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Hypersonic Velocity in Benzonitrile and Solutions of Benzonitrile in Carbon Tetrachloride

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The hypersonic velocity and dynamic isentropic compressibility of neat benzonitrile and solutions in carbon tetrachloride were measured by Brillouin spectroscopy in the temperature range from 293 to 373 K in the 5-6-GHz frequency region. Tables of the index of refraction for neat benzonitrile and solutions of benzonitrile in carbon tetrachloride are also given.

Introduction

The hypersonic velocity and dynamic isentropic compressibility of neat benzonitrile and solutions in carbon tetrachloride were measured from 293 to 373 K by using Brillouin light scattering in the 5-6-GHz frequency region. The measurements were made as part of a study of sound velocity in associated liquids. A large dispersion in the hypersonic velocity was observed. No one has previously reported these values as a function of temperature for neat benzonitrile or the solutions in the hypersonic frequency region.

Experimental Section

Purification of Materials**.** The benzonitrile and carbon tetrachloride were obtained from Baker and were redistilled. Volume precent solutions of 90%, 80%, and 60% of benzonitrile in carbon tetrachloride were made. The neat benzonitrile as well as the solutions were repeatedly filtered through fritted glass with pore size 4.5-5.0 μm into a fluorescence cell. The filtration was necessary in order to remove dust from the sample, which may obscure the Brillouin peaks.

Measurement of the Hypersonic Velocity**.** The experimental setup has been previously published (*1*). An argon ion laser operated at 514.5 nm was focused onto the sample cell, which was thermostated to ±0.1 K. The scattered light was focused through a Fabry-Perot interferometer with a long focal length lens. Output of the interferometer was focused with a second lens through a pinhole onto a photomultiplier tube (PMT). The output of the PMT was digitized and stored on an LSI 11/03 minicomputer.

The refractive indices of the benzonitrile solutions were measured as a function of temperature and the density data for the neat benzonitrile were taken from the literature (*2*). Additional density data were taken to complement previously reported data for the solutions (*3*).

The free spectral range (FSR) was 17.98 GHz for the neat benzonitrile and the 80% solution, and 18.78 GHz for the other solutions. The sound velocities were accurate to ±2% and the dynamic isentropic compressibilities to ±3%.

Table I. Hypersonic Velocity and Dynamic Isentropic Compressibility for Neat Benzonitrile

T, K	ω_s, GHz	C_s, ms^{-1}	χ_s, GPa
296.1	6.60	1572	0.404
298.7	6.56	1564	0.411
303.7	6.46	1542	0.425
306.9	6.45	1541	0.427
313.1	6.24	1494	0.458
319.5	6.18	1482	0.470
322.7	6.09	1462	0.484
326.9	6.01	1444	0.499
332.1	5.87	1413	0.524
336.1	5.86	1412	0.527
339.1	5.79	1397	0.541
342.2	5.75	1388	0.550
345.1	5.69	1374	0.562
348.5	5.59	1352	0.585
353.1	5.52	1337	0.601
356.1	5.45	1322	0.617
359.3	5.42	1315	0.626
362.9	5.34	1298	0.647
365.9	5.26	1279	0.667

Table II. Hypersonic Velocity and Dynamic Isentropic Compressibility for 90% (v/v) Benzonitrile in Carbon Tetrachloride

T, K	ω_s, GHz	C_s, ms^{-1}	χ_s, GPa
300.3	6.06	1450	0.456
303.7	6.03	1445	0.461
306.9	5.98	1435	0.473
313.1	5.90	1417	0.488
316.8	5.87	1412	0.496
319.5	5.78	1391	0.513
322.7	5.72	1378	0.525
326.9	5.67	1367	0.538
329.1	5.65	1364	0.543
336.1	5.52	1335	0.575
339.1	5.46	1322	0.590
342.2	5.44	1318	0.597
345.1	5.40	1310	0.609
348.5	5.33	1294	0.627
353.1	5.30	1289	0.639
356.1	5.22	1271	0.661
359.3	5.18	1262	0.675
362.9	5.12	1249	0.695
365.9	5.05	1232	0.717

Table III. Hypersonic Velocity and Dynamic Isentropic Compressibility for 80% (v/v) Benzonitrile in Carbon Tetrachloride

T, K	ω_s, GHz	C_s, ms^{-1}	χ_s, GPa
300.3	5.79	1391	0.472
306.9	5.72	1376	0.490
313.1	5.65	1362	0.508
322.7	5.49	1328	0.548
326.9	5.35	1295	0.582
332.1	5.32	1290	0.604
339.1	5.16	1254	0.640
342.2	5.10	1241	0.659
353.1	4.94	1206	0.718

Results and Discussion

The hypersonic velocity and dynamic isentropic compressibility for the benzonitrile solutions are given in Tables I-IV. The experimentally measured quantity in Brillouin light scattering is the adiabatic hypersonic frequency, ω_s. The adiabatic sound frequency is given by the frequency shift of the Brillouin peaks from the laser frequency relative to the splitting between adjacent orders of the Brillouin spectra. The splitting between the adjacent orders is the FSR and is used to calibrate the fre-

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Table IV. Hypersonic Velocity and Dynamic Isentropic Compressibility for 60% (v/v) Benzonitrile in Carbon Tetrachloride

T, K	ω_s, GHz	C_s, ms^{-1}	χ_s, GPa
300.3	5.49	1300	0.463
303.9	5.42	1313	0.476
306.9	5.33	1293	0.493
319.1	5.27	1284	0.507
322.7	5.15	1256	0.532
326.9	5.13	1253	0.537
332.1	5.02	1228	0.562
339.1	4.90	1202	0.592
345.1	4.81	1182	0.616

Table V. Index of Refraction (n) for Solutions of Benzonitrile in Carbon Tetrachloride

	n			
T, K	100% [a]	90% [a]	80% [a]	60% [a]
295.5	1.5276			
295.7		1.5221	1.5165	
295.9				1.5040
306.9	1.5226	1.5170	1.5115	1.4985
317.1	1.5178	1.5124	1.5063	1.4933
326.9	1.5139	1.5084	1.5025	1.4895
337.1	1.5093	1.5040	1.4972	1.4840
344.1	1.5064			
343.9		1.4995	1.4940	1.4805

[a] Concentration given as volume percent benzonitrile in carbon tetrachloride.

quency shift of the digitized data.

The hypersonic velocity, C_s, was calculated with eq 1

$$C_s = 2\pi\omega_s/q \tag{1}$$

where q is the scattering wave vector, given by

$$q = (4\pi n/\lambda) \sin (\theta/2) \tag{2}$$

and where n is the refractive index, λ is the wavelength of the incident light, and θ is the scattering angle which for our measurements was 90°. The refractive indices were measured in our laboratory as a function of temperature and are given in Table V. A thousand data points were taken over two spectral orders. All the spectra were fitted to a Lorenztian line shape by using a Simplex fitting routine from which the ω_s values were obtained.

The dynamic isentropic compressibility, χ_s, was calculated with

$$\chi_s = C_s^{-2}\rho^{-1} \tag{3}$$

where ρ is the density. Values for the density were measured in our laboratory to complement values in the literature (*3*). The refractive indices and densities were interpolated to the spectral temperature. From the uncertainty in the reported values of density and refractive indices the error is less than 1% and does not contribute significantly to the error in the reported velocity. The major source of error is in the uncertainty in the FSR (±2%) which produces systematic error in all data sets.

The values of the speed of sound as measured by ultrasonic absorption as reported in the literature are 1378 and 1428 ms^{-1} at 308 and 293 K, respectively (*4*, *5*). The reported values for the hypersonic velocity are greater than the ultrasonic values due to a relaxation processs in the hypersonic frequency region. A discussion of the relaxation mechanism has been given (*6*). Relaxation always gives rise to positive dispersion; therefore, we should expect that the hypersonic velocity should be greater than the ultrasonic velocity. This is in agreement with the observed results. The reported compressibility is the dynamic compressibility; that is, it also contains the contribution due to the shear modulus. In the hypersonic frequency region the shear modulus is, in general, not negligible.

Registry No. Benzonitrile, 100-47-0; carbon tetrachloride, 56-23-5.

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Vapor Pressures for Biphenyl, 4-Chlorobiphenyl, 2,2′,3,3′,5,5′,6,6′-Octachlorobiphenyl, and Decachlorobiphenyl

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Vapor pressures were determined by using a gas saturation technique for biphenyl, 4-chlorobiphenyl, 2,2′,3,3′,5,5′,6,6′-octachlorobiphenyl, and decachlorobiphenyl over the temperature ranges of 5.2–24.7, 4.2–24.9, 29.0–61.2, and 50.7–89.8 °C, respectively. Vapor pressures (in pascals ± standard deviation) at 25 °C were extrapolated or interpolated from the measured values, and these values are as follows: biphenyl, 1.19 ± 0.03; 4-chlorobiphenyl, 0.175 ± 0.006; 2,2′,3,3′,5,5′,6,6′-octachlorobiphenyl, (2.90 ± 0.20) × 10^{-5}; and decachlorobiphenyl, (5.30 ± 0.31) × 10^{-8}.

Introduction

In understanding and modeling the dynamics of polychlorinated biphenyls (PCBs) in the environment, one needs physical and chemical properties such as aqueous solubilities, vapor pressures, and melting points. Currently, vapor pressure data for the very highly chlorinated PCB congeners do not exist. In this report, vapor pressures determined by a gas saturation technique are reported for two highly chlorinated PCB congeners (2,2′,3,3′,5,5′,6,6′-octachlorobiphenyl and decachlorobiphenyl) and for 4-chlorobiphenyl and biphenyl.

Experimental Section

Compounds and Reagents. The 4-chlorobiphenyl and decachlorobiphenyl were obtained from Aldrich Chemical Co., Milwaukee, WI. The biphenyl and 2,2′,3,3′,5,5′,6,6′-octachlorobiphenyl were obtained from Ultra Scientific, Hope, RI. All compounds were used as received and had purities of 99% or greater. Fisher Scientific, Itasca, IL, pesticide-grade solvents

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