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ULTRASOUND ABSORPTION AND VELOCITY MEASUREMENT BY THE CORRELATION METHOD IN THE BINARY KNESER LIQUID MIXTURES

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Abstract: In a measurement area where the ultrasound waves are being diffused, if either of the transmitter or the receiver crystals is more movable with respect to each other, a Doppler shift of Δf occurs between the transmitted and received ultrasound frequencies. In this study, in order to establish an application to the theoretical method "Correlation Method" developed by M. Sedlacek [1] in a convenient experimental set up, calibration measurements have been performed for pure water and liquids CS_2, CCI_4, and $CHCI_3$ at (20±0.02) ^oC and (5, 15, 26, 36, 45) MHz frequencies. Then the measurements of ultrasound absorption and velocity have been taken in the mixtures of (CS_2+CCI_4) and (CCI_4+CHCI_3) which have been prepared "gravimetrically". $\alpha/f^2 = F(x)$ curve where x is the contraction of a component in the mixture and v=F(x) curve defined as "the characteristic sound curves" have been plotted. It has been observed from the plots that the curves of α/f^2 do not agree with the theoretical relation but in agreement with Bauer-Sette relation.

Key words: *ultrasound, absorption, velocity and liquid mixtures*

İKİLİ KNESER SIVI KARIŞIMLARINDA KORELASYON YÖNTEMİYLE ULTRASES SOĞURULMASI VE HIZ ÖLÇÜLERİ

Özet: Ultrases dalgalarının yayıldığı bir ölçü ortamında verici ve alici kristallerden biri diğerine göre hareketli olursa, verilen ve alınan ultrases dalgaları arasında Δf gibi bir dopler kayması oluşur. Bu frekans kaymasını esas alarak M. Sedlacek [1] "korelasyon yöntemi" denilen bir ölçü yöntemini geliştirmiştir. Çalışmamızda bu teorik yönteme uygunp bir deney düzeneğine de işlerlik kazandırmak için (20±0.02) ^oC de ve (5, 15, 26, 36, 45) MHz frekanslarında saf su, CS_2, CCI_4, ve $CHCI_3$ sıvılarında kalibrasyon ölçüleri yapıldı. Daha sonra "gravimetrik " olarak hazırlanan (CS_2+CCI_4) ve (CCI_4+CHCI_3) karışımlarında ultrases soğrulma ve hız ölçümleri alındı. Karışımdaki bir bileşenin konsantrasyonu x olmak üzere $\alpha/f^2 = F(x)$ ve karakteristik ses eğrileri olarak tanımlanan v=F(x) eğrileri çizildi. $\alpha/f^2 = F(x)$ eğrilerinin Pinkerton (2) tarafından ortaya konulan teorik bağıntıya uymadığı, Bauer-Sette (3) bağıntısına uyduğu görülmüştür.

Anahtar kelimeler: ultrases, absorpsiyon, hız, sıvı karışımlaır.

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1. INTRODUCTION

Up to now, not only measurements of physical size of the non-associated liquids and their mixtures, but also measurements of their sound absorption and velocity (α/f^2, v) have been made [1-4]. While it has been verified from these measurements that some of the size ranges of the mixture are equal to the sum of two components, it has been detected that the sound absorption do not agree with this rule. Non-associated liquids and showing thermal relaxation (Kneser) such as CCI_4, CS_2 etc., have a much bigger sound absorption in pure form than the other liquids. Mixing them with the same kind of liquid with small sound absorption, it has been observed that the absorption related with the mixture gets smaller [5-8].

A theory of sound absorption for binary Kneser liquid mixtures has been proposed by taking into account the experiment results of Grobenin [6], and has been obtained a relation with some hypothesis, which agrees roughly with the experiment results and which belongs to the sound absorption of the mixture. Then, it has been developed a thetorical model, which agrees with experimental data completely [3].

In this study, measurements of pure liquids of CCI_4, CS_2, $CHCI_3$ and of their binary mixtures at (20 ± 0,02) ^oC have been made by using “Correlation Method” which is more sensitive than other methods in sound absorption and velocity measurements. The values of experimental sound absorption have been compared with the values calculated from Pinkerton and Bauer-Sette relations. It has been observed that our measurement values agree with Bauer-Sette theory much better than the values obtained from the other methods.

The liquids, of which measurements of ultrasound absorption have been made, have been classified in accordance with the type of absorption and relaxation they possess [9]. In this classification, only the liquids showing “thermal relaxation” (Kneser liquids, CS_2, CCI_4, C_6H_6 ...) are of great importance. It has been concluded that the absorption values measured in these liquids are much bigger than the value calculated from the classical sound absorption relation and this difference results from the relaxation phenomenon. The reason of relaxation is not the structural transformations in these liquids but heat transformations in a very small scale. These heat transformations in small scale are formed with the ultrasound waves passing through the liquid. The energy received from the sound waves in a certain ultrasound frequency (frequency of relaxation) in the condition is exchanged during the inelastic collisions occurring between the excited and non-excited molecules. This result has also been verified by the measurements of ultrasound absorption done in the binary mixtures of the same liquids.

The ultrasound absorption measured in the mixture of two liquids of A and B, which is non-associate, does not agree with the ‘total rule’ verified by other physical parameters related with ideal liquid mixtures. The sound absorption measured in these liquid mixtures which do not yield reaction, is smaller than the sum of the absorption of its components:

$$(\alpha_{\text{mix.}})_{\text{measurement}} \langle (\alpha_{\text{A}} + \alpha_{\text{B}})_{\text{measurement}}$$

The case occurs as follows; the excessive sound absorption is mixed with the inner free degrees of the energy of surpass or a non-associated liquid, formed by the reverse action of passing, is mixed with other liquid of the same type, (CS_2 + CCI_4 , CCI_4 + $CHCI_3$,...,). Then the mixed molecules provide easy energy passing and sound absorption becomes less. Thus, in the maintenance of two-molecule inelastic collision, which is not elastic, the collision of two different molecules is more active than the collision of two similar ones.

The expression of the ultrasound absorption theory in binary Kneser liquid mixture is given by

$$\left(\frac{\alpha}{f^2}\right)_{\text{mix.}} = \frac{\left(\frac{\alpha}{f^2}\right)_B \alpha}{\left(\frac{v_A}{v_B}\right)(1-x)+x}\left[\frac{1-x}{\frac{\alpha_B v_B}{\alpha_A v_A}(1-x)+1}+x\right]$$

Formula 1

Where α_A, α_B are the coefficients of sound absorption of the liquids of A and B , and v_A and v_B are the sound velocities in the same liquids. x is the mole fraction of the liquid of B with the coefficient of small absorption.

The theory of ultrasound absorption in binary Kneser liquid mixtures has also been observed by E. Bauer and D. Sette [3]. In addition, the agreements with the theory of Pinkerton; by taking the reaction velocities and real heats of vibration belonging to the molecules into consideration and ignoring the collision of two excited molecules in the calculations, the formula (1) has been expressed as;

$$\left(\frac{\alpha_D/f^2}{\alpha_B/f^2}\right) = \frac{\alpha_D}{\alpha_B} = (1-dx)\left[\frac{xz}{1-g(1-x)}\frac{C_A}{C_B}+\frac{1-x}{1-x(r-1)}\right]$$

Formula 2

Where (1-x) is the mole fraction of the component B with little absorption, while x is the mole fraction of the component of A with higher absorption and z is the rate of frequencies of relaxation of two liquids $\left(f_r^B / f_r^A\right)$. g and r are coefficients and express how active the collision of different type of molecules than the collision of two same molecules in the energy transfer. Provided that $\alpha=\alpha_A$ for x=1, the coefficient of d can be found. C_A and C_B are real heats as the equivalence of inner free degrees of A, B and have been taken from G. Herzberg [10].

2. EXPERIMENTAL ARRANGEMENT

In liquids, either continuous sound waves or sound pulses are used in order to measure acoustic parameter of α/f^2 and the ultrasound velocity of v. The pulses prevent the spectral purity of sound waves and make the evaluation of experiment findings in a heterogeneous measurement condition more difficult. Apart from this, due to the indefiniteness formed during the comparison of two amplitude discharges with the phases on the screen of oscilloscope, the sensitivity of the method of pulse is limited [11]. Therefore; continuous sound waves are preferred for the measurement of two acoustic parameters ($v\alpha/f^2$). The sound waves are used as the network of diffraction in the optical method where continuous sound waves are used. However, the sensitivity is limited in the measurement of v and α/f^2 because of the difficulties rose in the evaluation of the design of optical diffraction.

The defects of all methods, in which other continuous sound waves and the ones with pulses are used, have been tried to be corrected in the "Correlation Method" of which theory has been developed by M. Sedlacek [1].

The absorption coefficient of ultrasound waves passing through the liquids in the frequency region of [5-36] MHz and the whole set up enabling to measure the velocity have been illustrated in the simplified scheme in Figure (1). Thus, the experiment set up is : the glass measuring bowl can be observed in three parts as the interpherometer encompassing with receiver-transmitter quartz crystals one of which is movable and two suspending quartz sticks; the electronic part including the signal generator, selective amplifier, mixer, circuit of filter and recorder; and thermostat keeping the heat of the measurement environment constant. These parts have been explained thoroughly in the previous studies [1, 11].

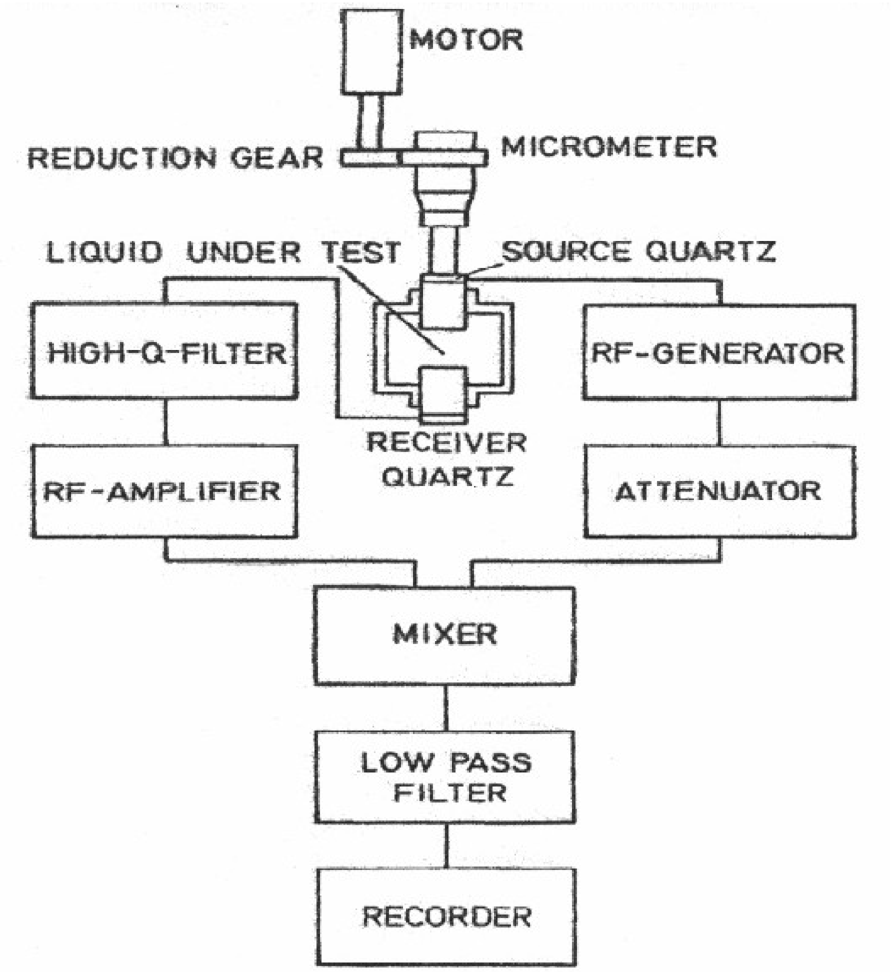

Figure 1. The scheme of experiment setup.

The plane ultrasound waves are obtained with the aid of alternative tension with the frequency of f_0 implemented on the transmitter crystal. These waves are absorbed while passing through the measuring liquid and reach to receiver crystal turning the sound waves to alternative tension. When transmitter crystal is driven with a small velocity (0.02 mm/s)with the aid of an engine, the “Doppler frequency shift” is formed between the main signal implemented on the transmitter crystal and the signal obtained from the receiver crystal, which is

$$\Delta f = f_0 \frac{c}{v_0} \qquad (c<<v)$$

Formula 3

Where c is the friction velocity of transmitter crystal and v is the ultrasound velocity in the liquid. The Doppler Shift is recorded with the aid of the printer of x-t after going through the phases of mixer and filter (Fig.2). The velocity of ultrasound is calculated from the frequency shift Δf and the absorption coefficient α is calculated from the signal sleeve (Fig.3).

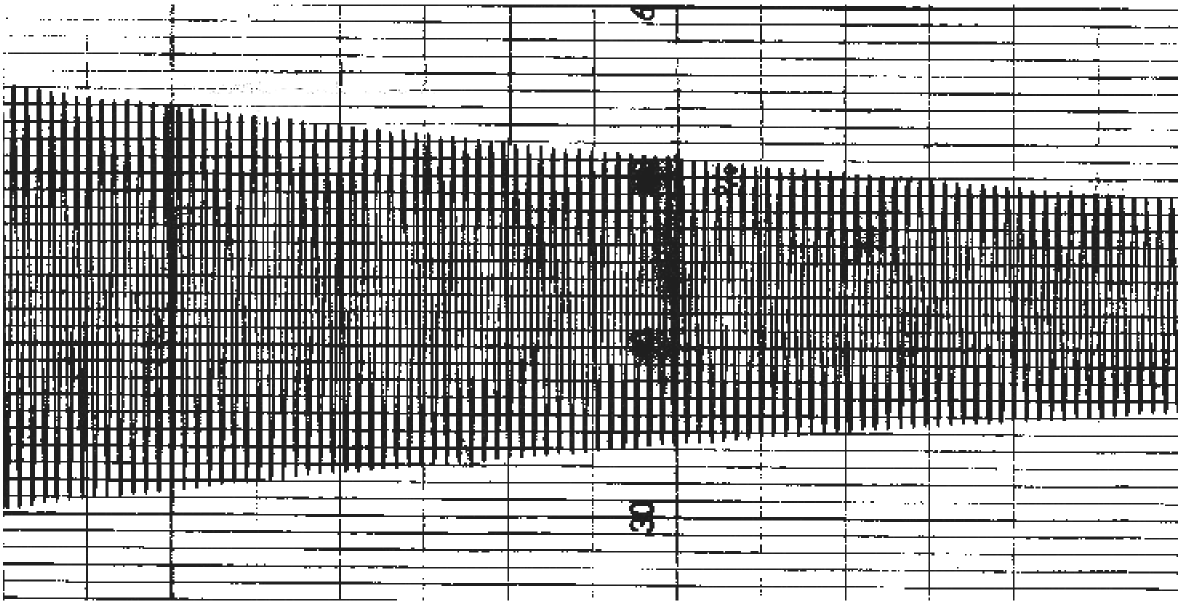

Figure 2. Displacement of source quartz for X_{CCl4}=0.3591 in the liquid mixture of CS_2 +CCl_4 at 15.76 MHz.

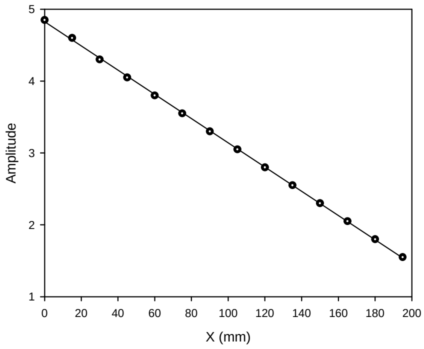

Figure.3. Displacement of source quartz for X_{CCl4}=0.3591 in the liquid mixture of CS_2 +CCl_4 at 15.76 MHz.

3. RESULTS AND DISCUSSION

In order to calibrate the measurement set up, the measurements of sound absorption and velocity of pure water and the Kneser liquids of CS_2, CCI_4, $CHCI_3$ have been made in the frequency interval of (5-36) MHz and at temperature of (20±0,02) ^oC. It has been observed that the values found go parallel with the values of literature. The relative errors in sound absorption and velocity measurements were 3% and 1%, respectively.

Binary liquid mixtures have been prepared with ‘gravimetric method’ which can weight 10^{-5} grams in scales, taking the Archimedes’ Principle of Elevation into consideration. Therefore, the sound absorption and velocity measurements of the liquid mixtures of CS_2+CCI_4 and CCI_4+CHCI_3 obtained in the frequency region of (5-36) MHz at (20±0,02) ^oC have been made. The theoretic (α/f^2) values calculated from the relations of (1) and (2) for the same mixtures have been shown in the Table (1) and (2) together with these measurement values. With the aid of these values; the graphs of $(\alpha/\alpha_B)_{teo.}=F(x)$ and $(\alpha/\alpha_B)_{exp.} = F(x)$ have been plotted (Figure 4 and 5). Also, the values of sound velocity measured in binary liquid mixtures and the “Characteristic sound curves” of v=F(x) have been plotted (Figure 6 and 7).

Table 1. The exchange of the sound velocity and experimental, theoretic ultrasound absorption in the liquid mixtures of CS_2+CCI_4 with concentration.

X_{CCI4}	α/f^2 $(cm^{-1}.s^2).10^{17}$	α_D/α_B	α_{BAU}/α_B	α_P/α_B	v(m/s)
0	5971,4	11,05	11,0	11,05	1163,1
0,0218	3617,5	6,69	6,69	10,8	1151,4
0,0771	1832,8	3,39	3,03	10,2	1126,8
0,1302	1233,7	2,28	1,97	9,7	1106,7
0,2462	772,6	1,43	1,07	8,53	1069,2
0,3450	608	1,12	0,90	7,51	1042,1
0,4348	517,3	0,95	0,79	6,59	1020,6
0,5148	492,6	0,91	0,77	5,77	1003,3
0,5917	469,9	0,87	0,78	4,98	989,6
0,6498	465,0	0,86	0,82	4,48	981
0,6731	454,3	0,84	0,80	4,80	976
0,8329	463,2	0,85	0,88	2,51	954,1
0,8875	501,9	0,93	0,92	1,96	948,7
0,9390	508,2	0,94	0,95	1,43	941,2
1	540	1,00	1,00	1,00	935,8

Table 2. The exchange of the experimental, theoretic sound absorption and sound velocity in the liquid mixtures of CCI_4+$CHCI_3$ with the concentration.

X_{CHCL4}	α/f^2 $(cm^{-1}.s^2).10^{17}$	α_D/α_B	α_{BAU}/α_B	α_P/α_B	v(m/s)
0	540	1,40	1,40	1,40	935,8
0,0929	494,7	1,29	1,19	1,38	939,8
0,1812	463,8	1,21	1,03	1,34	943,8
0,2674	447,7	1,17	0,92	1,32	948,4
0,3728	402	1,05	0,87	1,26	958,0
0,5305	382,3	1,00	0,74	1,23	962,9
0,6081	370,9	0,97	0,73	1,21	967,8
0,6646	363,6	0,95	0,74	1,20	972,8
0,7417	369,8	0,96	0,76	1,16	978,3
0,8037	367,9	0,963	0,79	1,13	983,6
0,8694	373,9	0,98	0,85	1,11	990,2
0,9663	379,2	0,89	0,95	1,08	999
1	382,7	1,00	1,00	1,07	1002,6

The mass distribution in the molecules is much bigger than the relation of sound absorption (3) measured in CCI_4, CS_2,… and in the non-associated liquids, which are approximately spherical. It has been concluded that this difference in absorption can occur from the energy transferred by the inelastic collisions, taking place between the liquid molecules excited with ultrasound energy and other molecules (thermal relaxation) [4,10]. The verification for this conclusion has been made by the measurements of sound absorption made in binary mixtures of the same liquids. When the liquid A with great absorption is mixed with a liquid B with little absorption in the same type, (CS_2+CCI_4 , CCI_4+$CHCI_3$ ...), the possibility of the occurrence of collisions, inelastic, is much bigger. Therefore, as the energy transfer is easier in collisions, the sound absorption belonging to the mixture gets smaller (Figure 4 and 5).

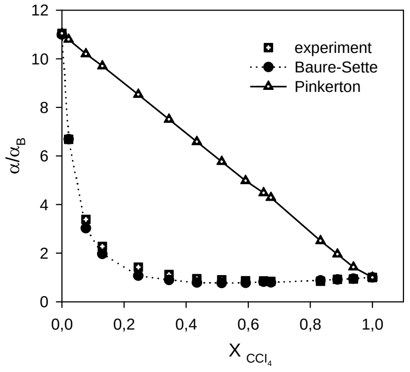

Figure 4. The change of $\left(\alpha/\alpha_B\right)_{Exp.}$ and $\left(\alpha/\alpha_B\right)_{Teo.}$ in the liquid mixtures of CS_2+CCI_4 with mole fraction of CCI_4.

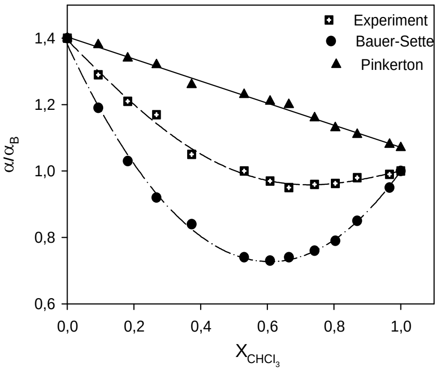

Figure 5. The change of $\left(\alpha/\alpha_B\right)_{Exp.}$ and $\left(\alpha/\alpha_B\right)_{Teo.}$ in the liquid mixtures of CCI_4 +$CHCI_3$ with mole fraction of $CHCI_3$.

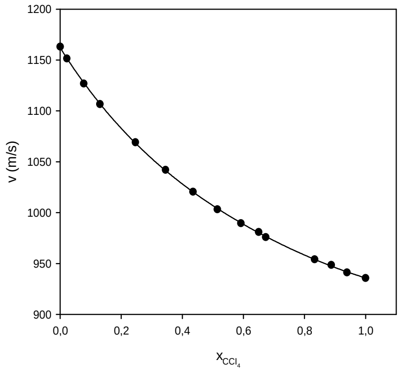

Figure 6. The change of sound velocity in the liquid mixtures of CS_2 + CCI_4 with mole fraction of CCI_4.

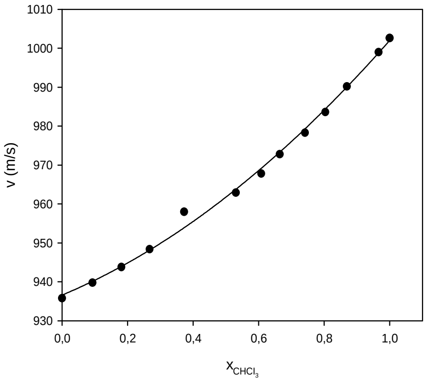

Figure 7. The change of sound velocity in the liquid mixtures of CCI_4 +$CHCI_3$ with mole fraction of $CHCI_3$.

As it is seen in the Figure (4 and 5), the adaptation of experimental curves of α/α_B = f (x) to the relation of Bauer-Sette is much better than Pinkerton's relation. But as Chloroform evaporates very rapidly in the mixture of (CCI_4 + $CHCI_3$) the mole fraction of X_{CHCL3} changes. Thus, the adaptation of the experiment values and values obtained from the relation of Bauer-Sette with each other is not good. The change in the values of sound absorption measured in the same mixtures with other methods is exponential against X_B mole fraction α/α_B. However, it is observed in this study that the curves of α/α_B = F (x) pass through a minimum in the value of a certain x. This case has also been explained theoretically for binary mixtures of the liquids which do not associate with the aid of quantum mechanism by D. Sette [8].

The variations in 'Characteristic sound curves' of v=F(x) seen in figure (6 and 7) are in compliance with the molecular structures of these mixtures.

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