# Ultrasonic Absorption in Mixtures of 1,2-Ethanediol with 1-Nonanol at $T = 298.15$ K

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**Abstract**    Ultrasonic absorption coefficients for (1,2-ethanediol + 1-nonanol) have been measured for various mole fractions between 0 and 1 at 298.15 K. The measurements of the absorption coefficients have been performed by the standard pulse technique in the frequency range of (30 to 80) MHz. The volume viscosity is derived from the measured quantities. The dependence upon the mixture composition is discussed.

**Keywords**    Absorption · Alcohols · Binary mixtures · Ultrasound

## 1 Introduction

As is well known, the ultrasonic absorption is a significant source of information on the molecular structure of a liquid and on physical and chemical processes occurring in the liquid phase. Modern methods permit measurements of absorption over a frequency range covering about six decades, i.e., from ca. 10 kHz to ca. 10 GHz (a concise review of ultrasonic broadband spectrometry of liquids can be found in [1]). However, measurements of the ultrasonic absorption are rather rare, especially in comparison with speed-of-sound measurements. It seems that three reasons are dominant: (i) measurements of ultrasound absorption have an essentially poorer accuracy than measurements of the speed of sound, (ii) measurements are more complicated (apparatus, procedure), and (iii) in practice, there is a lack of commercially available measurement instruments at moderate price.

From an acoustical point of view, very interesting are two (and more) component systems. If both components are capable of forming hydrogen bonds, various

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interactions, among them solute–solute, solvent–solvent, and solute–solvent associations, may lead to a variety of structures. As a consequence, different types of chemical processes may dominate the molecular motions, e.g., the formation of hydrogen-bonded dimers, trimers, or oligomers, and in general, multimers of different size and structure. Such systems are very interesting, but interpretation of results is not simple.

In this work, a study of the ultrasonic absorption and related properties for $\{x$ 1,2-ethanediol + (1-$x$) 1-nonanol$\}$ at $T = 298.15$ K is presented. The present work is a continuation of earlier studies of the above-mentioned system [2] (a study of 1-nonanol has been recently reported as well [3]). The system under test is so much more interesting because it exhibits limited miscibility characterized by the upper critical temperature point (UCTP). According to Zhuravleva and Zhukova [4,5], the UCTP for the system under test is equal to $T = 293$ K at a mole fraction $x = 0.819$ of 1,2-ethanediol, and a monotectic transformation occurs at $T = 260.6$ K.

From the measurement results and the data on density, shear viscosity, and speed of sound reported previously [2], the difference between the experimental absorption and classical values, the volume viscosity, and the ratio of the volume and shear viscosities are calculated. Their composition dependences are analyzed and discussed in terms of previous results reported in [2]. To the best of my knowledge, this ultrasound absorption study for the system under test has not been reported in the available literature.

## 2 Experimental

Apart from partial degassing (ultrasonic cleaner), 1,2-ethanediol (Fluka, mass fraction $\geq 0.995$) and 1-nonanol (Fluka, mass fraction $\geq 0.99$) were used without further purification. The water content in both chemicals was $\leq 10^{-3}$. The mixtures were prepared by weighing (Ohaus, Analytical Standard AS 200 balance) and stored in sealed flasks. The mole fractions of the mixtures were determined with an uncertainty of $5 \times 10^{-5}$. More details about component purity and mixture preparation can be found in [2].

The ultrasonic absorption measurements at atmospheric pressure were carried out with a measuring set designed and constructed in our laboratory. The standard pulse technique was used, i.e., a method which enables absolute measurements of $\alpha$ by variation of the sample thickness. The measurements within the frequency range of (30 to 80) MHz were executed for the pure components and mixtures at 298.15 K (platinum thermometer Ertco-Hart 850, NIST certified), i.e., above the miscibility gap. As a rule, the measurements were made at 4 to 7 frequencies covering always the range (30 to 80) MHz, i.e., exactly in the form of discrete values at (30.004, 36.062, 45.033, 52.499, 60.101, 69.941, and 79.142) MHz. Because the frequency was stabilized by quartz, the error in the frequency was negligibly small. The intensity of the ultrasonic field within the liquids was sufficiently small to avoid heating of the sample by absorption of sound energy. The thermal stabilization of the samples was controlled directly to within $\pm 0.05$ K by the use of a thermistor. Before the measurements, all samples were degassed using ultrasound (ultrasonic cleaner). In the present study, the

uncertainty in the ultrasound absorption coefficient $\alpha$ is estimated to be 2.5 %. More details about the apparatus and experimental procedures can be found elsewhere [6,7].

## 3 Results and Discussion

It appears that within the investigated frequency range the quotient $\alpha f^{-2}$ (the ultrasound absorption coefficient $\alpha$ per squared frequency $f$) is independent of frequency for all mixtures and components (for clarity, in Fig. 1 only some examples are presented). Therefore, the mean values of the quotients $\alpha f^{-2}$ in the investigated frequency range are calculated. The experimental mean values of $\alpha f^{-2}$ (their mean standard deviation is $1.5 \times 10^{-15}\,\text{s}^2 \cdot \text{m}^{-1}$) are summarized in Table 1. Only the $\alpha f^{-2}$ values for 1,2-ethanediol and 1-nonanol can be compared with those reported in the literature. A survey of the literature shows, however, that the measurements by various authors show considerable differences, sometimes without having a concrete reason for it. For example, according to Schaaffs [8], $\alpha f^{-2} = 120 \times 10^{-15}\,\text{s}^2 \cdot \text{m}^{-1}$ for 1,2-ethanediol in the frequency range from 5 MHz to 15 MHz at $T = 298.15$ K. On the other hand, according to Kishimoto and Nomoto [9], $\alpha f^{-2} = 386 \times 10^{-15}\,\text{s}^2 \cdot \text{m}^{-1}$ at $f = 8$ MHz and at the same temperature. In turn, according to Litovitz et al. [10], $\alpha f^{-2} = 153 \times 10^{-15}\,\text{s}^2 \cdot \text{m}^{-1}$ $(T = 297.15$ K, $f = 30$ MHz), and according to Jerie et al. [11], a relaxation in the frequency range from 20 MHz to 60 MHz and at $T = 293.15$ K is observed. The findings of Jerie et al. [11] seem rather doubtful, the more so as the relaxation for the pure 1-hexanol at the same conditions is also reported. Fortunately, $\alpha f^{-2}$ obtained in this work for 1-nonanol is consistent with values reported for 1-alkanols by Chari et al. [12] (e.g., $183 \times 10^{-15}\,\text{s}^2 \cdot \text{m}^{-1}$ and $230 \times 10^{-15}\,\text{s}^2 \cdot \text{m}^{-1}$ at $f = 21$ MHz for 1-octanol and 1-decanol, respectively). It must be pointed out that ultrasonic absorption spectra in a broad frequency range covering about six decades have been measured for various 1-alkanols as well. And several
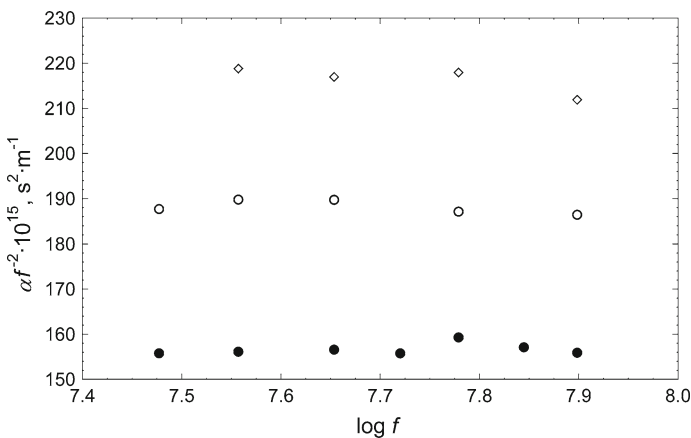


**Fig. 1** Semi-logarithmic plot of the ultrasonic absorption coefficient per squared frequency $\alpha f^{-2}$ as a function of log $f$ at $T = 298.15$ K for selected samples: ($\circ$) 1-nonanol, ($\bullet$) 1,2-ethanediol, and ($\diamond$) mixture at a mole fraction $x = 0.64413$ of 1,2-ethanediol

**Table 1** Means of the ultrasound absorption coefficients, $\alpha f^{-2}$, and classical coefficients of the ultrasound absorption, $\alpha_{cl} f^{-2}$, for $\{x$ 1,2-ethanediol$+(1-x)$ 1-nonanol$\}$ at $T = 298.15\,K$

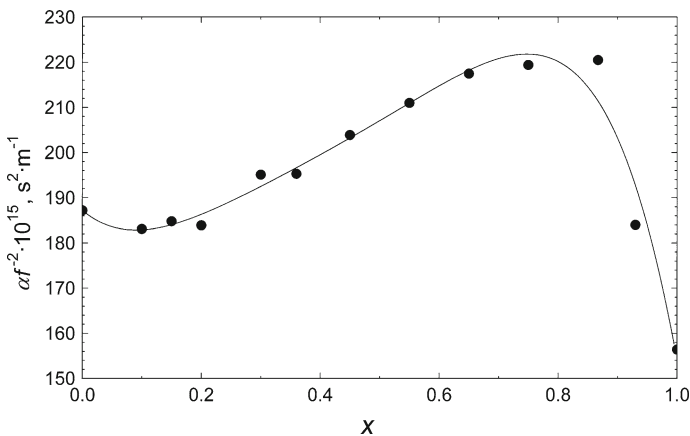| $x$ | $\alpha f^{-2} \times 10^{15}\,(s^2 \cdot m^{-1})$ | $\alpha_{cl} f^{-2} \times 10^{15}\,(s^2 \cdot m^{-1})$ |
|---|---|---|
| 0 | 187.8 | 119.3 |
| 0.10019 | 183.1 | 118.5 |
| 0.19791 | 183.9 | 121.3 |
| 0.29637 | 195.1 | 126.1 |
| 0.36408 | 195.3 | 130.1 |
| 0.45332 | 203.9 | 136.6 |
| 0.54316 | 211.0 | 143.3 |
| 0.64413 | 217.5 | 151.0 |
| 0.75168 | 219.4 | 156.7 |
| 0.93084 | 184.0 | 127.0 |
| 1 | 157.1 | 88.7 |



**Fig. 2** Plot of mean values of the ultrasound absorption coefficient per squared frequency $\alpha f^{-2}$ versus mole fraction $x$ for $\{x1, 2\text{-ethanediol} + (1-x)1\text{-nonanol}\}$ at $T = 298.15\,K$; line—polynomial fit

reports can be found in the literature (but often not in English), i.e., for methanol to 1-pentanol [13], 1-octanol and 1-nonanol [14], and 1-dodecanol [15].

For the system studied here, the composition dependence of the mean values of the quotient $\alpha f^{-2}$ is however s-shaped (Fig. 2). A pronounced relative maximum is characteristic for binary systems with a miscibility gap [16,17]. In such systems, the ultrasonic absorption predominantly results from fluctuations in concentration.

The experimental results are compared with values of the classical ultrasonic absorption. The ratio of the classical ultrasound absorption and the squared frequency was determined by the use of the Stokes formula (the Kirchoff term has been neglected),

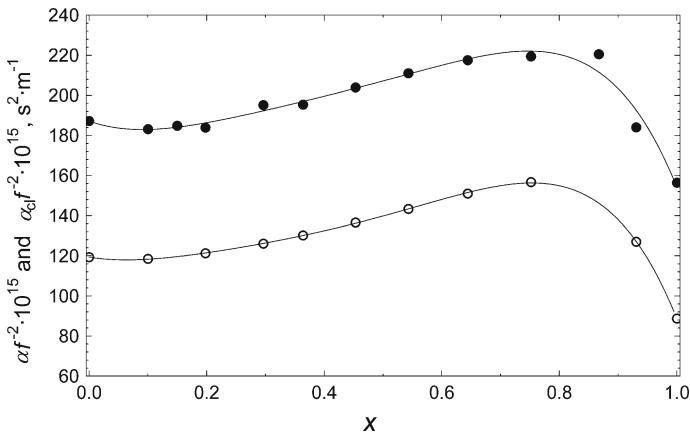$$\alpha_{cl} f^{-2} = 8\pi^2 \eta (3\rho c^3)^{-1} \qquad (1)$$

**Fig. 3** Plot of mean values of the ultrasonic absorption coefficient per squared frequency $\alpha f^{-2}$ (●) and plot of the classical coefficient of ultrasonic absorption per squared frequency $\alpha_{cl} f^{-2}$ (○) versus mole fraction $x$ for $\{x 1, 2\text{-ethanediol} + (1 - x)1\text{-nonanol}\}$ at $T = 298.15$ K; lines—polynomial fits

where $\eta$ is the steady-state Newtonian viscosity in the low-frequency limit (in other words, the dynamic or shear viscosity), $c$ is the speed of sound, and $\rho$ is the density. It appears that as shown in Fig. 3, the $\alpha f^{-2}(x)$ curve is reminiscent of the $\alpha_{cl} f^{-2}(x)$ curve. In other words, the differences between the experimental absorption and the classical values are almost composition independent. Moreover, both above-mentioned curves are reminiscent of the $\eta(x)$ curve [2] (in this case, however, there is a lack of a relative minimum for mixtures with a small concentration of 1,2-ethanediol). Thus, the shear viscosity is a predominant property in this case. In other words, this transport property (its concentration fluctuations) is reflected in the shape of the absorption curves. However, it seems that for the system under test, the concentration fluctuations are the primary reason for the composition dependences of both the viscosity and ultrasonic absorption. It is interesting that in the case of the speed of sound, no anomaly was detected even for temperatures in the immediate vicinity of the critical point, i.e., at 293.15 K [2]. Recently, Makowska and Szydłowski [18] reported a similar result for the (nitromethane + 1-pentanol) system.

In the next step, the volume viscosity $\eta_V$ has been calculated. Since there are no viscometers available which measure the volume viscosity, the $\alpha f^{-2}$ data are advantageously used to determine the $\eta_V$ values. For the calculation of $\eta_V$ values, the following relation was used:

$$\alpha f^{-2} = 2\pi^2 (\rho c^3)^{-1}(\eta_V + 4(3^{-1})\eta) \tag{2}$$

The $\eta_V$, $\eta_V/\eta$, and $\eta$ (taken from [2]) are summarized in Table 2. Apart from 1,2-ethanediol, in all cases the $\eta_V/\eta$ values are evidently smaller than 1. Moreover, the composition dependence of the viscosity ratio shows a distinct minimum at $x \approx 0.85$ (Fig. 4), i.e., in the vicinity of the critical composition. The viscosity ratio increases when going from this composition to mixtures with lower and higher 1,2-ethanediol content. It should be emphasized that this composition dependence is quite different

**Table 2** Shear and volume viscosities, $\eta$ and $\eta_V$, and ratio of viscosities $\eta_V/\eta$ for $\{x1, 2\text{-ethanediol} + (1 - x) 1\text{-nonanol}\}$ at $T = 298.15\,\text{K}$

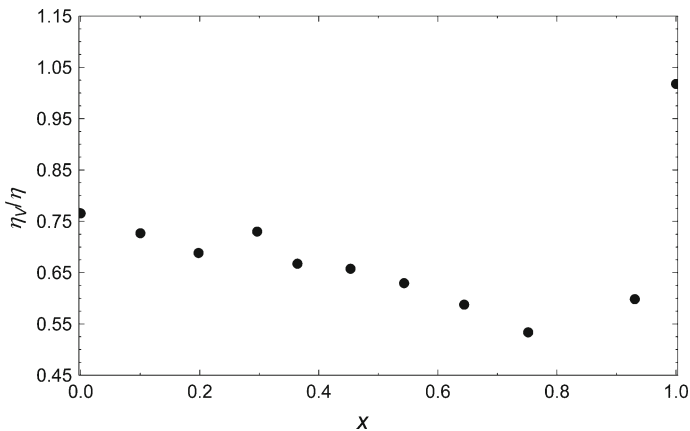| $x$ | $\eta$ (mPa · s) | $\eta_V$ (mPa · s) | $\eta_V/\eta$ |
|---|---|---|---|
| 0 | 9.494[a] | 7.27 | 0.77 |
| 0.10019 | 9.581[a] | 6.97 | 0.73 |
| 0.19791 | 10.006[a] | 6.89 | 0.69 |
| 0.29637 | 10.668[a] | 7.79 | 0.73 |
| 0.36408 | 11.256[a] | 7.51 | 0.67 |
| 0.45332 | 12.222[a] | 8.04 | 0.66 |
| 0.54316 | 13.410[a] | 8.44 | 0.63 |
| 0.64413 | 15.091[a] | 8.87 | 0.59 |
| 0.75168 | 17.316[a] | 9.24 | 0.53 |
| 0.93084 | 19.276[a] | 11.53 | 0.60 |
| 1 | 16.952[a] | 17.43 | 1.03 |

[a] Data from Ref. [2]



**Fig. 4** Plot of the ratio of the volume viscosity to shear viscosity, $\eta_V/\eta$, versus mole fraction $x$ for $\{x1, 2\text{-ethanediol} + (1 - x)1\text{-nonanol}\}$ at $T = 298.15\,\text{K}$

from those obtained for 1-butanol + 1,3-butanediol [19]. In this last case, over most of the composition range the viscosity ratio of the mixtures scatters slightly around $\eta_V/\eta = 1.3$. In other words, the ratio $\eta_V/\eta$ can be, in practice, assumed as composition independent. In this system (completely miscible), however, no peak ultrasonic absorption composition is observed as well. At the same time, according to Brai and Kaatze [20], over most of the composition range of the alkanol + water systems, the viscosity ratio scatters around 0.67 (both for systems with a miscibility gap (1-butanol, isobutanol, and *sec*-butanol) and for completely miscible systems (ethanol, 1-propanol, isopropanol, and *tert*-butanol). However, all miscible systems exhibit a relative maximum in their dependence of the ultrasonic absorption coefficient upon composition.

Simultaneously, a survey of the literature shows that the ratio of $\eta_V/\eta$ scatters around 1, as was found for different pure alcohols. According to Brai and Kaatze

[20], a structural relaxation process at very high frequencies may be a reason for the differences in the $\eta_V/\eta$ values (from 1.28 to 0.36) obtained for lower alkanols.

## 4 Conclusions

The results of this study confirm a previous finding [2] that stoichiometrically well-defined molecular complexes are rather not formed. Much more likely is the existence of concentration fluctuations. However, the rather narrow range of frequency used for ultrasonic absorption measurements at only one temperature (5 K above the UCTP), may lead to an over-simplified molecular picture. For these reasons, the experimental results here are not compared with the indications of the dynamical scaling theory of Bhattacharjee and Ferrell [21,23,23], or even with those of the Fixman [24–26] and Kawasaki [27,28] theories.

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