rho$ is comparable to the overall half-width at half-height Γ_{HV} of the depolarized peak. The quantity $q = (4\pi n/\lambda) \sin \theta/2$ is the magnitude of the scattering vector for light of vacuum wavelength λ traveling in a medium with refractive index n and scattered through an angle θ in the scattering plane; η is the shear viscosity and ρ is the mass density. The dip is due to coupling between the hydrodynamic shear modes of the fluid and molecular reorientation. The predicted form of the spectrum is[2b]

$$I_{\mathrm{HV}}(\omega) \propto \frac{\Gamma_{\mathrm{HV}}}{\Gamma_{\mathrm{HV}}^2 + \omega^2} \sin^2 \theta/2 + \Gamma_{\mathrm{HV}} \cos^2 \frac{\theta}{2} \times \frac{(q^4\eta^2/\rho^2)(1 - R) + \omega^2}{(\Gamma_{\mathrm{HV}}(q^2\eta/\rho) - \omega^2)^2 + \omega^2(\Gamma_{\mathrm{HV}} + (1 - R)(q^2\eta/\rho))^2} \quad (1)$$

where R is a parameter which is equal to the fraction of the total shear viscosity which is due to coupling to molecular reorientation.

The theory should apply to any fluid composed of optically anisotropic molecules. The quantity $q^2\eta/\rho$ is known to be comparable to Γ_{HV} for the *n*-alkanes liquids. Thus, the central dip is predicted to occur if the coupling parameter R is sufficiently large. We expect any optically anisotropic liquid to show the dip feature provided the value of $q^2\eta/\rho\Gamma$ is in the range of ~0.1 to 0.7 and the value of R is sufficiently large (~0.1 or greater). However, a recent paper[5] by Champion and Jackson reported that none of the I_{HV} spectra in the *n*-alkanes showed any evidence of this central dip. The purpose of the present paper is to demonstrate the observation of a central dip in the depolarized Rayleigh spectra of two *n*-alkanes. The spectra were fit to the form given in eq 1 and a value of R was determined. The results are then discussed in detail and compared to the work of Champion and Jackson.

Experimental Section

The spectra were obtained as described previously.[6] The incident light was at 5145 Å and the free spectral range of the Fabry-Perot interferometer was 7.41 GHz. Great care was taken to render the incident light highly polarized in the horizontal direction relative to the scattering plane. The scattering angle was $\theta = 90°$. A Glan-Thompson polarizer was used to isolate the HV component of the scattered light.

The spectra were recorded with a 1024-point multichannel analyzer and fit with a nonlinear least-squares program described previously.[7] The deconvoluted values of Γ_{HV}, $q^2\eta/\rho$, and R for each spectrum were obtained by comparing the fitted results with spectra obtained by convoluting the instrumental function with eq 1.

n-Hexadecane (99%) and *n*-docosane (99%) were obtained from the Chemical Samples Co. The liquids were filtered directly into square quartz cells. The samples were held in a thermostated aluminum block and the temperatures were controlled to ±0.2 °C.

Results and Discussion

The depolarized (I_{HV}) spectrum of *n*-hexadecane at 65 °C is shown in Figure 1. The central dip is clearly visible. This feature was studied from 40–80 °C, but the best spectra were obtained near 65 °C. The overall width of the peak was $\Gamma_{\mathrm{HV}} = 1.30 \pm 0.05$ GHz and agrees quite well with the value reported by Champion and Jackson.[5] The quantity $q^2\eta/\rho$ calculated from direct measurements is 186 MHz for *n*-hexadecane at 65 °C. The value obtained from the fit to the depolarized spectrum is $q^{2\eta/\rho} = 196 \pm 20$ MHz. The coupling parameter is measured to be $R = 0.33 \pm 0.02$. This value for R is in the same range as that measured in several previous studies of the depolarized Rayleigh dip in other liquids.[7-10] Although no dip was actually observed, Champion and Jackson estimated the value of R to be near 0.1 by comparing depolarized Rayleigh and flow birefringence data. The present results cast some doubt on the validity of that analysis.

The I_{HV} spectrum of *n*-docosane at 110 °C is shown in Figure 2. The overall width is $\Gamma_{\mathrm{HV}} = 1.05 \pm 0.05$ GHz. The calculated value of the shear width quantity is $q^{2\eta/\rho} = 187$ MHz. The value obtained by fitting the spectrum is 199 ± 20 MHz. The coupling parameter is found to be $R = 0.38 \pm 0.02$. The depolarized Rayleigh spectra of the *n*-alkanes are found to be in good quantitative agreement with the general theories.

The observation of the central dip feature in liquids depends on both physical considerations and experimental conditions. Keyes and Kivelson[3] have shown that no central dip exists when the quantity $q^2\eta/\rho\Gamma_{\mathrm{HV}}$ is greater than a critical value given by

$$\left(\frac{q^2\eta}{\rho\Gamma_{\mathrm{HV}}}\right)_{\mathrm{C}} = \frac{(1 - R)R + [(1 - R)^2 + \tan^2 \theta/2]^{1/2}R^{1/2}}{(1 - R)^3 + \tan^2 \theta/2} \quad (2)$$

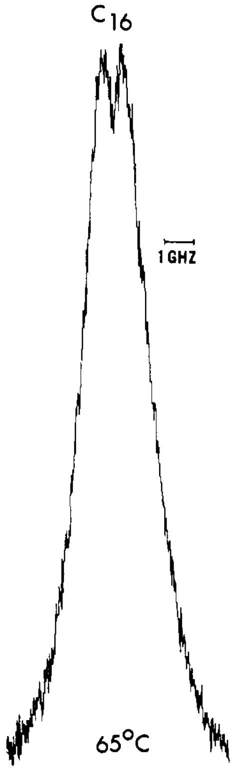

Figure 1. Depolarized (I_{HV}) spectrum of *n*-hexadecane at 65 °C.

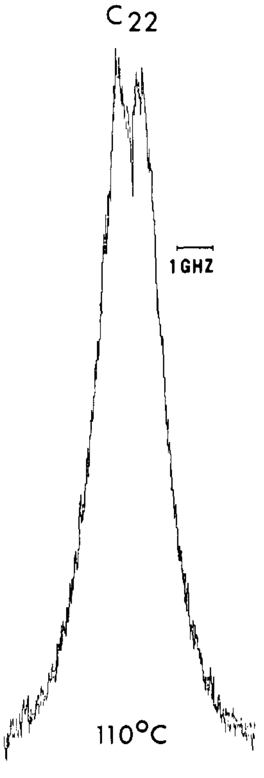

Figure 2. Depolarized (I_{IV}) spectrum of *n*-docosane at 110 °C.

For *n*-hexadecane, this critical value is equal to 0.7 and will be reached for $T \approx 32$ °C. In the present study clear demonstration of a central dip was possible above 40 °C. At 40 °C, the I_{HV} spectrum has a very flat top with a shallow central minimum. At much higher temperatures (small $q^2\eta/\rho\Gamma_{HV}$), the spectra can be expressed as

$$I_{HV}(\omega) \propto \frac{\Gamma_{HV}}{\Gamma_{HV}^2 + \omega^2} - R \cos^2 \theta/2 \, \frac{q^2\eta}{\rho\Gamma_{HV}} \, \frac{q^2\eta/\rho}{(q^2\eta/\rho) + \omega^2} \quad (3)$$

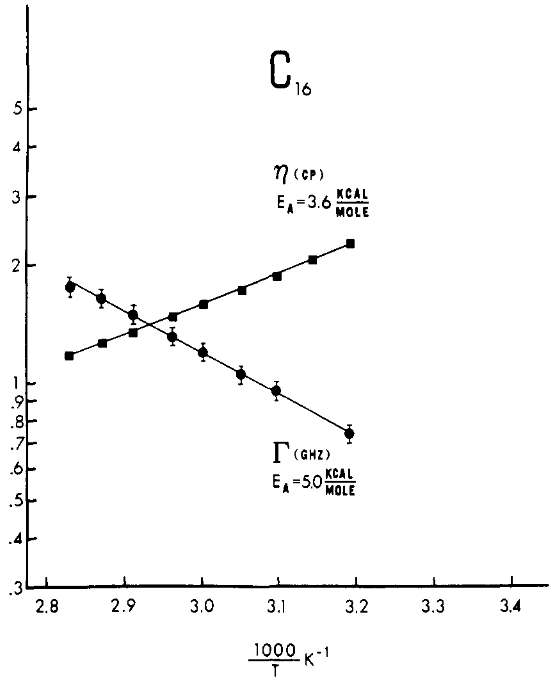

Figure 3. Shear viscosity η and half-width at half-height Γ_{HV} vs. $1/T$ for *n*-hexadecane. The apparent activation energy for η is 3.6 kcal mol^{-1} and Γ_{HV} is 5.0 kcal mol^{-1}.

As $q^2\eta/\rho\Gamma_{HV}$ becomes small, the integrated intensity of the dip feature vanishes.

For the *n*-alkanes, the temperature range over which the dip is clearly observed is limited. The primary reason for this behavior is shown in Figure 3. The log of the viscosity η and linewidth Γ_{HV} are plotted vs. $1/T$. The apparent activation energies for both η and Γ_{HV} are relatively high for a molecular fluid well above the glass-transition temperature. As a result the quantity $q^2\eta/\rho\Gamma_{HV}$ is only smaller than its critical value and also large enough to give a measureable dip for a narrow temperature interval.

The experimental conditions necessary to observe the central dip are very stringent. The polarization of the incident and scattered light must be precisely set to obtain only the I_{HV} spectrum. Leakage of the I_{VV} or I_{HH} components will yield excess intensity at $\Delta\omega = 0$ and obscure the dip. The liquid must be very pure and free from particulate matter. Also, stray light from cell windows or other external sources must be minimized. All the above experimental problems lead to excess scattering at $\Delta\omega = 0$ and will hide the dip.

In order to resolve the central dip it is desirable to have a free spectral range below 8 GHz and a finesse above 40. This yields an instrumental width less than or equal to 200 MHz. Such a resolution is sufficient to observe the dip near 65 °C. At much higher temperatures the width of the central dip is given by $q^2\eta/\rho$ and the above conditions are insufficient to resolve the narrow central feature.

Greater resolution can be obtained by using a smaller free spectral range, but the signal-to-noise ratio at the peak is greatly reduced. The need to optimize both resolution and peak signal-to-noise ratio eventually limits observation of the dip at higher temperatures. The spectra published by Champion and Jackson[5] for *n*-hexadecane at 60 °C lacked the necessary signal-to-noise ratio to clearly resolve the dip.

As the temperature is raised, the total depolarized intensity for the *n*-alkanes falls off as $T/(T - T_0)$.[11] When this fact is coupled with the reduction in peak intensity which decreases as $1/\Gamma_{HV}$, the observation of a central dip in the *n*-alkanes at higher temperatures becomes very difficult.

In the present work the signal-to-noise ratio was kept high by scanning very slowly (1 s/point) and by using 1024-point spectra. The free spectral range was chosen to optimize resolution and peak height. All the precautions noted above were taken. Thus the existence of the depolarized Rayleigh dip in the *n*-alkanes has been demonstrated. A full study of the depolarized Rayleigh spectra in a wider range of *n*-alkanes is presently being carried out. Also a discussion of the significance of the value of R and the correlation between the value of R and molecular structure is presented in a forthcoming paper.[12]

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Gas-Chromatographic Investigation of the Thermodynamic Interactions of Poly(dimethylsiloxane) or Poly(diethylsiloxane) with Some Solvents between 60 and 180 °C

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ABSTRACT: Gas–liquid chromatography has been used for the thermodynamic study of the interactions between poly(dimethyl- or (diethylsiloxane) and various aliphatic or aromatic hydrocarbons within the temperature range 60–180 °C. The experimental results related to PDMS are in good agreement with literature data obtained either by dynamic or static methods and restricted to the lower temperatures. The thermodynamic interaction parameters were discussed in terms of Flory and Prigogine–Patterson theories.

In the last 10 years, the study of the thermodynamics of interactions between polymers and solvents by "inverse gas chromatography" has received increased attention.[1] This dynamic method is now being applied to a growing number of complex systems even when the liquid–vapor equilibrium is not reached instantaneously (glassy or crystalline polymers as opposed to liquid polymers) and even when specific interactions may occur between polymers and solvents (as opposed to nonpolar systems).

Because of the conjugated effects of its low glass transition temperature and of its enhanced chain flexibility poly(dimethylsiloxane) (PDMS) behaves as a nearly ideal system with respect to inverse gas-chromatography experiments, and thus it has been investigated by several authors.[2-4] Most of these studies are related to the systems PDMS–hydrocarbons (linear or branched alkanes or aromatic hydrocarbons) within a narrow range of temperature (20–60 °C).

In the present work we have focused our interest on three points: the study of interactions between PDMS and aliphatic or aromatic hydrocarbons over a wide range of temperature up to 180 °C (the experimental variations of the activity coefficient of the probe at infinite dilution (Ω^∞) and of the Flory χ parameter with temperature were discussed according to Flory and to Prigogine–Patterson theories); the study of the influence of the chain structure using both linear samples and model PDMS networks; the comparison between PDMS and its next higher homologue poly(diethylsiloxane) (PDES), since the thermodynamics of PDMS solutions cannot be accurately described according to classical theories.

Experimental Section

Apparatus. The gas chromatograph used was a dual column apparatus (INTERSMAT IGC 15) fitted with a thermal conductivity detector; the column oven temperature was controlled to within ±0.05 °C. The flow rate of helium used as carrier gas (10–30 mL/min) was measured at the column outlet by a soap-bubble flowmeter; inlet pressure (850–1400 Torrs) was monitored to within 1 Torr with a mercury manometer. The outlet pressure was the atmospheric pressure.

Probe Molecules and Stationary Phases. The probe solutes were the best reagent grade and were used in most cases without further purification; chloroform was eluted over activated alumina and dioxane was distilled over the disodium–benzophenone complex.

The PDMS samples used as the stationary phase were obtained from the Rhône-Poulenc Co.; two samples were involved: PDMS $\overline{M}_n = 3 \times 10^4$, $\overline{M}_w/\overline{M}_n = 3$, $\mathrm{S_i}$–OH end groups; PDMS $M_n = 1.7 \times 10^4$, $\overline{M}_w/\overline{M}_n = 1.2$, $\mathrm{S_i}$–H end groups. They were heated for 24 h at 100 °C under vacuum (0.1 Torr) to remove any low-boiling component.

The PDMS network was prepared by polycondensation of PDMS bearing silane end groups ($\overline{M}_n = 3770$) and tetraallyloxyethane.[5] This sample may be considered as a model network; the fluctuations in the length of the elastic linear chains between two consecutive nodules were low and the functionality of the cross-linking points was constant and equal to 4.

The PDES sample (Dow Corning Co.) was a generous gift of Dr. Manley (Pulp and Paper Research Institute of Canada, Montréal), $\overline{M}_n = 1.12 \times 10^5$, $\overline{M}_w/\overline{M}_n = 2.5$. Its molar specific volume was measured by dilatometry between 25 and 85 °C. The experimental values fit the following relation obtained by second-order regression analysis

$$\frac{1}{v_{\mathrm{sp}}}\ (\mathrm{cm^3\ g^{-1}}) = 1.0046 - 6.2556 \times 10^{-4}t + 1.1648 \times 10^{-6}t^2 \quad (1)$$