

Table II. Comparison of Experimental and Calculated Diffusion Coefficients for C₃H₈-He

temp, °C	D ₁₂ , cm ² /s		
	exptl	from eq 3	D ₁₂ (calcd) - D ₁₂ (exptl)
21.3	0.3005 ± 0.0010	0.3002	-0.0003
30.3	0.3292 ± 0.0010	0.3295	+0.0003
40.1	0.3601 ± 0.0010	0.3633	+0.0022
51.0	0.4104 ± 0.0011	0.4036	-0.0068
60.3	0.4365 ± 0.0015	0.4403	+0.0038

lation between Yang and Hawkes' (4) values of 15 and 20 °C gave $D_{12} = 0.6446$ cm²/s. The expected reliability of either determination (4) is 0.2% or 0.0013, so that a difference of 0.0015 between the two measurements is satisfactory.

Propane in Helium

The new measured data for propane in helium are shown in Table I. These were fitted to the equation $\log D_{12} = A + B$

$\log T$ by using a linear least-squares regression and gave

$$\log D_{12} = -8.1277 + 3.0805 \log T \quad (3)$$

with a correlation coefficient of 0.9976. The coefficients require D_{12} to be in cm²/s and T to be in Kelvin. The number of significant figures quoted is required because the fitting of the two numbers is highly correlated so that rounding of either requires adjustment of the other. Individually, they could not be relied upon to the implied precision.

The experimental and fitted values are shown in Table II.

Registry No. Propane, 74-98-6; helium, 7440-59-7.

Literature Cited

- (1) Yang, F. J.; Hawkes, S. J.; Lindstrom, F. T. *J. Am. Chem. Soc.* **1976**, *98*, 5101.
- (2) Knox, J. H.; McLaren, L. *Anal. Chem.* **1964**, *36*, 1477.
- (3) Einstein, A. *Ann. Phys. (Leipzig)* **1905**, *17*, 549.
- (4) Yang, F. J.; Hawkes, S. J. *J. Chem. Eng. Data* **1979**, *24*, 354.

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Sound Velocity in Formamide

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The speed of sound and the isentropic compressibility of formamide were measured by Brillouin spectroscopy in the temperature range from 293 to 373 K.

Introduction

The speed of sound and the isentropic compressibility of formamide were measured from 293 to 373 K by using Brillouin light scattering. The measurements were made as part of a study of sound velocity in associated liquids. Brillouin spectroscopy has been shown to provide accurate values of the speed of sound and isentropic compressibility in liquids (1). A survey of the literature revealed that no one has previously reported these values as a function of temperature or by Brillouin light scattering.

Experimental Section

Purification of Materials. Spectroscopic-grade formamide obtained from Aldrich was used without further purification. The formamide was repeatedly filtered through fritted glass with a pore size of 4.5–5.0 μm into a fluorescence cell. The filtration is necessary in order to remove dust from the formamide which may obscure the Brillouin peaks.

Measurement of the Speed of Sound. A description of the experimental setup has been previously published (2). 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 photomul-

Table I. Speed of Sound and Isentropic Compressibility of Formamide

T, K	ω _s , GHz	C _s , ms ⁻¹	κ _s , GPa
296.1	6.60	1661	0.320
300.3	6.53	1646	0.327
303.7	6.51	1641	0.329
306.9	6.45	1628	0.336
309.9	6.41	1619	0.340
316.8	6.38	1614	0.344
319.5	6.35	1607	0.348
326.9	6.27	1588	0.358
329.4	6.22	1577	0.364
332.1	6.18	1568	0.369
336.1	6.17	1567	0.370
339.1	6.14	1560	0.375
342.2	6.12	1557	0.377
345.1	6.10	1552	0.380
348.5	6.05	1541	0.387
353.1	6.00	1531	0.393
356.1	5.99	1528	0.396
359.3	5.96	1523	0.399
362.7	5.92	1514	0.405
365.9	5.90	1508	0.409
368.7	5.85	1497	0.416
372.0	5.82	1491	0.420

tiplier tube (PMT). The output of the PMT was digitized and stored on an LSI 11/03 minicomputer.

The free spectral range (FSR) was 19.34 GHz. The sound velocities are accurate to ±2% and the isentropic compressibilities to ±3%.

Results and Discussion

The speed of sound and isentropic compressibilities for formamide as a function of temperature are given in Table I. The experimentally measured quantity in Brillouin light scattering is

the adiabatic sound 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 frequency shift of the digitized data.

The sound velocity was calculated with eq 1

$$C_s = 2\pi\omega_s/q \quad (1)$$

where C_s is the sound velocity and q is the scattered wave vector. The scattered wave vector is given by

$$q = (4\pi n/\lambda) \sin(\theta/2) \quad (2)$$

where n is the refractive index, λ is the wavelength of the incident light, and θ is the scattering angle. For our measurements the scattering angle was 90° . The refractive indices were obtained from published values (3).

A thousand data points were taken over two spectral orders. All the spectra were fitted to a Lorentzian line shape by using a Simplex fitting routine from which the ω_s values were obtained (4).

The isentropic compressibility, χ_s , was calculated with

$$\chi_s = C_s^{-2}\rho^{-1} \quad (3)$$

where ρ is the density. Values for the density as a function of temperature were also obtained from the literature (5). The

refractive indices and densities were interpolated from the values in the literature. From the given uncertainty in the reported values of density and refractive indices the error is much less than 1% and does not contribute significantly to the error in the reported velocities. The major source of error is in the uncertainty in the FSR ($\pm 2\%$) which produces systematic error in all the data.

The quoted value in the literature of the speed of sound for formamide at 298 K was 1622 ms^{-1} (6). This value was determined by ultrasonic methods and is within the quoted error of our value.

Registry No. Formamide, 75-12-7.

Literature Cited

- (1) Goodman, M. A.; Whittenburg, S. L. *J. Chem. Eng. Data* **1983**, *28*, 350.
- (2) Keegan, P. F.; Whittenburg, S. L. *J. Phys. Chem.* **1982**, *86*, 4622.
- (3) Boit, H. G. "Beilsteins Handbuch der Organischen Chemie"; Springer-Verlag: West Berlin, 1920; Vol. 2.
- (4) Gottfried, B. S.; Weisman, J. "Introduction to Optimization Theory"; Prentice-Hall: Englewood Cliffs, N.J., 1973; Chapter 8.
- (5) "International Critical Tables of Numerical Data, Physics, Chemistry and Technology"; McGraw-Hill: New York, 1933.
- (6) Helwege, K. H. "Landolt-Bornstein: Numerical Data and Functional Relationships in Science and Technology", 6th ed.; Springer-Verlag: New York, 1967.

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Vapor-Liquid Equilibria in Binary Systems Containing 1,3-Dioxolane at Isobaric Conditions. 4. Binary Mixtures of 1,3-Dioxolane with 1,4-Dioxane and 1,1,2,2-Tetrachloroethane

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Isobaric vapor-liquid equilibria (VLE) for the binary systems 1,3-dioxolane-dioxane and 1,3-dioxolane-tetrachloroethane were measured at 150, 300, 500, 650, and 740 mmHg by using a Stage-Müller distilling apparatus. The Redlich-Kister equation, with temperature-dependent parameters, was used to correlate the VLE data. A one-temperature-dependent-parameter equation is sufficient for the system 1,3-dioxolane-dioxane and for the system 1,3-dioxolane-tetrachloroethane at $P = 150$ and $P = 740$ mmHg, whereas a two-temperature-dependent-parameter equation is needed for the second system at $P = 300, 500,$ and 650 mmHg.

Isobaric vapor-liquid equilibria (VLE) data at several subatmospheric pressures were determined for the binary systems of 1,3-dioxolane (1) with 1,4-dioxane (2) and with 1,1,2,2-tetrachloroethane (tetrachloroethane) (2). This study is a continuation of the systematic acquisition of isobaric VLE data for binary systems containing 1,3-dioxolane as a common component (1-4).

Table I. Refractive Index-Composition Data for 1,3-Dioxolane-Dioxane

x_1	n_D^{25}	x_1	n_D^{25}
1.0000	1.3992	0.4446	1.4123
0.9189	1.4012	0.3720	1.4139
0.8305	1.4035	0.2306	1.4168
0.7197	1.4062	0.1662	1.4181
0.6272	1.4084	0.0951	1.4195
0.5410	1.4103	0.0000	1.4214

Experimental Section

The Fluka product 1,3-dioxolane (analytical grade, 99%) was purified by refluxing on sodium in inert gas flow and fractionated on a Vigreux column, following the procedure given in ref 1. Dioxane and tetrachloroethane (C. Erba RPE products) were used without purification. Their major impurity is water (0.02% and 0.05%, respectively). The refractive indices of dioxane and tetrachloroethane are $n_D^{20} = 1.4224$ (lit. (5) $n_D^{20} = 1.4224$) and $n_D^{20} = 1.4944$ (lit. (5) $n_D^{20} = 1.4940$), respectively. The isobaric VLE data were determined with a Stage-Müller distilling