

Ultrasonic velocity measurements in isobutyric acid - water binary mixtures over the temperature range from 300.15 to 313.15 K

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Abstract—We measured the ultrasonic velocity, U , density, ρ , and viscosity, η in Isobutyric acid - water binary liquid mixtures over the entire composition range at temperatures ranging from 300.15 to 313.15 K under atmospheric pressure. The experimental data values were analyzed to determine, various acoustical parameters: adiabatic compressibility, β , acoustic impedance, Z , free length, L_p , free volume, V_p , molar volume, V_m , relaxation time, τ , absorption coefficient, α/f^2 , internal pressure, π_b , Gibbs's free energy, ΔG , cohesive energy, CE , Wada's constant, W , Rao's constant, R_m and relative association, R_A . The variation of these parameters versus the mixture composition was explained on the basis of the intermolecular interactions between the components of the mixture.

Keywords: Binary Mixtures, Isobutyric Acid, Water, Molecular Interactions, Ultrasonic Velocity, Acoustical Parameters

INTRODUCTION

The isobutyric acid - water (IBA-W) system is convenient for studying nonequilibrium interfacial phenomena. The mutual miscibility of coexisting liquid phases of this binary liquid is very propitious for innovative separation and extraction processes [1,2]. Moreover, the advantage of studying (IBA-W) mixture which is stable is that it is characterized by a coexistence curve representing a readily accessible way of studying the mixing of molecules. Previously, we studied and reported data for this critical mixture: transport phenomena and physical properties [3,4], ionic structure [5], salvation phenomenon in a binary liquid [6], the effect of ions on the mixture (IBA+W) [7] and phase equilibrium properties occurring in the presence of added ions [8].

In chemical and industrial processes, materials are normally handled in fluid form and consequently, the physical, chemical and transport properties of fluids, are important. Therefore, data on some of the properties associated with the liquids and liquid mixtures such as ultrasonic velocity, density and viscosity find extensive application in solution theory and molecular dynamics. The practical need for thermodynamic data for research, design and set up of industrial processes remains to drive investigation in the study of multicomponent systems. Ultrasonic velocity measurements have been employed to investigate the nature of molecular interactions occurring in pure liquids, binary and ternary liquid mixtures [9-13]. It is therefore required to have a data source which gives the speed of sound and the density in the mixtures by simply specifying their concentration and temperature. Since the speed of sound

has often been measured in-house, a literature survey shows that ultrasonic studies have been made in a large number of binary liquid mixtures [14-20]; nevertheless, there are few numerically accessible data available for the (IBA-W) system [21-23]. Both Dunker et al. [21] and Belkoura et al. [22] have reported measurements of sound attenuation in the homogeneous phase near the critical mixing point of (IBA-W) mixture. The experimental results have been analyzed in terms of a theory of critical ultrasonic absorption proposed by Bhattacharjee and Ferrell, which contains no adjustable parameters [24]. Kaatze and Schreiber [23] studied the dependence upon frequency of the ultrasonic absorption coefficient for the (IBA-W) system of critical composition as a function of temperature; however, the data were presented in graphs instead of numerical values.

The spirit of the present work was to perform a detailed experimental study of the temperature and concentration dependence of ultrasonic velocity in Isobutyric acid - water (IBA-W) binary mixture. The ultrasonic velocity data were determined in the single phase as a function of six temperatures: 300.15 K, 302.15 K, 305.15 K, 308.15 K, 311.15 K and 313.15 K and of the whole composition x_1 in acid (IBA). These obtained values can be coupled with other experimental data such as density and shear viscosity to compute various acoustical parameters such as adiabatic compressibility, β , acoustic impedance, Z , free length, L_p , free volume, V_p , molar volume, V_m , relaxation time, τ , internal pressure, π_b , absorption coefficient, α/f^2 , relative association, R_A , Rao's constant, R_m , Wada's constant, W , Gibbs free energy, ΔG , and cohesive energy, EC .

EXPERIMENTAL SECTION

1. Materials

Water (CAS No 7732-18-5) was obtained from Merck while

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isobutyric acid (CAS No 79-31-2) was supplied by Reidel de Haen (Germany). The fraction purities are, respectively, 0.990 and 0.999. The purity of Isobutyric acid was confirmed by gas chromatography (GC). No further purification was carried out for all of the chemicals in the present work.

The isobutyric acid - water (IBA-W) system is appropriate for studying the critical phenomena. In fact, a two-phase equilibrium system can be easily prepared by equilibrating IBA and water below the upper critical solution temperature (UCST) of 27 °C. The IBA-rich phase will sit on the top, whereas the denser water-rich phase will form at the bottom. If the temperature of the equilibrated system is quickly raised above the UCST, thermal equilibrium is reached much faster than chemical equilibrium, so that a non-equilibrium interface persists for a long time with a sharp concentration gradient between the two fluids. Note that the critical mass fraction of the acid (IBA) was 0.38, which corresponds to a critical mole fraction $x_{lc}=0.1114$ [4]. We chose the (IBA-W) binary fluid since their component densities are very close to each other, and consequently this mixture does not have density gradients induced by gravity, and the critical temperature T_c of (IBA+W) is relatively low.

2. Equipment and Procedure

Solutions were prepared by weighing the chemicals directly into screw-capped Pyrex tubes. The weight is determined by using a digital electronic balance (Sartorius BP 221S) with a resolution of 10^{-3} g. Density, viscosity and ultrasonic velocity measurements were carried out soon after the samples preparation to avoid preferential evaporation. All transfers of material between the screw capped Pyrex tubes and the measuring apparatuses were made with syringes to reduce evaporation losses. Precautions were taken to prevent condensation of moisture into the samples during the temperature stabilization period. The cell, in which the isobutyric acid and water were mixed together, was immersed in a thermally stabilized water bath with thermal regulation in the order of 10^{-3} K over hours.

2-1. Density Measurement

The density measurements of the pure liquids and the mixtures were by means of an Anton Paar digital oscillating U-tube densimeter (model DMA 4500). Total uncertainty in the density measurement, as reported by the equipment manufacturers, was $\pm 10^{-5}$ g·cm⁻³ at a confidence level of 95%, and the accuracy for the density measurement was $\pm 5 \times 10^{-5}$ g cm⁻³ between 300.15 and 313.15 K. The instrument is fully automatic, and therefore the resonant frequency was automatically determined. The temperature in the cell was regulated to ± 0.01 K with a solid-state thermostat. The DMA cell was calibrated using the published density values data for both water [25,26] and methanol [27] at atmospheric pressure. Triplicate measurements of the density were made for all the mixtures and pure components.

2-2. Viscosity Measurement

The kinematic viscosities of the pure liquid and liquid-liquid mixture were measured with an (AVS/N-Schott Greäte) Ubbelohde viscometer suspended in a thermostatically controlled water bath at required temperature. Care was taken to prevent evaporation during the measurements. The viscometer was calibrated by using viscosity values taken from published values for methanol [27] and water [28]. An average of four or five sets of flow times

were taken for each liquid and liquid mixture. The uncertainty in viscosity measurements was within $\pm 1\%$. The measured values of kinematic viscosities were converted to dynamic viscosities η after multiplication by the density. The flow-time measurements were made with an electronic stop watch having precision of ± 0.01 s. Viscosity values are accurate within the range ± 0.003 mPa·s.

2-3. Ultrasonic Velocity Measurement

The velocity of ultrasonic waves in the liquid mixture was measured with an ultrasonic interferometer (Model-81, supplied by Mital Enterprises) operating at frequency range of 1 MHz to 4 MHz. The temperature around this device was maintained within 0.01 K in electronically controlled thermostatic water bath. The measuring cell is a specially designed double walled vessel with provision of temperature constancy. The high frequency generator excites a quartz crystal fixed at the bottom of the measuring cell, at its resonant frequency. The capacity of the measuring cell is 12 cc. A fine micrometer screw, with a least count of 0.001 mm at the top of the cell, can be raise (or) drop the reflector plate in the liquid through a known distance. The measuring cell is connected to the output terminals of the high frequency generator through a shielded cable. Ultrasonic waves, normal to quartz crystal, are reflected from the reflector plate. Stationary waves are formed in the region between reflector plate and the quartz crystal. The micrometer is slowly moving until a number of maximum readings (n) of the anode current goes through. The total distance moved by the micrometer is noted (d). The wavelength of the ultrasonic waves in the liquid is $\lambda=2d/n$. The velocity of ultrasonic waves in the liquid $U=\lambda f$, where f is the generator frequency.

THEORY AND CALCULATION

1. Acoustic Impedance (Z)

This parameter is studied in various fields; for example in the field of electricity acoustic impedance measures the ratio of the voltage and the current. Using Ohms [29] the analogical, impedance is written follows as:

$$Z = \frac{p_e}{U} \quad (1)$$

with p_e is the acoustic pressure, and U is ultrasonic velocity.

Beyer and Latcher [29] obtained a relation that related the mass density (ρ) with ultrasonic velocity (U) defined by:

$$Z = U\rho \quad (2)$$

2. Adiabatic Compressibility (β)

Taking into account the thermodynamics exchanges, the adiabatic compressibility of a fluid is defined by the following relation: $\beta=1/v \cdot (\partial v / \partial p)$.

The adiabatic compressibility (β) can be also determined by the ultrasonic velocity and mass density using the equation of Newton-Laplace [30].

$$\beta = \frac{1}{\rho U^2} \quad (3)$$

3. Free Length (L_f)

Free length (L_f) is another important parameter for the study of

intermolecular interactions in the liquid mixture that is defined as being the distance between the surfaces of neighboring molecules. This factor is determined by the empirical relation Jacobson [31].

$$K_f = K_T \beta^{1/2} \quad (4)$$

where K_T is the temperature dependent constant and whose numerical value is defined as follows [32]: $K_T = (93.875 + 0.375 \times T) \times 10^{-8}$.

4. Relaxation Time (τ)

The relaxation time of an ultrasonic wave is the result of a time interval between the passage of the wave and the molecules return to their equilibrium position. The relaxation time is calculated by the following equation [33].

$$\tau = \frac{4\eta}{3\rho U^2} \quad (5)$$

5. Free Volume (V_f)

The free volume was made to explain the movement of molecules, so that the liquid media molecules are not tight enough and

there is a free space (gap) between its molecules [34]. All of the gaps represent the free volume. This parameter was determined in terms of ultrasonic velocity (U) and the shear viscosity of the liquid (η) by the relation [35]:

$$V_f = \left(\frac{M_{eff} U}{K \eta} \right)^{\frac{3}{2}} \quad (6)$$

where, " $M_{eff} = x_1 M_1 + x_2 M_2$ where M_1, M_2 are, respectively, the molecular weights of two constituents and x_1, x_2 are their mole fractions" which is the effective molecular weight of the liquid, and 'K' is a constant equal to 4.28×10^9 when M_{eff} , U, η and V_f are given in c.g.s units and is independent of the nature of liquid and temperature.

6. Absorption Coefficient (α/f^2)

Generally, the propagation of the ultrasonic wave in a medium causes a decrease in its intensity with the distance; thus the absorption coefficient is a measurement tool that provides information to explain the physical phenomena where a chemical weakens the ultra-

Table 1. Ultrasonic velocity, U, mass density, ρ and shear viscosity, η , for the isobutyric acid - water mixture at 300.15 K, 302.15 K, 305.15 K, 308.15 K, 311.15 K and 313.15 K. x_1 is the Isobutyric acid (IBA) mole fraction

x_1	U (m·s ⁻¹)	ρ (10 ³ Kg·m ⁻³)	η (10 ⁻³ Pa·s)	U (m·s ⁻¹)	ρ (10 ³ Kg·m ⁻³)	η (10 ⁻³ Pa·s)	U (m·s ⁻¹)	ρ (10 ³ Kg·m ⁻³)	η (10 ⁻³ Pa·s)
T=300.15 K									
0.000	1501.20	0.9963	0.8498	1505.06	0.9958	0.8143	1512.26	0.9951	0.7647
0.037	1472.67	0.9981	1.3913	1474.85	0.9974	1.3172	1477.79	0.9965	1.2126
0.072	1413.70	0.9991	1.8784	1411.74	0.9984	1.7655	1408.82	0.9972	1.6050
0.102	1376.47	0.9995	2.1974	1374.29	0.9986	2.0608	1371.03	0.9973	1.8672
0.111	1373.19	0.9996	2.3615	1380.99	0.9988	2.2130	1373.36	0.9976	1.9931
0.131	1336.09	0.9997	2.4323	1334.49	0.9989	2.2800	1332.11	0.9977	2.0647
0.206	1304.10	0.9991	2.7789	1300.40	0.9979	2.6098	1296.60	0.9967	2.3733
0.297	1269.60	0.9960	2.8606	1264.66	0.9951	2.6993	1257.06	0.9935	2.4760
0.407	1237.00	0.9928	2.7094	1231.93	0.9915	2.5730	1224.13	0.9896	2.3845
0.501	1211.86	0.9881	2.4995	1206.60	0.9870	2.3845	1197.40	0.9849	2.2249
0.603	1188.46	0.9835	2.2542	1181.06	0.9818	2.1579	1172.93	0.9794	2.0239
0.705	1171.66	0.9770	2.0036	1165.33	0.9754	1.9221	1157.26	0.9729	1.8112
0.806	1154.80	0.9690	1.7385	1146.60	0.9672	1.6714	1136.80	0.9646	1.5844
0.904	1136.46	0.9581	1.4581	1128.93	0.9561	1.4064	1119.06	0.9532	1.3408
1.000	1127.20	0.9408	1.1875	1120.52	0.9387	1.1482	1109.60	0.9358	1.0991
T=308.15 K									
0.000	1519.32	0.9943	0.7194	1526.40	0.9935	0.6784	1529.72	0.9930	0.6535
0.037	1480.32	0.9955	1.1233	1482.45	0.9946	1.0432	1483.65	0.9940	0.9945
0.072	1405.91	0.9962	1.4761	1402.99	0.9952	1.3629	1401.05	0.9945	1.2939
0.102	1367.75	0.9960	1.7126	1364.46	0.9948	1.5778	1362.26	0.9940	1.4959
0.111	1369.53	0.9965	1.8270	1366.16	0.9953	1.6752	1364.24	0.9946	1.5841
0.131	1329.70	0.9964	1.8916	1327.33	0.9952	1.7410	1325.74	0.9944	1.6501
0.206	1291.90	0.9953	2.1750	1288.20	0.9942	2.0024	1285.40	0.9935	1.8994
0.297	1249.66	0.9921	2.2779	1242.80	0.9902	2.1033	1238.13	0.9889	2.0003
0.407	1216.20	0.9875	2.2093	1207.66	0.9858	2.0514	1202.33	0.9846	1.9578
0.501	1188.33	0.9830	2.0744	1180.20	0.9809	1.9367	1173.93	0.9794	1.8537
0.603	1160.86	0.9769	1.8970	1151.53	0.9746	1.7815	1144.86	0.9731	1.7096
0.705	1147.66	0.9701	1.7021	1136.80	0.9680	1.6068	1130.60	0.9665	1.5460
0.806	1126.80	0.9620	1.4905	1114.46	0.9594	1.4137	1108.26	0.9576	1.3647
0.904	1109.06	0.9502	1.2671	1098.00	0.9474	1.2087	1091.73	0.9455	1.1724
1.000	1097.06	0.9326	1.0471	1086.26	0.9297	1.0083	1080.92	0.9275	0.9841
T=311.15 K									
T=313.15 K									

sonic intensity. This coefficient is proportional to the frequency of ultrasound; it can be calculated from the relation [36]:

$$\alpha/f^2 = \frac{8\pi^2\eta}{3\rho U^3} \quad (7)$$

7. Internal Pressure (π_i)

The internal pressure is the force of cohesive of liquid due to the forces of interatomic attractions and intermolecular between molecules. A general expression for the internal pressure in terms of temperature, pressure and their mutual dependence based on the thermodynamic state equation is:

$$\pi_i = T \left(\frac{\partial p}{\partial T} \right) - p$$

In liquids pure and binary, Suryanarayana and Kuppuswami [37] used an indirect alternative method relating the shear viscosity, mass density and ultrasonic velocity given by the relation:

Table 2. Values of acoustic impedance, Z, adiabatic compressibility, β , and free length, L_f , for the mixture isobutyric acid - water at 300.15 K, 302.15 K, 305.15 K, 308.15 K, 311.15 K and 313.15 K

X _i	Z (10 ³ kg·m ⁻² ·s ⁻¹)	β (10 ⁻¹⁰ Kg ⁻¹ ·m·s ²)	L _f (10 ⁻¹¹ m)	Z (10 ³ kg·m ⁻² ·s ⁻¹)	β (10 ⁻¹⁰ Kg ⁻¹ ·m·s ²)	L _f (10 ⁻¹¹ m)	Z (10 ³ kg·m ⁻² ·s ⁻¹)	β (10 ⁻¹⁰ Kg ⁻¹ ·m·s ²)	L _f (10 ⁻¹¹ m)
T=300.15 K									
0.000	1495.6456	4.4538	4.3565	1498.7387	4.4332	4.3623	1504.8499	4.3942	4.3666
0.037	1469.8719	4.6197	4.4369	1471.0154	4.6093	4.4480	1472.6177	4.5951	4.4653
0.072	1412.4277	5.0081	4.6197	1409.4812	5.0256	4.6445	1404.8753	5.0525	4.6823
0.102	1375.7818	5.2806	4.7437	1372.3660	5.3021	4.7706	1367.3282	5.3343	4.8111
0.111	1372.6407	5.3053	4.7548	1379.3328	5.2498	4.7470	1370.0639	5.3147	4.8022
0.131	1335.6892	5.6035	4.8866	1333.0221	5.6214	4.9122	1329.0461	5.6483	4.9507
0.206	1302.9263	5.8853	5.0080	1297.6692	5.9260	5.0435	1292.3212	5.9679	5.0888
0.297	1264.5216	6.2288	5.1520	1258.4632	6.2833	5.1933	1248.8891	6.3697	5.2573
0.407	1228.0936	6.5826	5.2963	1221.4586	6.6456	5.3409	1211.3990	6.7435	5.4093
0.501	1197.4389	6.8912	5.4190	1190.9142	6.9592	5.4655	1179.3193	7.0816	5.5433
0.603	1168.8504	7.1987	5.5386	1159.5647	7.3019	5.5984	1148.7676	7.4216	5.6748
0.705	1144.7118	7.4559	5.6367	1136.6629	7.5495	5.6926	1125.8983	7.6749	5.7708
0.806	1119.0012	7.7386	5.7426	1108.9915	7.8643	5.8101	1096.5573	8.0220	5.8999
0.904	1088.8423	8.0813	5.8683	1079.3700	8.2066	5.9352	1066.6880	8.3774	6.0292
1.000	1060.4698	8.3657	5.9707	1051.8321	8.4847	6.0349	1038.3637	8.6793	6.1368
T=302.15 K									
0.000	1510.6599	4.3570	4.3715	1516.4784	4.3201	4.3764	1519.0120	4.3036	4.3835
0.037	1473.6586	4.5840	4.4840	1474.4448	4.5750	4.5036	1474.7481	4.5704	4.5174
0.072	1400.5675	5.0785	4.7200	1396.2556	5.1048	4.7573	1393.3442	5.1226	4.7825
0.102	1362.2790	5.3670	4.8518	1357.3648	5.3994	4.8926	1354.0864	5.4212	4.9199
0.111	1364.7366	5.3503	4.8443	1359.7390	5.3832	4.8853	1356.8731	5.4022	4.9113
0.131	1324.9131	5.6762	4.9897	1320.9588	5.7034	5.0284	1318.3159	5.7217	5.0544
0.206	1285.8281	6.0199	5.1385	1280.7284	6.0612	5.1838	1277.0449	6.0919	5.2154
0.297	1239.7877	6.4545	5.3207	1230.6206	6.5385	5.3840	1224.3868	6.5965	5.4271
0.407	1200.9975	6.8462	5.4798	1190.5112	6.9554	5.5530	1183.8141	7.0258	5.6009
0.501	1168.1284	7.2040	5.6212	1157.6582	7.3192	5.6964	1149.7470	7.4089	5.7516
0.603	1134.0441	7.5961	5.7721	1122.2811	7.7379	5.8571	1114.0633	7.8404	5.9167
0.705	1113.3450	7.8263	5.8590	1100.4224	7.9939	5.9531	1092.7249	8.0943	6.0118
0.806	1083.9816	8.1871	5.9925	1069.2129	8.3921	6.0996	1061.2698	8.5022	6.1614
0.904	1053.8288	8.5561	6.1260	1040.2452	8.7551	6.2302	1032.2307	8.8738	6.2946
1.000	1023.1182	8.9093	6.2512	1009.8959	9.1157	6.3572	1002.5533	9.2278	6.4189
T=305.15 K									
0.000	1510.6599	4.3570	4.3715	1516.4784	4.3201	4.3764	1519.0120	4.3036	4.3835
0.037	1473.6586	4.5840	4.4840	1474.4448	4.5750	4.5036	1474.7481	4.5704	4.5174
0.072	1400.5675	5.0785	4.7200	1396.2556	5.1048	4.7573	1393.3442	5.1226	4.7825
0.102	1362.2790	5.3670	4.8518	1357.3648	5.3994	4.8926	1354.0864	5.4212	4.9199
0.111	1364.7366	5.3503	4.8443	1359.7390	5.3832	4.8853	1356.8731	5.4022	4.9113
0.131	1324.9131	5.6762	4.9897	1320.9588	5.7034	5.0284	1318.3159	5.7217	5.0544
0.206	1285.8281	6.0199	5.1385	1280.7284	6.0612	5.1838	1277.0449	6.0919	5.2154
0.297	1239.7877	6.4545	5.3207	1230.6206	6.5385	5.3840	1224.3868	6.5965	5.4271
0.407	1200.9975	6.8462	5.4798	1190.5112	6.9554	5.5530	1183.8141	7.0258	5.6009
0.501	1168.1284	7.2040	5.6212	1157.6582	7.3192	5.6964	1149.7470	7.4089	5.7516
0.603	1134.0441	7.5961	5.7721	1122.2811	7.7379	5.8571	1114.0633	7.8404	5.9167
0.705	1113.3450	7.8263	5.8590	1100.4224	7.9939	5.9531	1092.7249	8.0943	6.0118
0.806	1083.9816	8.1871	5.9925	1069.2129	8.3921	6.0996	1061.2698	8.5022	6.1614
0.904	1053.8288	8.5561	6.1260	1040.2452	8.7551	6.2302	1032.2307	8.8738	6.2946
1.000	1023.1182	8.9093	6.2512	1009.8959	9.1157	6.3572	1002.5533	9.2278	6.4189
T=311.15 K									
0.000	1510.6599	4.3570	4.3715	1516.4784	4.3201	4.3764	1519.0120	4.3036	4.3835
0.037	1473.6586	4.5840	4.4840	1474.4448	4.5750	4.5036	1474.7481	4.5704	4.5174
0.072	1400.5675	5.0785	4.7200	1396.2556	5.1048	4.7573	1393.3442	5.1226	4.7825
0.102	1362.2790	5.3670	4.8518	1357.3648	5.3994	4.8926	1354.0864	5.4212	4.9199
0.111	1364.7366	5.3503	4.8443	1359.7390	5.3832	4.8853	1356.8731	5.4022	4.9113
0.131	1324.9131	5.6762	4.9897	1320.9588	5.7034	5.0284	1318.3159	5.7217	5.0544
0.206	1285.8281	6.0199	5.1385	1280.7284	6.0612	5.1838	1277.0449	6.0919	5.2154
0.297	1239.7877	6.4545	5.3207	1230.6206	6.5385	5.3840	1224.3868	6.5965	5.4271
0.407	1200.9975	6.8462	5.4798	1190.5112	6.9554	5.5530	1183.8141	7.0258	5.6009
0.501	1168.1284	7.2040	5.6212	1157.6582	7.3192	5.6964	1149.7470	7.4089	5.7516
0.603	1134.0441	7.5961	5.7721	1122.2811	7.7379	5.8571	1114.0633	7.8404	5.9167
0.705	1113.3450	7.8263	5.8590	1100.4224	7.9939	5.9531	1092.7249	8.0943	6.0118
0.806	1083.9816	8.1871	5.9925	1069.2129	8.3921	6.0996	1061.2698	8.5022	6.1614
0.904	1053.8288	8.5561	6.1260	1040.2452	8.7551	6.2302	1032.2307	8.8738	6.2946
1.000	1023.1182	8.9093	6.2512	1009.8959	9.1157	6.3572	1002.5533	9.2278	6.4189
T=313.15 K									
0.000	1510.6599	4.3570	4.3715	1516.4784	4.3201	4.3764	1519.0120	4.3036	4.3835
0.037	1473.6586	4.5840	4.4840	1474.4448	4.5750	4.5036	1474.7481	4.5704	4.5174
0.072	1400.5675	5.0785	4.7200	1396.2556	5.1048	4.7573	1393.3442	5.1226	4.7825
0.102	1362.2790	5.3670	4.8518	1357.3648	5.3994	4.8926	1354.0864	5.4212	4.9199
0.111	1364.7366	5.3503	4.8443	1359.7390	5.3832	4.8853	1356.8731	5.4022	4.9113
0.131	1324.9131	5.6762	4.9897	1320.9588	5.7034	5.0284	1318.3159	5.7217	5.0544
0.206	1285.8281	6.0199	5.1385	1280.7284	6.0612	5.1838	1277.0449	6.0919	5.2154
0.297	1239.7877	6.4545	5.3207	1230.6206	6.5385	5.3840	1224.3868	6.5965	5.4271
0.407	1200.9975	6.8462	5.4798	1190.5112	6.9554	5.5530	1183.8141	7.0258	5.6009
0.501	1168.1284	7.2040	5.6212	1157.6582	7.3192	5.6964	1149.7470	7.4089	5.7516
0.603	1134.0441	7.5961	5.7721	1122.2811	7.7379	5.8571	1114.0633	7.8404	5.9167
0.705	1113.3450	7.8263	5.8590	1100.4224	7.9939	5.9531	1092.7249	8.0943	6.0118
0.806	1083.9816	8.1871	5.9925	1069.2129	8.3921	6.0996	1061.2698	8.5022	6.1614
0.904	1053.8288	8.5561	6.1260	1040.2452	8.7551	6.2302	1032.2307	8.8738	6.2946
1.000	1023.1182	8.9093	6.2512	1009.8959	9.1157	6.3572	1002.5533	9.2278	6.4189

$$\pi_i = bRT \left(\frac{K\eta}{U} \right)^{1/2} \frac{\rho^{2/3}}{M^{7/6}} \quad (8)$$

where 'b' is the packing factor which is equal

assumed a simple relation related the ultrasonic velocity and mass density for a liquid given as follows:

$$R_m = V_m U^{1/3} \quad (10)$$

10. Wada's Constant (W)

Wada's constant is also called molar compressibility, which is dependent on adiabatic compressibility and mass density, is given by relation [40]:

$$W = \frac{(M\beta^{-1/7})}{\rho} \quad (11)$$

11. Gibbs Free Energy (ΔG)

The Gibbs free energy is calculated by using the relation [41]:

$$\Delta G = k_B T \ln\left(\frac{\tau k_B T}{h}\right) \quad (12)$$

where, τ is the relaxation time, ' k_B ' is the Boltzmann constant, T is

the absolute temperature and 'h' is Planck's constant.

12. Cohesive Energy (CE)

The concept of cohesive energy (CE) has been used to compare the interaction in the liquid. If the intermolecular forces are small, the cohesive energy is low and the molecules have relatively flexible chains. The cohesive energy is calculated by using the relation:

$$CE = \pi_i V_m \quad (13)$$

where π_i is the internal pressure and V_m is the molar volume.

RESULTS AND DISCUSSION

The values of ultrasonic velocity, U , density, ρ and viscosity, η , of Isobutyric acid - water binary liquid mixtures over the entire composition range at temperatures 300.15 K, 302.15 K, 305.15 K, 308.15 K, 311.15 K and 313.15 K are given in Table 1. The acoustical parameters such as adiabatic compressibility, β , acoustic imped-

Table 3. Values of relaxation time, τ , free volume, V_f and molar volume, V_m , for the mixture isobutyric acid - water at 300.15 K, 302.15 K, 305.15 K, 308.15 K, 311.15 K and 313.15 K

X_1	V_m (10^{-6} m 3 ·mol $^{-1}$)	V_f (10^{-8} m 3 ·mol $^{-1}$)	τ (10^{-12} s)	V_m (10^{-6} m 3 ·mol $^{-1}$)	V_f (10^{-8} m 3 ·mol $^{-1}$)	τ (10^{-12} s)	V_m (10^{-6} m 3 ·mol $^{-1}$)	V_f (10^{-8} m 3 ·mol $^{-1}$)	τ (10^{-12} s)
T=300.15 K				T=302.15 K				T=305.15 K	
0.000	18.0769	2.0260	0.5046	18.0860	2.1682	0.4813	18.0987	2.3997	0.4480
0.037	20.6429	1.1498	0.8570	20.6574	1.2509	0.8095	20.6761	1.4205	0.7429
0.072	23.0780	0.8161	1.2543	23.0942	0.8938	1.1830	23.1219	1.0279	1.0812
0.102	25.1728	0.7064	1.5471	25.1955	0.7759	1.4569	25.2283	0.8965	1.3280
0.111	25.8014	0.6557	1.6705	25.8221	0.7290	1.5490	25.8531	0.8458	1.4124
0.131	27.2013	0.6518	1.8173	27.2230	0.7169	1.7089	27.2558	0.8296	1.5550
0.206	32.4798	0.6709	2.1806	32.5189	0.7340	2.0621	32.5580	0.8427	1.8885
0.297	38.9856	0.8077	2.3758	39.0209	0.8760	2.2614	39.0837	0.9882	2.1029
0.407	46.8782	1.1058	2.3780	46.9397	1.1876	2.2798	47.0298	1.3185	2.1440
0.501	53.7700	1.4760	2.2966	53.8299	1.5738	2.2126	53.9447	1.7262	2.1007
0.603	61.2916	2.0227	2.1637	61.3977	2.1395	2.1009	61.5482	2.3312	2.0027
0.705	69.0179	2.7955	1.9918	69.1311	2.9510	1.9348	69.3088	3.1928	1.8534
0.806	76.8943	3.9310	1.7938	77.0374	4.1257	1.7526	77.2451	4.4131	1.6947
0.904	84.9394	5.7031	1.5711	85.1170	5.9606	1.5389	85.3760	6.3196	1.4977
1.000	93.6543	8.6352	1.3246	93.8639	9.0017	1.2989	94.1547	9.4714	1.2719
T=308.15 K				T=311.15 K				T=313.15 K	
0.000	18.1132	2.6483	0.4179	18.1278	2.9122	0.3908	18.1370	3.0903	0.3750
0.037	20.6968	1.5973	0.6866	20.7156	1.7886	0.6364	20.7281	1.9240	0.6060
0.072	23.1452	1.1619	0.9995	23.1684	1.3055	0.9277	23.1847	1.4084	0.8838
0.102	25.2612	1.0169	1.2255	25.2917	1.1458	1.1359	25.3121	1.2381	1.0813
0.111	25.8817	0.9597	1.3033	25.9129	1.0890	1.2024	25.9311	1.1818	1.1410
0.131	27.2913	0.9435	1.4316	27.3243	1.0657	1.3240	27.3462	1.1529	1.2588
0.206	32.6038	0.9554	1.7458	32.6399	1.0769	1.6182	32.6629	1.1618	1.5428
0.297	39.1389	1.1100	1.9604	39.2140	1.2407	1.8337	39.2655	1.3303	1.7593
0.407	47.1298	1.4641	2.0167	47.2111	1.6191	1.9024	47.2686	1.7250	1.8340
0.501	54.0489	1.8957	1.9925	54.1646	2.0798	1.8901	54.2476	2.2035	1.8311
0.603	61.7057	2.5294	1.9213	61.8513	2.7458	1.8380	61.9467	2.8955	1.7872
0.705	69.5088	3.4611	1.7762	69.6596	3.7201	1.7126	69.7677	3.9095	1.6685
0.806	77.4538	4.7729	1.6271	77.6637	5.0824	1.5819	77.8097	5.3139	1.5471
0.904	85.6455	6.7870	1.4455	85.8987	7.1757	1.4110	86.0713	7.4477	1.3871
1.000	94.4778	10.0134	1.2439	94.7725	10.4409	1.2255	94.9973	10.7486	1.2108

Table 4. Values of internal pressure, π_i , Rao's constant, R_m , and Wada's constant, W , for the mixture isobutyric acid - water at 300.15 K, 302.15 K, 305.15 K, 308.15 K, 311.15 K and 313.15 K

x_i	π_i (N·m ⁻²)	R_m (10 ⁻⁴ m ³ ·mol ⁻¹ (m·s ⁻¹) ^{1/3})	W (10 ⁻⁴ m ³ ·mol ⁻¹ (kg ⁻¹ ·m·s ²) ^{-1/7})	π_i (N·m ⁻²)	R_m (10 ⁻⁴ m ³ ·mol ⁻¹ (m·s ⁻¹) ^{1/3})	W (10 ⁻⁴ m ³ ·mol ⁻¹ (kg ⁻¹ ·m·s ²) ^{-1/7})	π_i (N·m ⁻²)	R_m (10 ⁻⁴ m ³ ·mol ⁻¹ (m·s ⁻¹) ^{1/3})	W (10 ⁻⁴ m ³ ·mol ⁻¹ (kg ⁻¹ ·m·s ²) ^{-1/7})
T=300.15 K									
0.000	84057.2071	2.0698	3.9176	82697.0644	2.0727	3.9222	80703.8528	2.0774	3.9299
0.037	92927.8889	2.3486	4.4504	90912.7413	2.3514	4.4549	87952.7752	2.3551	4.4609
0.072	96713.8868	2.5901	4.9183	94407.1972	2.5907	4.9193	90930.2613	2.5920	4.9215
0.102	95771.2293	2.8002	5.3243	93382.3888	2.8012	5.3260	89798.5582	2.8027	5.3283
0.111	96576.8634	2.8678	5.4536	93797.7280	2.8756	5.4662	90076.5896	2.8737	5.4632
0.131	93420.8433	2.9960	5.7048	91057.0114	2.9972	5.7067	87520.5157	2.9990	5.7097
0.206	82205.7596	3.5486	6.7642	80245.7110	3.5495	6.7657	77334.4914	3.5503	6.7670
0.297	68420.3162	4.2214	8.0536	66996.1048	4.2198	8.0509	64928.5250	4.2181	8.0481
0.407	54491.6065	5.0322	9.6079	53518.6857	5.0319	9.6074	52132.2817	5.0309	9.6058
0.501	45166.0372	5.7327	10.9485	44472.4760	5.7307	10.9454	43489.0762	5.7283	10.9414
0.603	37264.1017	6.4923	12.4024	36774.6671	6.4900	12.3987	36033.5864	6.4909	12.4002
0.705	30908.4403	7.2760	13.8960	30524.6108	7.2748	13.8940	29977.4002	7.2767	13.8970
0.806	25670.6691	8.0673	15.3998	25397.2084	8.0632	15.3929	25035.0357	8.0618	15.3907
0.904	21220.6718	8.8639	16.9060	21020.6334	8.8628	16.9041	20777.3411	8.8638	16.9058
1.000	17315.1758	9.7468	18.5487	17165.1186	9.7493	18.5527	17008.9750	9.7476	18.5500
T=308.15 K									
0.000	78820.3738	2.0823	3.9378	77065.7182	2.0872	3.9458	76016.2033	2.0898	3.9499
0.037	85354.6340	2.3588	4.4670	82946.2107	2.3621	4.4723	81440.9783	2.3641	4.4756
0.072	88091.6545	2.5929	4.9228	85503.1230	2.5937	4.9241	83864.5221	2.5943	4.9251
0.102	86875.3705	2.8041	5.3306	84231.8278	2.8052	5.3325	82567.1742	2.8060	5.3337
0.111	87147.0046	2.8742	5.4640	84296.6435	2.8753	5.4658	82518.7331	2.8760	5.4669
0.131	84597.4744	3.0011	5.7131	81958.3546	3.0029	5.7161	80306.3878	3.0041	5.7181
0.206	74826.7595	3.5510	6.7682	72545.3772	3.5515	6.7690	71153.9914	3.5514	6.7689
0.297	63015.7715	4.2157	8.0443	61232.4309	4.2161	8.0448	60158.0727	4.2163	8.0452
0.407	50766.4498	5.0307	9.6054	49511.9896	5.0276	9.6003	48749.1931	5.0263	9.5982
0.501	42512.3325	5.7249	10.9357	41560.7631	5.7240	10.9343	40988.1149	5.7226	10.9320
0.603	35351.2506	6.4851	12.3908	34677.1924	6.4830	12.3872	34252.9305	6.4804	12.3830
0.705	29412.3740	7.2774	13.8983	28950.8884	7.2701	13.8863	28628.9503	7.2682	13.8831
0.806	24585.0156	8.0598	15.3875	24266.0096	8.0521	15.3748	24031.9293	8.0522	15.3750
0.904	20445.4697	8.8652	16.9081	20224.9588	8.8618	16.9024	20077.2410	8.8626	16.9039
1.000	16822.0416	9.7441	18.5442	16716.0521	9.7423	18.5413	16635.0930	9.7494	18.5529
T=311.15 K									
T=313.15 K									

ance, Z, free length, L_f , free volume, V_f , molar volume, V_m , relaxation time, τ , internal pressure, π_i , absorption coefficient, α/f^2 , relative association, R_A , Rao's constant, R_m , Wada's constant, W , Gibbs's free energy, ΔG , and cohesive energy, EC , are presented in Tables 2-6.

Table 1 clearly shows that, except the viscosity, η , all the measured parameters, sound velocity, U , and density, ρ , decrease with the increasing concentration. This result is expected since the molecular interactions between water and isobutyric acid, are strong [4]. The following factors may be regarded as primarily responsible for volume contraction: Specific interactions which are assumed to be strong (hydrogen bonding), accommodation of one component into the structural network of the other component and non-specific interactions such as the dipole-dipole interactions between the component molecules. These forces are weak and physical. As depicted in Fig. 1, the curves showing the ultrasonic velocity evolution, U , versus the Isobutyric acid (IBA) mole fraction x_i have

similar character at temperatures from 300.15 K to 313.15 K. These experimental results exhibit a monotonic drop of the ultrasonic velocity with increasing (IBA) composition. This behavior can be similarly explained in terms of molecular interactions that cause the existence gaps of matter in the binary mixture (IBA-W) that take the effect of the propagation of the ultrasound wave for higher Isobutyric acid composition. According to the results of many investigators, Hyne [42] suggest that the addition of another component in binary mixture (component-water) "buttresses" the structure of water.

On the other hand, the evolution of the viscosity, h , highlights a maximum value in isobutyric acid mole fraction range of (0.10-0.45). This predicted behavior is similar to that reported in the literature [43,44]. In fact, close to the critical point of the studied (IBA-W) system which is characterized by the critical temperature $T_c=300.095$ K and critical acid mole fraction $x_{lc}=0.1114$ [4,45], the

Table 5. Values of absorption coefficient, α/f^2 , Gibbs free energy, ΔG , and cohesive energy, CE , for the mixture isobutyric acid - water at 300.15 K, 302.15 K, 305.15 K, 308.15 K, 311.15 K and 313.15 K

X_1	α/f^2 (10^{-14} Np·m $^{-1} \cdot s^2$)	ΔG (10^{-24} KJ·mol $^{-1}$)	EC (KJ·mol $^{-1}$)	α/f^2 (10^{-14} Np·m $^{-1} \cdot s^2$)	ΔG (10^{-24} KJ·mol $^{-1}$)	EC (KJ·mol $^{-1}$)	α/f^2 (10^{-14} Np·m $^{-1} \cdot s^2$)	ΔG (10^{-24} KJ·mol $^{-1}$)	EC (KJ·mol $^{-1}$)
T=300.15 K									
0.000	0.6636	4.7629	1.5195	0.6313	4.6250	1.4957	0.5848	4.4105	1.4606
0.037	1.1487	6.9574	1.9183	1.0835	6.7938	1.8780	0.9924	6.5412	1.8185
0.072	1.7514	8.5359	2.2320	1.6541	8.3763	2.1803	1.5150	8.1222	2.1025
0.102	2.2187	9.4055	2.4108	2.0926	9.2450	2.3528	1.9120	8.9883	2.2655
0.111	2.4013	9.7233	2.4918	2.2141	9.5009	2.4221	2.0300	9.2477	2.3288
0.131	2.6848	10.0723	2.5412	2.5277	9.9106	2.4788	2.3042	9.6530	2.3854
0.206	3.3007	10.8277	2.6700	3.1301	10.6943	2.6095	2.8750	10.4717	2.5179
0.297	3.6938	11.1829	2.6674	3.5296	11.0792	2.6142	3.3021	10.9247	2.5376
0.407	3.7947	11.1868	2.5545	3.6530	11.1131	2.5122	3.4573	11.0064	2.4518
0.501	3.7408	11.0425	2.4286	3.6196	10.9882	2.3939	3.4631	10.9205	2.3460
0.603	3.5936	10.7953	2.2840	3.5112	10.7721	2.2579	3.3704	10.7191	2.2178
0.705	3.3557	10.4524	2.1332	3.2774	10.4286	2.1102	3.1613	10.3927	2.0777
0.806	3.0662	10.0185	1.9739	3.0172	10.0160	1.9565	2.9426	10.0155	1.9338
0.904	2.7289	9.4692	1.8025	2.6908	9.4736	1.7892	2.6418	9.4948	1.7739
1.000	2.3196	8.7618	1.6216	2.2882	8.7664	1.6112	2.2627	8.8065	1.6015
T=308.15 K									
0.000	0.5430	4.1995	1.4277	0.5053	3.9934	1.3970	0.4839	3.8685	1.3787
0.037	0.9155	6.3115	1.7666	0.8473	6.0883	1.7183	0.8063	5.9439	1.6881
0.072	1.4034	7.9094	2.0389	1.3052	7.7075	1.9810	1.2451	7.5751	1.9444
0.102	1.7687	8.7766	2.1946	1.6433	8.5774	2.1304	1.5668	8.4473	2.0899
0.111	1.8785	9.0385	2.2555	1.7373	8.8218	2.1844	1.6509	8.6797	2.1398
0.131	2.1252	9.4379	2.3088	1.9689	9.2356	2.2395	1.8743	9.1045	2.1961
0.206	2.6674	10.2819	2.4396	2.4797	10.0978	2.3679	2.3692	9.9841	2.3241
0.297	3.0965	10.7752	2.4664	2.9124	10.6347	2.4012	2.8048	10.5518	2.3621
0.407	3.2732	10.8958	2.3926	3.1095	10.7928	2.3375	3.0110	10.7316	2.3043
0.501	3.3098	10.8444	2.2977	3.1612	10.7648	2.2511	3.0790	10.7248	2.2235
0.603	3.2670	10.6896	2.1814	3.1507	10.6449	2.1448	3.0815	10.6198	2.1219
0.705	3.0549	10.3554	2.0444	2.9737	10.3413	2.0167	2.9130	10.3226	1.9974
0.806	2.8503	9.9823	1.9042	2.8018	10.0001	1.8846	2.7555	9.9959	1.8699
0.904	2.5728	9.4790	1.7511	2.5367	9.5092	1.7373	2.5081	9.5242	1.7281
1.000	2.2381	8.8398	1.5893	2.2270	8.9036	1.5842	2.2111	8.9364	1.5803
T=311.15 K									
T=313.15 K									

viscosity is expected to exhibit the following:

$$\eta \approx \eta_0 (Q \xi)^z \approx \eta_0 (Q \xi_0)^z t^{-y} \quad (14)$$

where $t = (T - T_c)/T_c$ is the reduced temperature, η_0 is the non-critical background viscosity, $\xi = \xi_0 t^{-n}$ is the correlation length, ξ_0 is the correlation length amplitude, $z=0.052$ is a universal (dynamic) critical exponent [46], which has the same value for all systems belonging to the same dynamic universality class, $y=0.0398$ and $n=0.63$ are universal critical exponents [44,47] and Q is a system dependent inverse length.

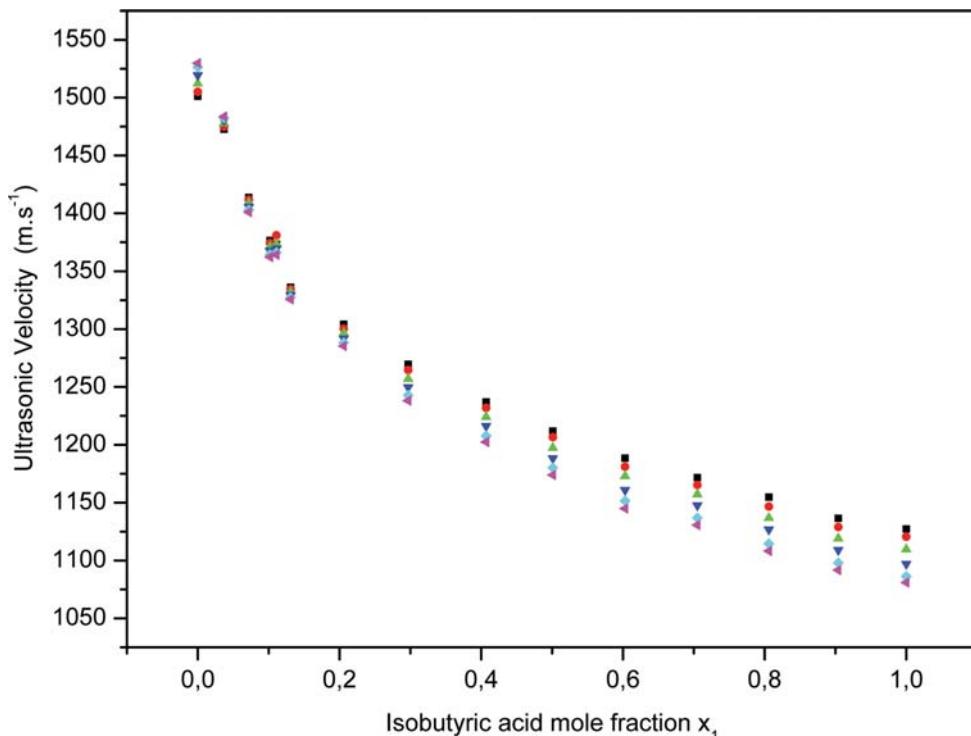
The correlation length ξ describing the molecular correlation diverges at $T=T_c$ where all IBA molecules are correlated with water molecules. As a matter of fact, in the vicinity of the critical point (IBA-W) mixture, the correlations fluctuations of concentrations become more and more important. The molecules of the constituents organize in entities of spherical shapes whose radius is characterized by the correlation length. This phenomenon leads to the

presence of the material which causes an increase of the ultrasonic velocity in the mixture (IBA-W). Far from the critical region, the ultrasonic velocity in the mixture decreases in a linear manner. The result obtained can be interpreted in terms of the correlation; molecule-molecule interaction weakens when the temperature T moves away from T_c .

The acoustic impedance, Z , is a significant parameter of the ultrasonic velocity. This factor translates the ability of ultrasound penetration in the medium studied; it is also useful in the design of ultrasonic transducers which serves to assess the absorption of ultrasound in a medium. From Fig. 2, the acoustic impedance, Z , variation versus the isobutyric acid mole fraction x_1 has a similar character for all studied temperatures from 300.15 K to 313.15 K. The acoustic impedance, Z , values decrease sharply with increasing the acid concentration; this non-linearly supports the strong molecular interaction as suggested by Oswal et al. [48]. Once an acoustic wave travels in a medium, there is a variation of pressure

Table 6. Relative association, R_A , values for the isobutyric acid - water mixture at 300.15 K, 302.15 K, 305.15 K, 308.15 K, 311.15 K, and 313.15 K

X_1	300.15 K	302.15 K	305.15 K	308.15 K	311.15 K	313.15 K
0.000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.037	0.9954	0.9948	0.9937	0.9926	0.9914	0.9909
0.072	0.9829	0.9814	0.9787	0.9763	0.9740	0.9726
0.102	0.9746	0.9729	0.9700	0.9672	0.9646	0.9631
0.111	0.9739	0.9746	0.9708	0.9681	0.9655	0.9641
0.131	0.9652	0.9637	0.9611	0.9586	0.9561	0.9548
0.206	0.9568	0.9544	0.9515	0.9483	0.9457	0.9441
0.297	0.9454	0.9429	0.9387	0.9349	0.9307	0.9281
0.407	0.9342	0.9314	0.9268	0.9222	0.9177	0.9151
0.501	0.9235	0.9207	0.9157	0.9109	0.9062	0.9030
0.603	0.9132	0.9094	0.9043	0.8982	0.8930	0.8897
0.705	0.9029	0.8994	0.8943	0.8886	0.8832	0.8800
0.806	0.8912	0.8871	0.8814	0.8758	0.8696	0.8661
0.904	0.8764	0.8723	0.8664	0.8605	0.8544	0.8509
1.000	0.8583	0.8543	0.8482	0.8415	0.8355	0.8319

**Fig. 1.** The measured ultrasonic velocity of binary mixture isobutyric acid-water as a function of mole fraction of acid in the single phase region at different temperatures: (■) T=300.15 K, (●) T=302.15 K, (▲) T=305.15 K, (▼) T=308.15 K, (◆) T=311.15 K, (◀) T=313.15 K.

and instantaneous velocity from particle to particle. This is governed by the inertial and elastic properties of the medium. Referring to Fig. 3, the values of adiabatic compressibility (β) increase with the increase in the acid content within the whole range of mixture composition. This suggests making and breaking of hydrogen bonding [49]. In fact, the smaller the attractive force among the molecules, the greater will be the compressibility [50]. In the water-rich region, the water molecules become more tightly packed, and

the result is a reduction of the adiabatic compressibility, β , to a minimum value. In the acid-rich region, the adiabatic compressibility, β , reached maximum values in binary mixture (IBA-W) at higher composition, indicating the possibility of low molecular interaction due to steric hindrance and no specific interaction (dipole-dipole).

In a binary mixture, the free length, L_f , is a measure of intermolecular attraction between the components of solution. On analyzing Table 2, it is noticed that this parameter reflects a similar trend

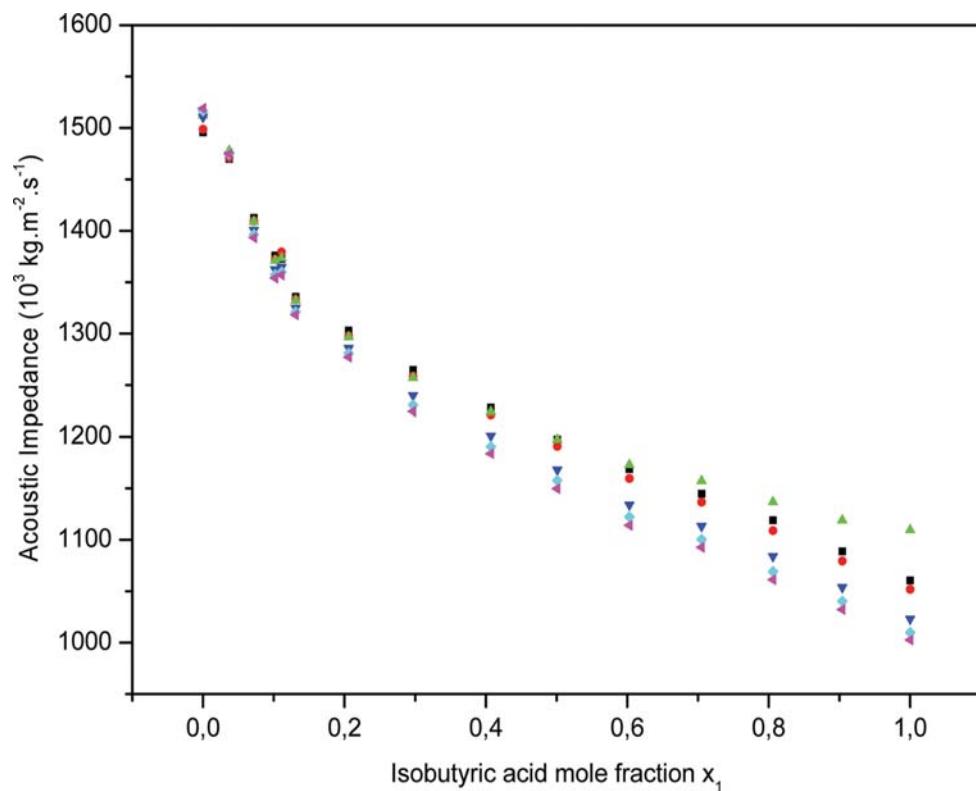


Fig. 2. Acoustic impedance, Z , variation versus isobutyric acid mole fraction x_1 for binary mixture isobutyric acid-water at different temperatures: (■) $T=300.15$ K, (●) $T=302.15$ K, (▲) $T=305.15$ K, (▼) $T=308.15$ K, (◆) $T=311.15$ K, (◀) $T=313.15$ K.

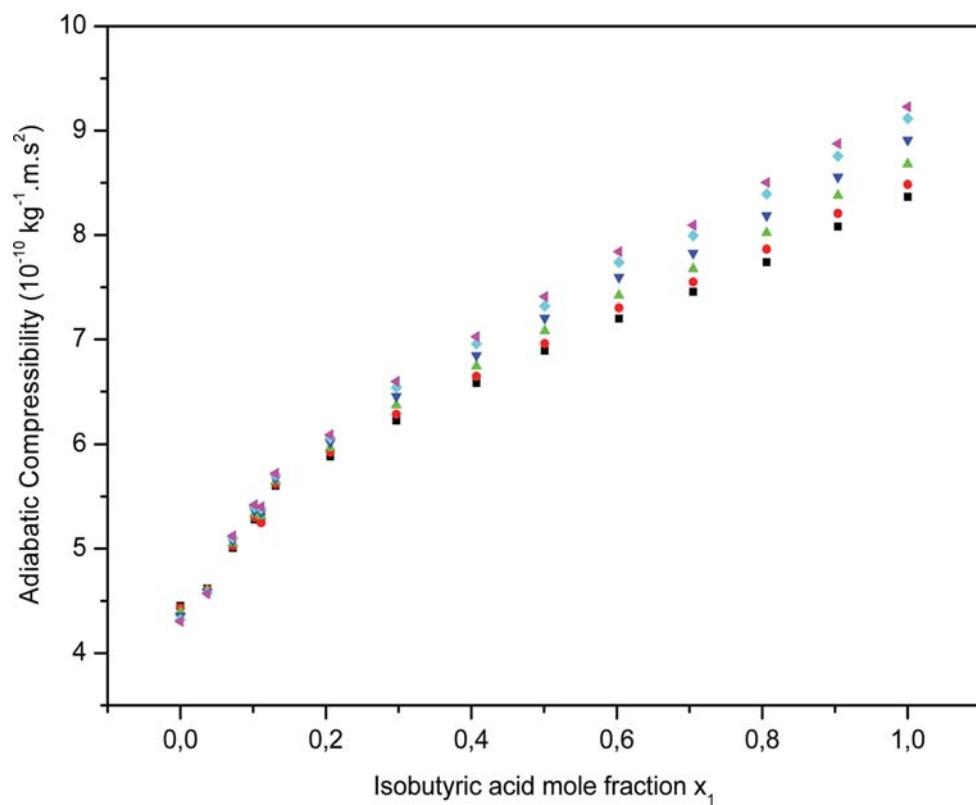


Fig. 3. Adiabatic compressibility, β , plotted against isobutyric acid mole fraction x_1 for binary mixture isobutyric acid-water at different temperatures: (■) $T=300.15$ K, (●) $T=302.15$ K, (▲) $T=305.15$ K, (▼) $T=308.15$ K, (◆) $T=311.15$ K, (◀) $T=313.15$ K.

as that of adiabatic compressibility [51]. The free length between the molecules of the system takes low values in the water-rich region. This experimental finding shows that the intermolecular distance between the molecules of the mixture (water-rich region) decreases due to the presence of a significant number of hydrogen bonds, leading to strong correlation between molecules. In the acid-rich region, intermolecular distance becomes larger than that in the water-rich region; this result can be interpreted by the presence of non-specific interaction (dipole-dipole) between component molecules.

The order of the relaxation time, τ , is of 10^{-12} s, which is due to the structural relaxation process, and such sort of situation is due to rearrangement of molecules because of the cooperative process. In the water-rich region, the relaxation time increases until reaching its maximum where $0.2 \text{ M} < x_1 < 0.5 \text{ M}$, due to the strong interaction between the solvent molecules. The increase of the relaxation time in this region indicates that during the passage of the ultrasonic wave, the molecules of the system (IBA-W) require a very short interval of time for relax. In the acid-rich region, the relaxation time changes its position in which values are greater than that obtained in the water-rich region. This result shows that during the passage of the ultrasonic wave, the molecules of the system take a significant time to return to an equilibrium position due to weak interaction between the solute and solvent molecules.

In the water-rich region, the free volume, V_f , goes through a minimum $x_1=0.1 \text{ M}$ in the neighborhood of acid critical composition; the decrease in the free volume indicates that the molecules are coming closer and the fact is confirmed from the free length values, which confirms the increasing magnitude of the interaction. The free volume changes its variation in the acid-rich region: it increases

with the increase in acid composition, which is expected since the molecular interaction between water and isobutyric acid is low.

Gibbs free energy, ΔG , increases with the increase in mole fraction of acid, and we notice that the Gibbs free energy is a maximum $x_1=0.3 \text{ M}$. This observation confirms that the molecules get rearranged due to a cooperative process [52], which increases the energy that leads to dissociation.

In the water-rich region, the cohesive energy (CE) of the binary mixture (IBA-W) increases with increase of mole fraction x_1 and is a maximum at $x_1=0.3 \text{ M}$; the six curves having a similar behavior in the selected temperature range from 300.15 to 313.15 K. This result allows us to say that the energy of all bonds present in the mixture (IBA-W) is very large due to the strong attractions between water molecules. The cohesive energy abruptly changes its direction in the rich region isobutyric acid, indicating that the intermolecular forces between the acid and water molecules are weak.

The values of the relative association, R_A , for the binary mixture (IBA-W) decrease with an increase of acid composition. This result may be due to the disruption of water molecules linked by hydrogen bridges on addition of isobutyric acid.

The curves of Fig. 4 representing the variation of the Internal pressure, π_i , as a function of the acid molar fraction at different selected temperatures from 300.15 K to 313.15 K show the influence of the temperature is remarkable in the water-rich region. The internal pressure increases with increase of acid composition and reaches its maximum at $x_1=0.1 \text{ M}$, close to the critical point, then decreases abruptly for strong acid compositions. As explained above, the correlation length ζ diverges at $T=T_C$ and all of the molecules of (IBA) are correlated with water molecules. This phenome-

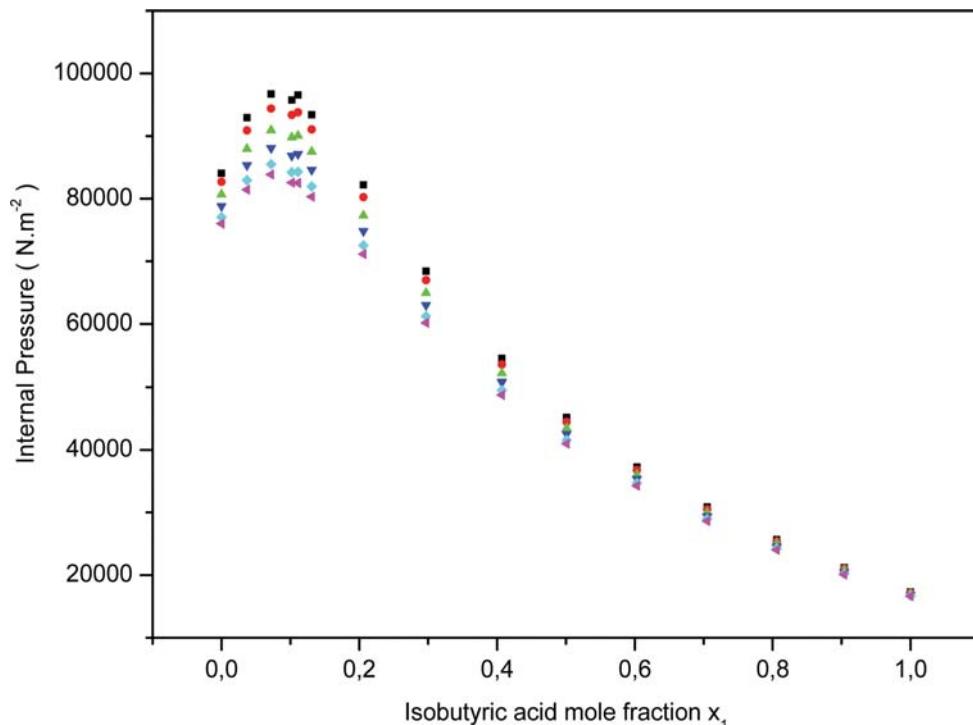


Fig. 4. Change in the internal pressure, π_i , as a function of mole fraction of acid of binary mixture isobutyric acid with water for different temperatures: (■) $T=300.15 \text{ K}$, (●) $T=302.15 \text{ K}$, (▲) $T=305.15 \text{ K}$, (▼) $T=308.15 \text{ K}$, (◆) $T=311.15 \text{ K}$, (◀) $T=313.15 \text{ K}$.

non has been known for a long time in critical mixtures. This behavior shows that the cohesive forces existing between the molecules depend on the mixture composition and temperature.

As portrayed in Figs. 5 and 6, the curves showing the Rao's constant, R_m , and Wada's constant, w , versus isobutyric acid mole fraction have the same character from 300.15 to 313.15 K. These acous-

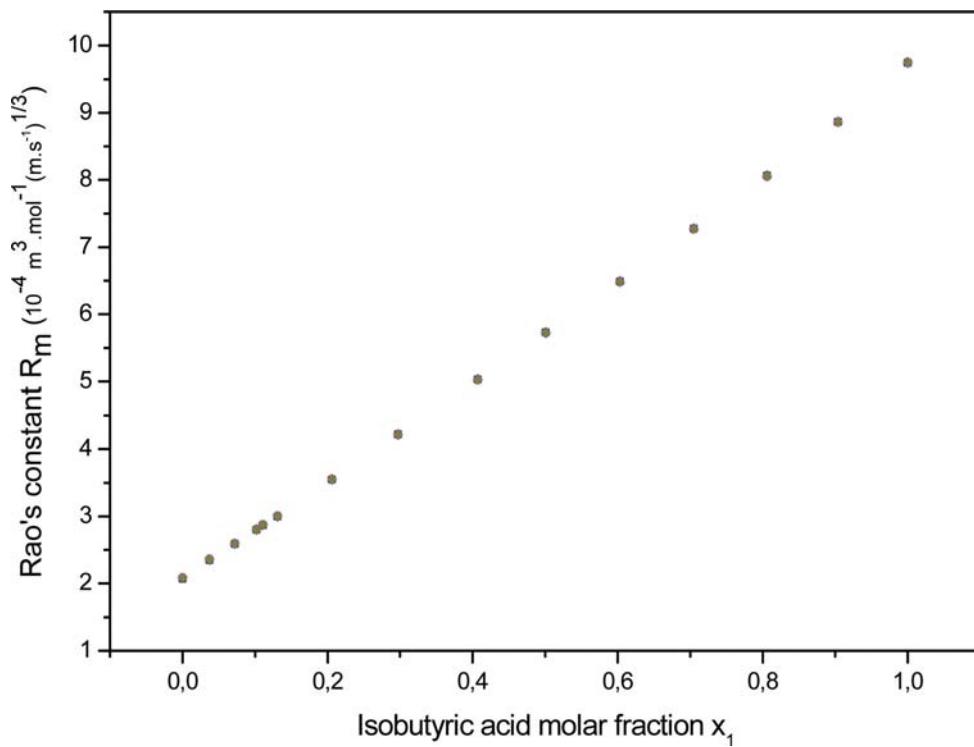


Fig. 5. Rao's constant R_m in the aqueous solution of isobutyric acid against the mole fraction of acid for six temperatures: (■) $T=300.15\text{ K}$, (●) $T=302.15\text{ K}$, (▲) $T=305.15\text{ K}$, (▼) $T=308.15\text{ K}$, (◆) $T=311.15\text{ K}$, (◀) $T=313.15\text{ K}$.

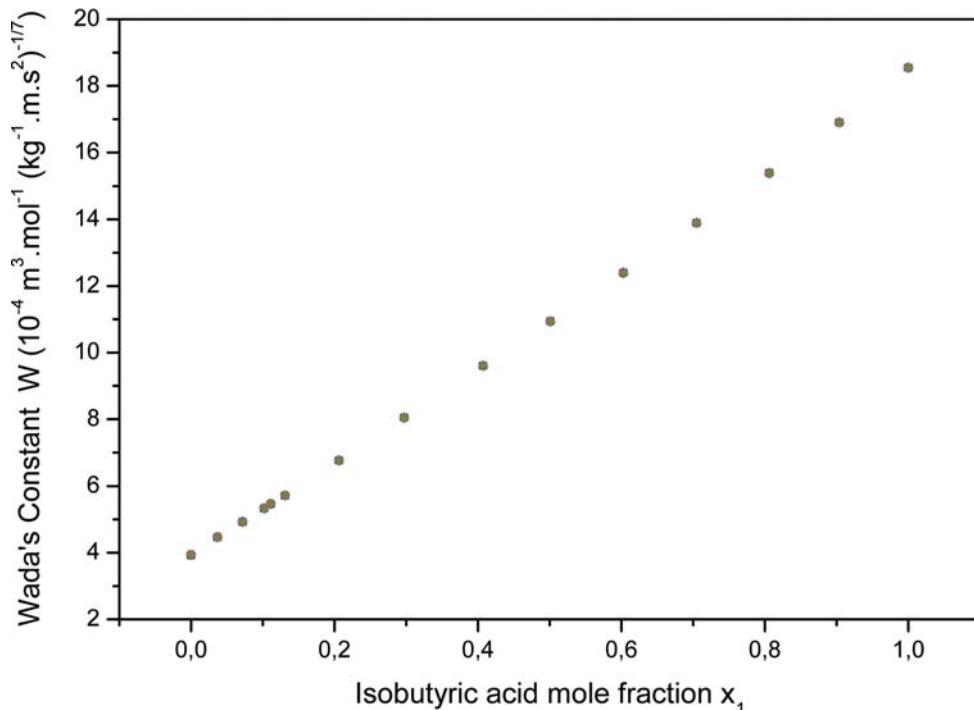


Fig. 6. Wada's constant, W , in the aqueous solution of isobutyric acid against the mole fraction of acid for six temperatures: (■) $T=300.15\text{ K}$, (●) $T=302.15\text{ K}$, (▲) $T=305.15\text{ K}$, (▼) $T=308.15\text{ K}$, (◆) $T=311.15\text{ K}$, (◀) $T=313.15\text{ K}$.

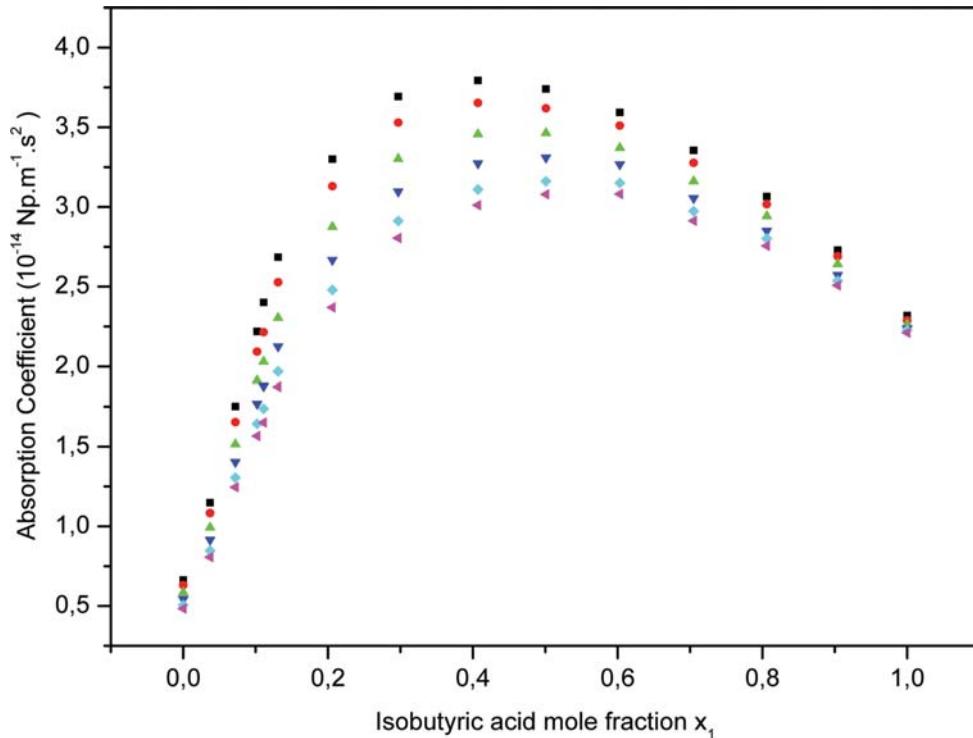


Fig. 7. Absorption coefficient, α/f^2 , of the aqueous solution of isobutyric acid against the mole fraction of acid for six temperature: (■) $T=300.15\text{ K}$, (●) $T=302.15\text{ K}$, (▲) $T=305.15\text{ K}$, (▼) $T=308.15\text{ K}$, (◆) $T=311.15\text{ K}$, (◀) $T=313.15\text{ K}$.

tical parameters exhibit linear behavior over the entire range of composition, no change with temperature. This result is expected since aggregate and complex formation between the water and isobutyric acid are absent.

From Fig. 7, the absorption coefficient (α/f^2) evolution versus the isobutyric acid mole fraction x_1 has the same character from 300.15 to 313.15 K, although it decreases with temperature. In the water-rich region, the absorption factor (α/f^2) passes through a broad maximum, and decreases slowly in the acid-rich region. It can be suggested that the intensity of the ultrasound wave decreases as the intermolecular distance between the solute and the solvent molecules increases. This result indicates that there is a structural change due to a strong intermolecular attraction between the molecules of the components.

CONCLUSION

Our aim was to establish the importance of solution study. Accurate measurements of the ultrasonic velocity, density and viscosity in isobutyric acid - water liquid mixture over the entire composition range were performed at temperatures ranging from 300.15 to 313.15 K and at atmospheric pressure. Related acoustical parameters were found to be in good agreement with each other, which confirms the presence of strong intermolecular interaction between the components of molecules.

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