

Acoustical Properties of Aqueous Solutions of Urea: Reference Data for the Ultrasonic Spectrometry of Liquids

R. Hagen, R. Behrends, and U. Kaatze*

Drittes Physikalisches Institut, Georg-August-Universität, Bürgerstrasse 42–44, 37073 Göttingen, Germany

The density, sound velocity, and ultrasonic attenuation coefficient of aqueous solutions of urea were measured at temperatures between 10 °C and 35 °C and at concentrations ranging from 0 to 9 mol/L (≈ 21.7 mol %) urea. The data are correlated using simple empirical expressions, and the isentropic compressibilities are calculated. These urea solutions provide a favorable set of reference data for acoustical measurements of liquids with sound velocity between 1500 $\text{m}\cdot\text{s}^{-1}$ and 1700 $\text{m}\cdot\text{s}^{-1}$.

Introduction

Acoustical relaxation spectrometry is a powerful tool for the study of the molecular dynamics of liquids. Being available now in the broad frequency range from about 10 kHz to 5 GHz, acoustical attenuation measurements are capable of significant contributions to our knowledge of the fast kinetics in liquid systems and to our understanding of complex critical phenomena of liquids.^{1–6} Beyond the well-established position in basic research, ultrasonic spectrometry is now becoming a routine analytical technique, providing a nondestructive way to measure the properties of liquid materials.^{7–9}

Two main groups of methods for the accurate ultrasonic spectrometry of liquids can be distinguished.^{9,10} At frequencies between about 1 MHz and 10 GHz, pulse-modulated waves transmitted through the liquid are recorded at variable transmitter–receiver spacing. Because of the variations of the sample length, this method enables absolute measurements of the attenuation coefficient α of the sonic wave within the liquid. At smaller frequencies ν ($10 \text{ kHz} \leq \nu \leq 20 \text{ MHz}$), cavity resonator methods are applied in which the path length of the acoustic field interactions with the sample is effectively enlarged by multiple reflections. The half-power bandwidths $\Delta\nu_n$, $n = 1, 2, 3, \dots$, of the cavity resonance peaks with resonance frequencies ν_n are measured to yield, on ideal conditions, the attenuation coefficient as

$$\alpha(\nu_n) = \pi \Delta\nu_{n,\text{ideal}}/c_s \quad (1)$$

Here, c_s denotes the sound velocity. In addition to the sample losses, however, real cells are also subject to radiation energy losses at the back faces of the transducers and to dissipation of energy by diffraction. In measurements, including plano-concave and biconcave cells as well as spherical resonators, all instrumental losses are considered by energy arguments using a suitable quality factor relation.¹¹ The instrumental losses have to be found from calibration measurements using liquids of a precisely known attenuation coefficient. Close agreement of the sound velocity of the reference with that of the sample liquid is mandatory. For sound velocities smaller than 1500 $\text{m}\cdot\text{s}^{-1}$, methanol–water mixtures are available as a refer-

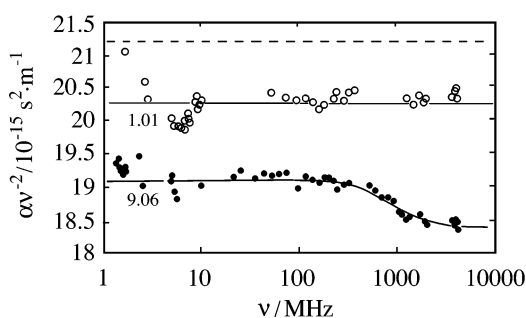


Figure 1. Ultrasonic attenuation spectra in the frequency-normalized format α/ν^2 vs ν for 1.01 M (○) and 9.06 M (●) solutions of urea in water at 25 °C (ref 12). The low-amplitude high-frequency relaxation term ($d(\alpha/\nu^2)/d\nu < 0$, $\nu > 200$ MHz) in the spectrum of the concentrated solution has been assigned to noncritical concentration fluctuations.¹² The dashed line shows the attenuation of water ($\alpha/\nu^2 = 21.24 \times 10^{15} \text{ s}^2\cdot\text{m}^{-1}$) at 25 °C.

ence. For higher sound velocities, no such reference liquids exist. We therefore investigated solutions of urea in water with sound velocities up to 1700 $\text{m}\cdot\text{s}^{-1}$ and measured their attenuation coefficient by an absolute method. These liquids offer favorable conditions for the use as reference standards because they do not show relaxation phenomena in the relevant frequency range. As illustrated by Figure 1, only at very high urea concentrations does a relaxation term with a small amplitude exist at frequencies above 200 MHz. In addition to this advantage, aqueous solutions of urea are easy to handle, harmless, and inexpensive.

Experimental Section

Materials. Urea ($\geq 99.5\%$) was supplied by Fluka (Deisenhofen, Germany) and was used without further purification. All solutions were prepared with deionized, additionally distilled, and degassed water by weighing appropriate amounts of urea and of water into suitable flasks, using a precision balance (Sartorius BP61S, $\pm 10^{-4}$ g). For simplicity, and in order to need only accurate weighing procedures in the sample preparation, we used as a primary concentration the quantity c_* in moles of solute per kilogram of solution. The molar concentration c has been calculated afterward with the aid of the density of the solution. The density ρ has been measured with a pycnometer (25 cm^3) that had been calibrated against

* To whom correspondence may be addressed. E-mail: uka@physik3.gwdg.de.

Table 1. Frequency-Normalized Ultrasonic Attenuation Coefficient α/v^2 , Density ρ , Sound Velocity c_s , and Adiabatic Compressibility κ_s for Aqueous Solutions of Urea at Different Solute Concentrations and Temperatures^a

$c^*/\text{mol kg}^{-1}$ $\pm 0.001\%$	$c/\text{mol L}^{-1}$ $\pm 0.1\%$	$\vartheta/^\circ\text{C}$ $\pm 0.05\text{ K}$	$\alpha/v^2/\text{s}^2\text{ m}^{-1}$ ± 0.5	$\rho/\text{g cm}^{-3}$ $\pm 0.1\%$	$c_s/\text{m s}^{-1}$ $\pm 0.07\%$	$\kappa_s/10^{-10}\text{Pa}^{-1}$ $\pm 0.15\%$
0	0	10	35.32	0.9997	1447.28	4.776
0	0	15	29.46	0.9991	1465.94	4.658
0	0	25	21.28	0.9990	1496.70	4.477
0	0	35	16.30	0.9940	1519.83	4.355
2	2.065	15	26.21	1.032	1527.2	4.153
2	2.059	25	19.36	1.030	1548.9	4.048
2	2.051	35	15.07	1.026	1564.8	3.982
3	3.148	15	25.02	1.049	1557.2	3.931
3	3.139	25	18.78	1.047	1574.8	3.853
3	3.124	35	14.78	1.041	1587.1	3.812
4	4.275	10	28.43	1.069	1578.8	3.754
4	4.269	15	24.25	1.067	1587.6	3.718
4	4.253	25	18.41	1.063	1601.1	3.669
4	4.232	35	14.60	1.058	1610.9	3.643
5	5.421	15	23.85	1.084	1617.0	3.527
5	5.405	25	18.19	1.081	1627.1	3.494
5	5.378	35	14.59	1.076	1633.2	3.486
7	7.839	15	23.82	1.120	1676.8	3.176
7	7.802	25	18.51	1.115	1680.3	3.178
7	7.765	35	15.01	1.109	1680.9	3.191
8	9.106	15	24.34	1.138	1706.5	3.017
8	9.069	25	19.13	1.134	1706.3	3.030
8	9.021	35	15.62	1.128	1704.1	3.054

^a Density¹⁵ and sound velocity¹⁶ data for water are taken from the literature. ^b c^* denotes the concentration in moles of urea per kg solution.

deionized, distilled, and degassed water and also an Anton Paar DMA 5000 vibrating tube density meter with built-in reference oscillator.

Ultrasonic Attenuation Coefficient and Sound Velocity. Since, according to the spectra displayed in Figure 1, no relaxation occurs at frequencies below 200 MHz, absolute measurements of the ultrasonic attenuation coefficient α have been performed between 100 MHz and 200 MHz. In this frequency range, the experimental errors in the variable path-length pulse-modulated wave transmission method are particularly small. One reason for the high accuracy at those frequencies is the favorably small wavelength, allowing for the neglect of any diffraction effects due to the finite cell diameter.

By use of this variable path-length method, the liquid was contained between disk-shaped piezoelectric transducer crystals, operated as a transmitter and a receiver, respectively. The sample thickness was precisely varied by shifting, with the aid of a stepping motor and with a resolution of 100 nm in the position, the receiver unit in the direction of wave propagation.¹³ Smooth run and backlash-free guiding was guaranteed by high-precision ball bush guides. To avoid errors by small instabilities and nonlinearities in the electronic apparatus, calibration procedures were routinely run in which the specimen cell was replaced by a specially designed high precision below cut off piston attenuator.

Fluctuations in the frequencies of measurements were negligibly small. The temperature of the liquid was controlled to within 0.03 K, and it was measured with an accuracy of 0.02 K. Temperature gradients within the cell did not exceed 0.05 K, corresponding with an error of less than 0.1% in the attenuation coefficient data. A careful analysis of the data obtained at different frequencies and repeated measurements, especially such with cells of different dimensions and different fundamental frequency of transducer thickness vibrations as well as with different below cut off piston attenuators, indicated an experimental error $\Delta\alpha/\alpha$ of less than 0.5% in the attenuation coefficient of the liquid.

The sound velocity c_s of the samples has been measured at frequencies between 800 kHz and 15 MHz from the

distances of a series of resonance frequencies of a biplanar cavity resonator cell. The nonequidistant distribution of resonance frequencies has been considered by the relation¹¹

$$c_s = 2\pi l(v_n - v_{n-1})/\arccos\left(\frac{(g_n^2 - 1)(1 - g_{n-1}^2) - 4g_n g_{n-1}}{(g_n^2 + 1)(g_{n-1}^2 + 1)}\right) \quad (2)$$

where

$$g_m = \frac{\rho c_s}{\rho_t c_d} \tan(\pi v_m / v_d) \quad (3)$$

In these equations l is the cell length and ρ_t , c_t , and v_t are the transducer density, sound velocity, and fundamental frequency, respectively. In the derivation of eqs 2 and 3, identical transmitter and receiver transducers have been assumed. Temperature fluctuations and gradients within the resonator cell ($<0.05\text{ K}$) resulted in an uncertainty $\Delta c_s/c_s$ of less than 0.01% in the sound velocity data. The difference $v_n - v_{n-1}$ in the resonance frequency of successive resonance peaks has been measured with an error of less than 10^{-4} , corresponding with an uncertainty of smaller than 0.01% in c_s . The main sources of possible experimental errors have been small disturbances in the cell geometry and cell adjustment that might have resulted from the cleaning and refilling procedure when the sample was exchanged for the reference liquid. Imperfect wetting of the transducer surfaces, covered with a gold layer, may also affect the resonance frequencies. These effects have been investigated by repeated measurements including refilling of the cell. The uncertainty from such disturbances was smaller than $\Delta c_s/c_s = 0.05\%$, so that a total uncertainty of 0.07% in the sound velocity results. This number has been verified by twin resonator cell velocimetry¹⁴ with an uncertainty of less than 0.01%.

Results and Discussion

In Table 1 the ultrasonic attenuation coefficient values at $v \leq 200\text{ MHz}$ are displayed in the format of frequency independent α/v^2 data (Figure 1), for each concentration

and temperature taken as a mean from the measurements at different frequencies. Also given in the table are the density and sound velocity data as well as isentropic compressibilities $\kappa_S = -(1/V)(\partial V/\partial p)_S$ as calculated according to the Newton–Laplace equation

$$\kappa_S = c_s^{-2} \rho^{-1} \quad (4)$$

Since we are interested in reference data, the results of the α/ν^2 , ρ , and c_s measurements are not discussed in terms of physical models but are analytically represented by polynomials $P(c, T)$, allowing for easy interpolations of the experimental values. A nonlinear least-squares regression analysis has been used for this purpose. With the notation $\vartheta = T - 273.16$ K, the following polynomial was appropriate for a description of the experimental α/ν^2 data within the limits of experimental error

$$P_{\alpha/\nu^2}(c^*, T) = a_{00} + a_{01}\vartheta + a_{02}\vartheta^2 + a_{10}c^* + a_{11}c^*\vartheta + a_{12}c^*\vartheta^2 + a_{20}c^{*2} + a_{21}c^{*2}\vartheta + a_{22}c^{*2}\vartheta^2 \quad (5)$$

where

$$\begin{aligned} a_{00} &= (49.08 \pm 0.26) \text{ s}^2 \cdot \text{m}^{-1} \\ a_{01} &= (-1.566 \pm 0.03) \text{ s}^2 \cdot \text{m}^{-1} \cdot \text{K}^{-1} \\ a_{02} &= (0.0180 \pm 0.0006) \text{ s}^2 \cdot \text{m}^{-1} \cdot \text{K}^{-2} \\ a_{10} &= (-4.22 \pm 0.35) \text{ s}^2 \cdot \text{m}^{-1} \cdot \text{mol}^{-1} \cdot \text{kg} \\ a_{11} &= (0.186 \pm 0.03) \text{ s}^2 \cdot \text{m}^{-1} \cdot \text{mol}^{-1} \cdot \text{kg} \\ a_{12} &= (-0.0025 \pm 0.0006) \text{ s}^2 \cdot \text{m}^{-1} \cdot \text{K}^{-2} \cdot \text{mol}^{-1} \cdot \text{kg} \\ a_{20} &= (0.319 \pm 0.05) \text{ s}^2 \cdot \text{m}^{-1} \cdot \text{mol}^{-2} \cdot \text{kg}^2 \\ a_{21} &= (-0.013 \pm 0.004) \text{ s}^2 \cdot \text{m}^{-1} \cdot \text{K}^{-1} \cdot \text{mol}^{-2} \cdot \text{kg}^2 \\ a_{22} &= (0.0002 \pm 0.0001) \text{ s}^2 \cdot \text{m}^{-1} \cdot \text{K}^{-2} \cdot \text{mol}^{-2} \cdot \text{kg}^2 \end{aligned}$$

For the sound velocity

$$P_{c_s}(c^*, T) = b_{00} + b_{01}\vartheta + b_{02}\vartheta^2 + b_{03}\vartheta^3 + b_{10}c^* + b_{11}c^*\vartheta + b_{12}c^*\vartheta^2 + b_{20}c^{*2} + b_{21}c^{*2}\vartheta \quad (6)$$

with

$$\begin{aligned} b_{00} &= (1403 \pm 1) \text{ m} \cdot \text{s}^{-1} \\ b_{01} &= (4.94 \pm 0.2) \text{ m} \cdot \text{s}^{-1} \cdot \text{K}^{-1} \\ b_{02} &= (-0.053 \pm 0.01) \text{ m} \cdot \text{s}^{-1} \cdot \text{K}^{-2} \\ b_{03} &= (0.0002 \pm 0.0002) \text{ m} \cdot \text{s}^{-1} \cdot \text{K}^{-3} \\ b_{10} &= (39.15 \pm 0.25) \text{ m} \cdot \text{s}^{-1} \cdot \text{mol}^{-1} \cdot \text{kg} \\ b_{11} &= (-0.622 \pm 0.02) \text{ m} \cdot \text{s}^{-1} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \cdot \text{kg} \\ b_{12} &= (0.00392 \pm 0.0004) \text{ m} \cdot \text{s}^{-1} \cdot \text{K}^{-2} \cdot \text{mol}^{-1} \cdot \text{kg} \\ b_{20} &= (-0.223 \pm 0.03) \text{ m} \cdot \text{s}^{-1} \cdot \text{mol}^{-2} \cdot \text{kg}^2 \\ b_{21} &= (0.0096 \pm 0.001) \text{ m} \cdot \text{s}^{-1} \cdot \text{K}^{-1} \cdot \text{mol}^{-2} \cdot \text{kg}^2 \end{aligned}$$

The density can be represented by

$$P_\rho(c^*, T) = c_{00} + c_{01}\vartheta + c_{10}c^* + c_{11}c^*\vartheta + c_{20}c^{*2} \quad (7)$$

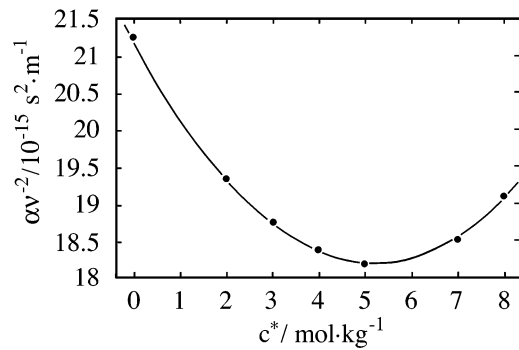


Figure 2. Frequency-normalized ultrasonic attenuation at $\nu \leq 200$ MHz for aqueous solutions of urea at 25 °C displayed as a function of c^* .

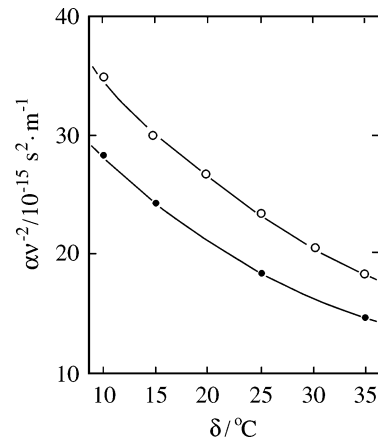


Figure 3. Frequency-normalized ultrasonic attenuation for water (deg) and an aqueous solution of urea (●, $c^* = 4$ mol·kg⁻¹) plotted vs temperature ϑ .

Here

$$\begin{aligned} c_{00} &= (1.0039 \pm 0.0004) \text{ g} \cdot \text{cm}^{-3} \\ c_{01} &= (-2.81 \pm 0.14) \times 10^{-4} \text{ g} \cdot \text{cm}^{-3} \cdot \text{K}^{-1} \\ c_{10} &= (0.0171 \pm 0.0001) \text{ g} \cdot \text{cm}^{-3} \cdot \text{mol}^{-1} \cdot \text{kg} \\ c_{11} &= (-4.23 \pm 0.3) \times 10^{-5} \text{ g} \cdot \text{cm}^{-3} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \cdot \text{kg} \\ c_{20} &= (1.13 \pm 0.1) \times 10^{-4} \text{ g} \cdot \text{cm}^{-3} \cdot \text{mol}^{-2} \cdot \text{kg}^2 \end{aligned}$$

Graphs of the P_{α/ν^2} function are presented in Figures 2 and 3 to show the dependence of the normalized attenuation coefficient upon urea concentration and temperature, respectively. Figure 4 presents the isentropic compressibility data. Obviously, the anomalous temperature dependence in the compressibility of water, for which $d\kappa_S/dT < 0$ at temperatures below 65 °C, exists also for aqueous solutions of urea. Only at the highest solute concentrations ($c \geq 7$ mol/L) does the slope in the κ_S vs T relation at room temperature change to adopt positive values, as common to normal liquids.

Conclusions

Aqueous solutions of urea are favorable reference materials for the ultrasonic spectrometry of liquids. They are available for the sound velocity range between about 1500 m·s⁻¹ and 1700 m·s⁻¹, as is characteristic for many aqueous systems. Since urea solutions do not display relaxation properties below 200 MHz, their ultrasonic attenuation

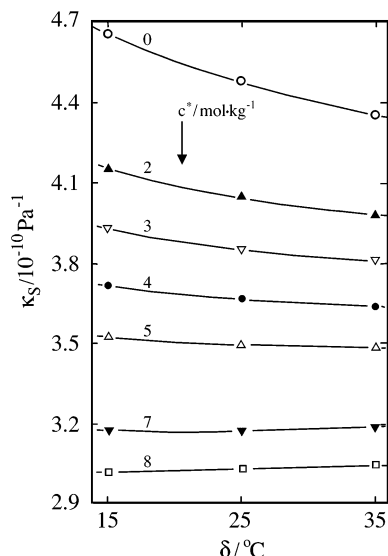


Figure 4. Isentropic compressibility κ_s of solutions of urea in water as a function of temperature ϑ .

coefficient can be determined by absolute measurements, utilizing the frequency range of the highest possible accuracy in the α data. In this range, the experimental error $\Delta\alpha/\alpha$ is smaller than 0.5%. The attenuation coefficient of the urea solutions is even smaller than that of water, thus offering optimum conditions for the precise determination of the instrumental loss in cavity resonator measurements.

Acknowledgment

We wish to thank Barbara Eberhardt for the measurements of the density.

Literature Cited

- (1) Stuehr, J. E. In *Investigation of Rates and Mechanisms of Reactions*; Bernasconi, C. F., Ed.; Wiley: New York, 1986.

- (2) Strehlow, H. *Rapid Reactions in Solutions*; VCH: Weinheim, 1992.
- (3) Kaatze, U.; Hushcha, T.; Eggers, F. Ultrasonic Broadband Spectrometry of Liquids: A Research Tool in Pure and Applied Chemistry and Chemical Physics. *J. Solution Chem.* **2000**, *29*, 299–368.
- (4) Anisimov, M. A. *Critical Phenomena in Liquids and Liquid Crystals*; Gordon and Breach: Philadelphia, 1992.
- (5) Behrends, R.; Telgmann, T.; Kaatze, U. The Binary System Triethylamine-Water Near Its Critical Consolute Point: An Ultrasonic Spectrometry, Dynamic Light Scattering, and Shear Viscosity Study. *J. Chem. Phys.* **2002**, *117*, 9828–9837.
- (6) Menzel, K.; Mirzaev, S. Z.; Kaatze, U. Crossover Behavior in Micellar Solutions with Lower Critical Demixing Point: Broadband Ultrasonic Spectrometry of the Isobutoxyethanol-Water System. *Phys. Rev. E* **2003**, *68*, 011501-1-11.
- (7) Povey, M. J. W. *Ultrasonic Techniques for Fluid Characterization*; Academic: San Diego, 1997.
- (8) Povey, M. J. W. Ultrasonics of Food. *Contemp. Phys.* **1998**, *39*, 467–78.
- (9) Buckin, V.; Smyth, C. High-Resolution Ultrasonic Resonator Measurements for Analysis of Liquids. *Semin. Food Anal.* **1999**, *4*, 113–130.
- (10) Kaatze, U.; Behrends, R.; Lautscham, K. Acoustic Relaxation Spectrometers for Liquids. *Ultrasonics* **2001**, *39*, 393–406.
- (11) Labhardt, A.; Schwarz, G. A High Resolution and Low Volume Ultrasonic Resonator Method for Fast Chemical Relaxation Measurements. *Ber. Bunsen. Phys. Chem.* **1976**, *80*, 83–92.
- (12) Rupprecht, A.; Kaatze, U. Solution Properties of Urea and Its Derivatives in Water: Evidence from Ultrasonic Relaxation Spectra. *J. Phys. Chem. A* **2002**, *106*, 8850–8858.
- (13) Kaatze, U.; Lautscham, K.; Brai, M. Acoustical Absorption Spectroscopy of Liquids Between 0.15 and 3000 MHz: II. Ultrasonic Pulse Transmission Methods. *J. Phys. E: Sci. Instrum.* **1988**, *21*, 98–103.
- (14) Lautscham, K.; Wente, F.; Schrader, W.; Kaatze, U. High Resolution and Small Volume Automatic Ultrasonic Velocimeter for Liquids. *Meas. Sci. Technol.* **2000**, *11*, 1432–1439.
- (15) Kell, K. S. In *Water, A Comprehensive Treatise, Vol. 1: The Physics and Physical Chemistry of Water*; Franks, F. Ed.; Plenum: New York, 1972.
- (16) Bilaniuk, N.; Wong, G. S. K. Speed of Sound in Pure Water as a Function of Temperature. *J. Acoust. Soc. Am.* **1993**, *93*, 1609–1612.

Received for review January 9, 2004. Accepted March 19, 2004. Financial assistance by the Deutsche Forschungsgemeinschaft, Bonn, Germany, is gratefully acknowledged.

JE049971A