Ultrasonic Velocity and Adiabatic Compressibility in Mixtures of Water and 2-Chloroethanol

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In the present investigation the ultrasonic velocity in mixtures of water and 2-chloroethanol has been measured by an interferometric method at 4 Mc/s and at the temperatures 0°, 9°, 18°, and 25°C. From the measured velocities and the densities of the mixtures, the adiabatic compressibilities have been determined at 0° and 25°C. It has been shown that the values of the adiabatic compressibility, which can be calculated from Jacobson's empirical formula by means of parameters evaluated from the experimental values, are in fairly good agreement with the experimental values.

Finally it has been shown that the ultrasonic velocity in the mixtures with compositions below about 40 wt.% 2-chloroethanol is linearly dependent on $((n_D^2 - 1)/(n_D^2 + 2))$, where n_D is the refractive index of the Na-D-line. In a similar way, the mixtures with compositions above 40 wt. % 2-chloroethanol are linearly dependent on this quantity. When $((n_D^2 - 1)/(n_D^2 + 2))$ can be expressed as a power function of the volume fraction φ_2 of 2-chloroethanol in the two concentration regions, it is possible to express the ultrasonic velocity in the two sections as functions of the volume fraction of 2-chloroethanol, thus $v_u = a_1 \varphi_2{}^n + a_2$.

The velocity *versus* composition curves of binary mixtures of associated molecules, *e.g.* alcohols, with water have been reported by several investigators [1-3] to exhibit a maximum at an intermediate concentration. Also the ultrasonic absorption expressed by a/f^2, where a is the absorption coefficient and f the frequency, showed a marked peak at an intermediate concentration. The maxima for the velocity and for the absorption, respectively, are most frequently at different concentrations. When the temperature coefficient for the ultrasonic velocity in water at the temperatures in question is positive and the temperature coefficient of the other component is negative, then the curves showing the velocity for different temperatures intersect as illustrated in Fig. 2.[4]

The absorption of ultrasonic waves in mixtures of water and 2-chloroethanol has been reported in a previous paper.[5] In the present investigation
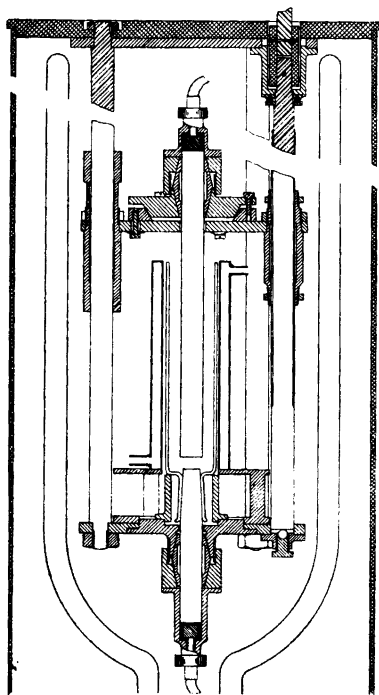
Fig. 1. The interferometer in cross-section. The diameter of the upper quartz delay rod is 15 mm.

the ultrasonic velocity at 4 Mc/s has been measured in mixtures of water and 2-chloroethanol in the temperature range 0°—25°C.

EXPERIMENTAL

The measurements of the ultrasonic velocity were performed by using an interferometric method.[6] A cross-section of the interferometer is shown in Fig. 1.

In the construction of the interferometer, which also can be used for measurements of the ultrasonic absorption, allowance was made for the necessary frequency range and the temperature range. The transducers are X-cut 4 Mc/s quartz crystals (10 mm diameter), which are bonded to the plane terminating faces of the fused quartz delay rods.

For absorption measurements, the liquid vessel is placed on the lowest rod with a tapered ground joint. For velocity measurements, this vessel is replaced by a similar one provided with a plane reflecting bottom-disc. In the mechanical design, the production of small displacements of the upper rod and the alignment of the transducers has been taken into consideration.[7] When the path-length is 100 mm, it is possible to make absorption measurements in the frequency range 12—100 Mc/s as well as the velocity measurements at 4 Mc/s. The Dewar flask ensures that the temperature can be lowered, *e.g.* to —30°C, and also that it can be kept constant within 0.1°C. The temperature controlling liquid flows from a thermostat between the inner and outer walls of the double wall container, which encircle the liquid vessel. The temperature of the liquid in the vessel is measured by a platinum resistance thermometer attached to the upper fused quartz delay rod.

For the velocity measurements, the transducer is excited by a variable "Vackar" oscillator, which is a variant of Colpitts circuit with great stability. Also a crystal con-

trolled 4 Mc/s Pierce oscillator [8] and a mixer section is included, so it is possible to control the deviation of the frequency from 4 Mc/s.

The frequency of the crystal controlled oscillator has been measured to 4000.64 Kc/s with a Hewlett-Packard counter 524/D1.

The necessity for having a variable oscillator arises when the system is cooled. The cooling results in a frequency shift of the oscillating part. Even when the system is cooled to 0°C, however, the change in frequency is still so small that it can be neglected. With the uncertainties on the frequency and pathlength taken into consideration, the accuracy in the measured velocity could be estimated to about 0.25 %.

The detecting and amplifying circuits are adopted from Gucker and Haag.[9]

In principle, it is possible to count the number of half wavelengths over a given pathlength automatically with the available apparatus, but in the present work they have been counted with a mechanical counter.

The densities of the mixtures have been measured with a "Mohr-Westphal" balance. The accuracy is of the order of 0.001 g/ml.

The 2-chloroethanol was supplied by "Merck". The mixtures were prepared from a fraction which distilled in the range 128.4—128.7°C at 760 mm Hg. The refractive index $n_D^{20} = 1.4422$. The boiling point of 2-chloroethanol is 128.6°C and $n_D^{20} = 1.4421$. Distilled water has been used for the preparation of the mixtures.

EXPERIMENTAL RESULTS

The ultrasonic velocity was measured for mixtures of water and 2-chloroethanol with compositions ranging from 12—80 wt. % 2-chloroethanol and also in the pure components. The measurements were made exclusively at the fundamental frequency of the quartz crystal 4 Mc/s and for the temperatures 0°, 9°, 18°, and 25°C. The experimental results are arranged in Table 1.

Table 1. Velocity of ultrasonic waves (4 Mc/s) in mixtures of water and 2-chloroethanol.

wt.%	Mole fraction x_2	Sound velocity v_u m.s^{-1}			
		0°C	9°C	18°C	25°C
0	0	1409	1449	1479	1500
12.1	0.03	1504	1527	1539	1550
20.1	0.05	1557	1564	1570	1570
27.0	0.08	1583	1583	1580	1574
40.3	0.13	1575	1569	1563	1555
48.3	0.17	1559	1551	1541	1535
56.4	0.22	1549	1541	1528	1513
80.5	0.48	1506	1482	1459	1438
100.0	1.00	1445	1411	1382	1358

Fig. 2 shows the characteristic lines for the above mentioned temperatures.

It appears that the ultrasonic velocity in the mixtures of water and 2-chloroethanol exhibits a maximum at an intermediate concentration and that the temperature coefficient changes sign as the concentration of 2-chloroethanol is increased beyond the value corresponding to the maximum. The results are thus in accordance with the results reported for mixtures of water and alcohols.
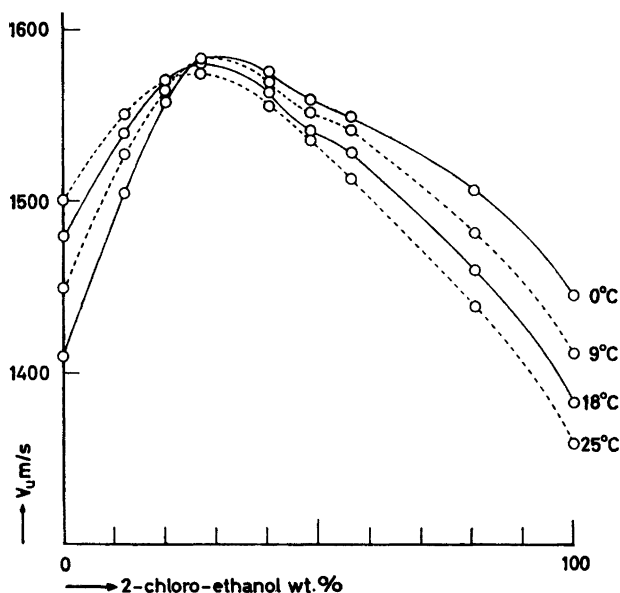
Fig. 2. The velocity *versus* composition curves for mixtures of water and 2-chloroethanol.

THE ADIABATIC COMPRESSIBILITY

The low frequency adiabatic compressibility $\varkappa_S(0)$ of the mixtures can be computed from the general expression

$$\varkappa_S(0) = (\varrho v_u^2)^{-1}$$

where ϱ is the density and v_u the velocity of sound. The adiabatic compressibility of a non-ideal mixture can be written [10]

$$\varkappa_S(0) = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_S = -\frac{1}{x_1 v_1^0 + x_2 v_2^0}\left(\frac{\partial(x_1 v_1^0 + x_2 v_2^0)}{\partial p}\right)_S + \varkappa_S^E(0)$$

where v is the mean molar volume of the mixture, x_1, x_2 the mole fractions of the components and v_1^0, v_2^0 the molar volumes of the pure components. $\varkappa_S^E(0)$ is the excess adiabatic compressibility. By carrying out the differentiation we get

$$\varkappa_S(0) = \frac{x_1 v_1^0}{x_1 v_1^0 + x_2 v_2^0}\varkappa_S(0)_1 + \frac{x_2 v_2^0}{x_1 v_1^0 + x_2 v_2^0}\varkappa_S(0)_2 + \varkappa_S^E(0)$$

$$= (1 - \varphi_2)\varkappa_S(0)_1 + \varphi_2\varkappa_S(0)_2 + \varkappa_S^E(0),$$

where φ_2 is the volume fraction of the second component in the binary mixture, 2-chloroethanol. The excess adiabatic compressibility $\varkappa_S^E(0)$ indicates the deviation in compressibility from that in a mixture in the ideal state.

In the present case the water molecules are associated with hydrogen bonds and it is not unreasonable to assume the same sort of association in the

2-chloroethanol. In the mixtures of water and 2-chloroethanol we must further take association between the water and the 2-chloroethanol into account. When the association in the mixtures probably is the main cause of the deviation from ideality, we can use $\varkappa_S^E(0)$ as a correction term, which gives the change in adiabatic compressibility due to the prevailing association condition.

Jacobson [11] has given the following expression for the correction term,

$$\varkappa_S^E(0) = (1 - \varphi_2)(1 - \vartheta)Q\xi$$

where ϑ designates a hydrogen bonding factor, Q a ratio between the "effective" inside surfaces of the components and ξ a compressibility change factor.

To introduce a molecule into the water structure a number of hydrogen bonds must be broken to form a cavity. The number of hydrogen bonds broken is proportional to the interface between the components, which is effective in breaking the bonds. The "effective" interface is proportional to the internal surface of the second component and inversely proportional to the inside surface of the water.

When the change in compressibility is caused by breaking of hydrogen bonds, then $\varkappa_S^E(0)$ is proportional to $Q\xi$, where Q is the ratio between the effective inside surfaces of the components and ξ is the change in compressibility if all the hydrogen bonds present at the temperature considered are broken. If only the breaking of the water structure is considered, while the association of the second component is neglected, then $\varkappa_S^E(0)$ will also be proportional to the volume fraction of water $(1 - \varphi_2)$. When water contains more hydrogen bonds than other substances, the neglect of the association of the second component should not introduce any great error. When, however, the second component is associated in itself and forms hydrogen bonds with water, then the mutual association must be taken into consideration.

The mutual association can be taken into account by the hydrogen bonding factor ϑ. ϑ is defined as the fraction of bonds between water and the second component per molecular surface of the substance in relation to the mean value for water on an equally large inside surface of water at the existing temperature. The term $(1 - \vartheta)$ then indicates the degree of breaking of the association. $\varkappa_S^E(0)$ can then be written as shown above. Q is calculated by considering the inside surfaces of the components of the mixture. The inside surface in one mole of a substance is given by the expression

$$A_{c_i} = f_i(36\pi N\ (v_i^0)^2)^{1/3}$$

where f_i is a form factor and N Avogadros number. A molecule of non-spherical form has a surface related to the spherical by means of the form factor $f_i \geq 1$, which gives the ratio between the surface of the molecule and the surface of a sphere with the same volume.

The surface effective in breaking the hydrogen bonds is reduced, when the concentration of the second component increases. This reduction in surface should be a function of φ_2 and is written as φ_2^μ, where μ is a constant connected with the substance.

When finally the total inside "effective" surfaces of the components per milliliter are $A_1 = A_{c_1}\ (1 - \varphi_2)/v_1^0$ and $A_2 = A_{c_2}\ \varphi_2(1 - \varphi_2^\mu)/v_2^0$ we get

Table 2. The adiabatic compressibility in mixtures of water and 2-chloroethanol at 0°C. Calculated values of $\varkappa_S^E(0)$ and v_u are included.

wt.%	volume fraction φ_2	sound velocity $v_u \times 10^{-5}$ cm s^{-1}	Density ϱ g cm^{-3}	$\varkappa_S(0) \times 10^{12}$ cm^2 dyne^{-1}	$\varkappa_S(0)_{id} \times 10^{12}$ cm^2 dyne^{-1}	$\varkappa_S^E(0) \times 10^{12}$ cm^2 dyne^{-1} exp.	calc.	$v_u \times 10^{-5}$ cm s^{-1} calc.
0	0	1.409	1.000	50.37	50.37			
12.1	0.102	1.504	1.028	43.01	49.23	− 6.22	− 5.45	1.491
20.1	0.170	1.557	1.049	39.32	48.47	− 9.15	− 7.48	1.525
27.0	0.231	1.583	1.067	37.40	47.78	−10.38	− 8.72	1.549
40.3	0.355	1.575	1.100	36.64	46.39	− 9.75	− 9.96	1.580
48.3	0.433	1.559	1.118	36.81	45.52	− 8.71	−10.05	1.588
56.4	0.514	1.549	1.137	36.66	44.62	− 7.96	− 9.70	1.587
80.5	0.772	1.506	1.189	37.08	41.73	− 4.65	− 5.95	1.587
100.0	1.000	1.445	1.222	39.18	39.18			1.533

Table 3. The adiabatic compressibility in mixtures of water and 2-chloroethanol at 25°C. Calculated values of $\varkappa_S^E(0)$ and v_u are included.

wt.%	volume fraction φ_2	sound velocity $v_u \times 10^{-5}$ cm s^{-1}	Density ϱ g cm^{-3}	$\varkappa_S(0) \times 10^{12}$ cm^2 dyne^{-1}	$\varkappa_S(0)_{id} \times 10^{12}$ cm^2 dyne^{-1}	$\varkappa_S^E(0) \times 10^{12}$ cm^2 dyne^{-1} exp.	$\varkappa_S^E(0) \times 10^{12}$ cm^2 dyne^{-1} calc.	$v_u \times 10^{-5}$ cm s^{-1} calc.
0	0	1.500	0.997	44.58	44.58			
12.1	0.103	1.550	1.022	40.72	44.65	−3.93	−3.74	1.547
20.1	0.172	1.570	1.040	39.00	44.70	−5.70	−5.13	1.559
27.0	0.234	1.574	1.055	38.27	44.74	−6.47	−5.96	1.563
40.3	0.359	1.555	1.083	38.18	44.83	−6.65	−6.78	1.558
48.3	0.438	1.535	1.099	38.62	44.88	−6.26	−6.82	1.546
56.4	0.518	1.513	1.117	39.11	44.94	−5.83	−6.57	1.528
80.5	0.788	1.438	1.166	41.48	45.12	−3.64	−3.81	1.441
100.0	1.000	1.358	1.198	45.27	45.27			

$$Q = \frac{\varphi_2}{1 - \varphi_2}(1 - \varphi_2{}^\mu)\frac{f_2}{f_1}\left[\frac{v_1{}^0}{v_2{}^0}\right]^{1/3} = \frac{\varphi_2}{1 - \varphi_2}(1 - \varphi_2{}^\mu)Q'$$

In the present case the water molecule has been assumed to be spherical and therefore $f_1 = 1$. The form factor, f_2, for the 2-chloroethanol molecule, has been estimated by assuming a model of the molecule composed of a hemisphere with the radius of a methanol molecule, a cylindrical part also with the radius of a methanol molecule, and of height equal to twice its radius, together with another hemisphere of radius $99/74 = 1.338$ (ratio of atomic radii of chlorine and oxygen) times the radius of methanol.

With the above mentioned assumptions about the breaking of hydrogen bonding in mixtures of water and 2-chloroethanol, it has been possible on the basis of the available experimental results to evaluate the parameters, which in turn can be used to calculate the excess adiabatic compressibility $\varkappa_S{}^E(0)$.

The experimental values of $\varkappa_S(0)$ and $\varkappa_S{}^E(0)$ at $0°$ and $25°C$, together with the calculated values of $\varkappa_S{}^E(0)$ and v_u are given in the Tables 2 and 3. In Table 4 are the values of the parameters used for the calculation of $\varkappa_S{}^E(0)$.

Table 4. The parameters used for the calculations of the excess adiabatic compressibility $\varkappa_S{}^E(0)$.

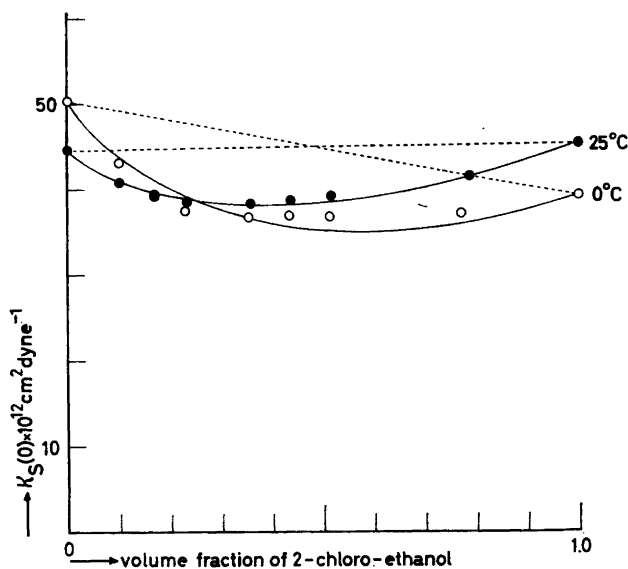| Temp.	$v_2{}^0$	f_2	Q'	ϑ	μ	$\xi_m \times 10^{12}$ cm^2 × dyne^{-1}
0°C	65.89	1.10	0.714	0.21	0.25	-218
25°C	67.21	1.10	0.710	0.21	0.25	-149

Fig. 3. The adiabatic compressibility $\varkappa_S(0)$ plotted *versus* the volume fraction of 2-chloro-ethanol. The full lines are calculated values, the circles are experimental points.

In Fig. 3 is shown a plot of $\varkappa_S(0)$ *versus* the volume fraction of 2-chloro-ethanol φ_2. It appears that the empirical formula in this case also, is able to account for the change in the adiabatic compressibility and thus the sound velocity when the compositions of the mixtures are changed. The change in temperature has not caused any serious break down of the formula.

THE CONNECTION WITH THE MOLAR REFRACTION

The results of the present investigation have so far been interpreted by means of Jacobson's empirical formula and thus by the ideas of the influence of the change in hydrogen bonding on the adiabatic compressibility, and the relation between this change and the fraction of the surfaces of the volume per molecule, which is effective in breaking the bonds.

The problem has, however, been approached in a different manner, which has a close connection with theories of intermolecular forces.[12,13] Schaaffs has concluded from his theories of ultrasonic velocities in homologous sequences of pure organic liquids, that the very simple formula $v_u = v_\infty sr = v_\infty s V_m (v_m^\circ)^{-1}$ holds, where s is called the "collision factor". This "collision factor" is defined as the ratio of the van der Waals' excluded volume b and $V_m = \frac{1}{6}\pi D^3$ the volume of a molecule considered as a rigid sphere of diameter D. Thus $s = b/V_m \leq 4$. r expresses "the filling up of volume" and is defined as the ratio of the "effective" volume V_m of a molecule and the volume per molecule, thus $r = V_m(v_m^\circ)^{-1}$. $v_\infty = 1600$ ms^{-1} is a limit to which the velocity converges with increasing filling up of the available volume. The above formula, which also could be written $v_u = Wr - v_u(0)$, where W is a constant, has been derived on the basis of the resemblance of the volume of a molecule $V_m N$ per mole to the molar refraction
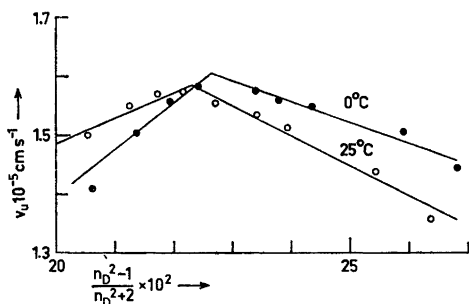
$$R = \frac{n^2 - 1}{n^2 + 2} v^\circ$$

Fig. 4. The ultrasonic velocity v_u in the mixtures of water and 2-chloroethanol plotted *versus* $\dfrac{n_D^2 - 1}{n_D^2 + 2}$.
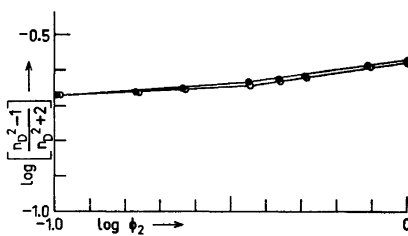
Fig. 5. log $\left(\dfrac{n_D^2 - 1}{n_D^2 + 2}\right)$ plotted *versus* the logarithm of the volume fraction of 2-chloroethanol, φ_2. The experimental points are, ● at 0°C and ○ at 25°C.

where n is the refractive index. Therefore we can assume a similarity of $(n^2 - 1)/(n^2 + 2)$ and r.

The refractive index n_D of the Na-D-line, has for the above mentioned reasons been measured in the mixtures of water and 2-chloroethanol at the temperatures 0° and 25°C.

In Fig. 4 is shown a plot of the ultrasonic velocity v_u in the mixtures *versus* $(n_D^2 - 1)/(n_D^2 + 2) \simeq r$. It is evident that the experimental points are distributed along two straight lines, which intersect at a value of r corresponding to a mixture of about 40 wt. % 2-chloroethanol.* It can be shown that the intersecting lines at the respective temperatures can be represented by

$$v_u 10^{-5} = 4.217\ r + 0.644\ (25°\text{C};\, < 40\ \text{wt.\%}\ 2\text{-chloroethanol})$$
$$v_u 10^{-5} = -5.081\ r + 2.718\ (25°\text{C};\, \geqq 40\ \text{wt.\%}\ 2\text{-chloroethanol})$$
$$v_u 10^{-5} = 7.870\ r - 0.176\ (0°\ \text{C};\, < 40\ \text{wt.\%}\ 2\text{-chloroethanol})$$
$$v_u 10^{-5} = -3.497\ r + 2.396\ (0°\ \text{C};\, \geqq 40\ \text{wt.\%}\ 2\text{-chloroethanol})$$

In Fig. 5 is shown a plot of log $((n_D^2 - 1)/(n_D^2 + 2))$ *versus* the logarithm of the volume fraction of 2-chloroethanol, φ_2. The experimental points are also here distributed along two intersecting lines.

From the available data it can be deduced that]

$$r = 0.2395\varphi_2^{0.0532}\ (25°\text{C};\, < 40\ \text{wt.\%}\ 2\text{-chloroethanol})$$
$$r = 0.2632\varphi_2^{0.143}\ (25°\text{C};\, \geqq 40\ \text{wt.\%}\ 2\text{-chloroethanol})$$
$$r = 0.2436\varphi_2^{0.0571}\ (\ 0°\text{C};\, < 40\ \text{wt.\%}\ 2\text{-chloroethanol})$$
$$r = 0.2673\varphi_2^{0.132}\ (\ 0°\text{C};\, \geqq 40\ \text{wt.\%}\ 2\text{-chloroethanol})$$

From the above established expressions it is now possible to derive expressions for the sound velocities in the mixtures with < 40 wt.% and ≥ 40 wt.% 2-chloroethanol as functions of the volume fraction of 2-chloroethanol, φ_2. Thus

$$v_u 10^{-5} = 1.010\ \ \varphi_2^{0.0532} + 0.644\ (25°\text{C};\, < 40\ \text{wt.\%})$$
$$v_u 10^{-5} = -1.337\ \ \varphi_2^{0.143}\ + 2.718\ (25°\text{C};\, \geqq 40\ \text{wt.\%})$$
$$v_u 10^{-5} = 1.917\ \ \varphi_2^{0.0571} - 0.176\ (\ 0°\text{C};\, < 40\ \text{wt.\%})$$
$$v_u 10^{-5} = -0.9347\ \varphi_2^{0.132}\ + 2.396\ (\ 0°\text{C};\, \geqq 40\ \text{wt.\%})$$

It may then be concluded that in the present case the sound velocity in the mixtures can be represented by an expression of the form $v_u = a_1\, \varphi_2^n + a_2$, and it is tempting to assume that the mixtures with less than 40 wt.% 2-chloroethanol behave as solutions of water-2-chloroethanol complexes in water, whereas the mixtures with more than 40 wt.% are solutions of water-2-chloroethanol complexes in 2-chloroethanol.

In the Tables 5 and 6 are given the experimental values of n_D and r, and also, for comparison, the sound velocities recalculated from the derived expressions.

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* 40 wt. % corresponds to 6.7 moles of water per mole 2-chloroethanol.

Table 5. The ultrasonic velocities in the mixtures calculated from the expression $v_u = a_1\varphi_2{}^n + a_2$ at 0°C.

wt.%	φ_2	n_D	$\dfrac{n_D{}^2 - 1}{n_D{}^2 + 2}$	$v_u \times 10^{-5}$ cm s^{-1} (calc.)	$v_u \times 10^{-5}$ cm s^{-1}
0	0	1.3342	0.2063		
12.1	0.102	1.3479	0.2138	1.507	1.504
20.1	0.170	1.3577	0.2194	1.557	1.557
27.0	0.231	1.3662	0.2241	1.587	1.583
40.3	0.355	1.3841	0.2339	1.581	1.575
48.3	0.433	1.3913	0.2378	1.559	1.559
56.4	0.514	1.4020	0.2435	1.540	1.549
80.5	0.772	1.4313	0.2590	1.493	1.506
100.0	1.000	1.4490	0.2682	1.461	1.445

When $(n_\infty{}^2 - 1)/(n_\infty{}^2 + 2)$, with the value of n extrapolated to infinite wavelength, is proportional to the electronic polarisability α_e,[14] then the established relation between the sound velocity and $(n_D{}^2 - 1)/(n_D{}^2 + 2)$

Table 6. The ultrasonic velocities in the mixtures calculated from the expression $v_u = a_1\varphi_2{}^n + a_2$ at 25°C.

wt.%	φ_2	n_D	$\dfrac{n_D{}^2 - 1}{n_D{}^2 + 2}$	$v_u \times 10^{-5}$ cm s^{-1} (calc.)	$v_u \times 10^{-5}$ cm s^{-1}
0	0	1.333	0.2055		
12.1	0.103	1.345	0.2126	1.539	1.550
20.1	0.172	1.354	0.2174	1.564	1.570
27.0	0.234	1.362	0.2216	1.579	1.574
40.3	0.359	1.372	0.2271	1.563	1.555
48.3	0.438	1.385	0.2341	1.530	1.535
56.4	0.518	1.394	0.2394	1.501	1.513
80.5	0.788	1.422	0.2543	1.426	1.438
100.0	1.000	1.440	0.2636	1.381	1.358

suggests an association with the dielectric constants of the mixtures of the polar substances and thereby the formation of complexes by hydrogen bonding. The two different ways of establishing the dependence of the sound velocity on the volume fraction of the second component are thus in fact attached both of them to the polar character of the molecules and the formation of complexes. Jacobson in particular lays stress on the certain regions near the "surface" of the molecules in which the polarity is localized, whereas the connection with the refractive index suggests a change in the effective dipole moment of the water molecules consequent to a break down of the highly coordinated structure of water due to formation of complexes by hydrogen bonding with alcohol molecules.[15]

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