

EFFECT OF TEMPERATURE AND IONS CONCENTRATION ON THE DENSITY AND SPEED OF SOUND OF NATURAL MINERAL WATERS FROM THE REGION OF SOUTH RUSSIA

Misirkhan Talybov¹, Ilmutdin Abdulagatov²

¹Azerbaijan Technical University

²Dagestan State University, RUSSIA

misirkhantalibov@yahoo.com

ilmutdina@gmail.com

Abstract

Density (ρ), and speed of sound (W) of natural mineral waters from the region of south Russia (North Caucasus, Essentuki wells ESN^o1, ESN^o2, ESN^o4, and ESN^o17) have been measured as a function of temperature. The measurements were made over the temperature range from (278 to 343) K at atmospheric pressure. Anton Paar DSA 5000 M sound-speed analyzer has been employed to the simultaneously measurements of the density and speed of sound of the mineral water samples. The combined expanded uncertainty of the density, speed of sound, atmospheric pressure (P_0), and temperature (T) measurements at the 95 % confidence level with a coverage factor of $k = 2$ is estimated to be $\pm 0.005 \text{ kg}\cdot\text{m}^{-3}$ (or 0.01 %), 0.1 %, and 15 mK, respectively. The measured temperature behavior of density, and speed of sound for natural mineral waters were compared with the values for pure water (IAPW formulation) and for various binary aqueous salt (NaCl, Na₂CO₃, Na₂SO₄, etc.) solutions. The measured values of density, and speed of sound were used to develop correlation models for the temperature and ion species concentration dependences (Riedel's characteristic constants of the ions determination). The measured properties as a function temperature at atmospheric pressure have been used as a reference data for prediction of the high-pressure thermodynamic behavior.

Keywords: mineral water, geochemistry, density, chemical composition

I. Introduction

Multicomponent aqueous salt solutions play a major role in both natural and industrial processes. Most of Earth surface is covered by water. Natural mineral water is a multicomponent aqueous solution containing varying amounts of dissolved solids and gases. According to the European Legislation (2009/54/EC Directive), physical and chemical characterization is used to make a classification of the different mineral waters [1]. The exploitation of thermal and mineral water resources requires availability of reliable thermodynamic and transport property data at high temperatures and high pressures. For example, these data are needed for estimate the likelihood of scaling and corrosion developing within the wells and surface equipment, and to predict the commercial lifetime of the exploitation project. The temperature dependence of the density of geothermal and mineral waters has also to be considered when defining the dimensions of the pumping systems because buoyancy effect decreases pumping requirements. Use of pure water or geothermal brine models (synthetic brines like binary or ternary aqueous salt solutions) properties instead of their natural mineral water values, in practical application (engineering calculations), leads to inaccuracy and incorrect estimation of the practical

calculations, for example, pumping requirements. This work is a part of our long-term continuing program of experimental study and modeling of the thermodynamic (*PVT*, heat capacity, vapor-pressure), acoustic (speed of sound) and transport (viscosity and thermal conductivity) properties of natural thermal and mineral waters at high-temperature and high-pressure [2-5]. In our recent publications [2-5] we have experimentally studied density, speed of sound, and viscosity of natural geothermal and mineral waters from various regions over the world (Azerbaijan, Turkey, and Germany) with different chemical compositions. The present results are considerably expanding the available data base on density of natural geothermal and mineral waters from various regions of the South Russia and around the world with various chemical compositions.

II. Methods

The chemical composition was obtained with the ionic chromatograph Dionex 100 + ICS 100. The pH, was determined at 293.15 K using the standard NF T 90-008.

The density and speed of sound of the natural mineral water samples at atmospheric pressure at elevated temperatures have been simultaneously measured with a sound-speed analyzer DSA 5000 M (Anton Paar Instrument, Austria). The method (experimental details, the physical basis and theory of the method, procedure of measurements, uncertainty assessment, etc.) and apparatus have been described in our several previous publications [2,4,5]. Only a brief review and essential information will be given here. The two-in-one instrument is equipped with a density and a sound velocity cell thus combining the proven Anton Paar oscillating U-tube method with a highly accurate measurement of sound velocity. Both cells are temperature-controlled by a built-in Peltier thermostat. The temperature, where located the U-tube, was controlled with a solid-state thermostat, working via Peltier effect with a precision of ± 0.005 K. The temperature of the experimental cell was measured using the (ITS-90) PRT100 thermometer with an uncertainty of 0.03 K. The sample is introduced into the sound velocity-measuring cell that is bordered by an ultrasonic transmitter on the one side, by a receiver on the other side. The transmitter sends sound waves of a known period through the sample. The speed of sound can be calculated by determining of the period of received sound waves and by considering the distance between the transmitter and receiver. The digital density analyzer in these instruments uses a U-shaped vibrating tube (VTD). The working principle of an oscillation-type densimeter is based on the law of harmonic oscillation, in which a U-tube is completely filled with the sample under study and subjected to an electromagnetic force. Density measurements with a VTD are based on the dependence of the period of oscillation of a unilaterally fixed U-tube on its mass. Due to complexity of the geometry of the vibrating tube it requires very carefully calibration with a reference fluid of well-known density. The accuracy of the method is limited by the calibration procedure. The calibration of the VTD is very important step of the measurements and should be performed very carefully and frequently to keep the high accuracy using a few (minimum 2) references fluids (such as water, benzene, nitrogen, air, and toluene) whose *PVT* properties are well known. In the present study the calibration was performed using a few reference fluids such as air, double distilled, deionized and degassed water, benzene, and toluene with well-known *PVT* properties [6]. The reference data Lemmon et al. [6] were used to determine the temperature dependence of the calibration parameters in the working equation of the method [2,4,5]. Further information about the details of the experimental technique for density and speed of sound measurements has been provided in our previous works [2,4,5]. The density and speed of sound measuring ranges for DMA 5000 instrument are from (0 to 3000) $\text{kg}\cdot\text{m}^{-3}$ and from (1000 to 2000) $\text{m}\cdot\text{s}^{-1}$, respectively in the temperature range from (278.15 to 343.15) K. The uncertainties of the density and speed of sound measurements are 0.01 % and 0.10 %, with repeatability of $0.001 \text{ kg}\cdot\text{m}^{-3}$ and $0.10 \text{ m}\cdot\text{s}^{-1}$, respectively.

III. Results and Discussion

I. Chemical Composition

Thermal and mineral water samples was distributed directly from Essentuki springs. Chemical composition and pH of the mineral water samples taken from the EMW (ESN₀₁, ESN₀₂, ESN₀₄, and ESN₀₁₇) are presented in Table 1. The pH of the mineral water samples under study ranges from (6.2 to 7.5).

Table 1. Chemical composition (mg/L) of natural mineral waters from Essentuki wells

Species	Sample: ESN ₀₁	Sample: ESN ₀₂	Sample: ESN ₀₄	Sample: ESN ₀₁₇
	pH=6.9-7.2	pH=7.2	pH=6.2-6.9	pH=7.0-7.5
	mg/L	mg/L	mg/L	mg/L
Cations				
Al ⁺	<0.1	<0.1	<0.1	<0.1
As ⁺	<0.1	<0.1	<0.1	<0.1
B⁺⁺	1.4	1.6	5.7	10.3
Ba⁺	7.0	<0.1	1.9	1.6
Ca²⁺	86	407	124	101
Cd ⁺	<0.1	<0.1	<0.1	<0.1
Co ⁺	<0.1	<0.1	<0.1	<0.1
Cr ⁺	<0.1	<0.1	<0.1	<0.1
Cu ⁺	<0.1	<0.1	<0.1	<0.1
Fe ²⁺	<0.1	<0.1	<0.1	<0.1
Hg ⁺	<0.1	<0.1	<0.1	<0.1
K⁺	6.7	63.3	15.8	11.7
Li ⁺	0.2	1.7	0.7	1.2
Mg²⁺	15	53.8	52.8	66.5
Mn ⁺	<0.1	0.2	<0.1	<0.1
Mo ⁺	<0.1	<0.1	<0.1	<0.1
Na²⁺ (Max)	539	948	2020	6620
Ni ⁺	<0.1	<0.1	<0.1	<0.1
P ⁺	<0.1	<0.1	<0.1	<0.1
Pb ⁺	<0.1	<0.1	<0.1	<0.1
S⁺	7.1	275	0.4	0.3
Sb	<0.1	<0.1	<0.1	<0.1
Se ⁺	<0.1	<0.1	<0.1	<0.1
Si⁺	7.1	22.7	5.6	3.5
Sr⁺	2.6	8.8	4.9	7.1
Ti ⁺	<0.1	<0.1	<0.1	<0.1
Tl ⁺	<0.1	<0.1	<0.1	<0.1
V ⁺	<0.1	<0.1	<0.1	<0.1
Zn ⁺	<0.1	<0.1	<0.1	<0.1
Total:	674	1784	2233.7	6825.1
Anions				
Cl ⁻	400	1009	1660	2268
Nitrate	<0.1	<0.1	<0.1	<0.1
Sulfate	31.5	849	1.3	0.8
Total:	431.6	1849.1	1661.4	2268.9
Total Dissolved Salt (TDS)	1105.6	3633.1	3895.1	9094.0

Due to pressure difference between underground and the near surface conditions (0.101 MPa), degassing (no stable components like dissolved gases such as CO₂, CH₄, H₂S, N₂, H₂ and O₂) occurs during production. Thus, in general, the mineral water samples are chlorine rich with Na and Ca, *i.e.*, the Na⁺, Ca²⁺, and Cl⁻ are dominant ions.

II. Density

Density measurements were performed at atmospheric pressure as a function of temperature from (278.15 to 343.15) K. The measured density data are presented in Table 2 and depicted in Figs. 1 to 3 in the $\rho(T, S)$ (where S is the TDS concentration), and $\rho(T, \chi_{NaCl})$ projections together with the values for pure water calculated from IAPWS fundamental equation of state (IAPWS, Wagner and Pruß) [7]. As can be noted from Fig. 1, the thermodynamic behavior of the mineral and thermal waters (also, for all aqueous salt solutions) governs by the properties of pure water (see Fig. 1), *i.e.*, the temperature dependence of the measured properties (density, and speed of sound) of mineral waters is determined through the pure water properties. Figure 1 also includes the values of density for the same mineral water samples measured using SVM 3000 visco-densimeter. As one can see from Fig. 1, the agreement between the both set of measurements is good enough, the average absolute deviations (AAD) are 0.008 % (ES№1), 0.014 % (ES№2), 0.009 % (ES№4), and 0.015% (ES№17). This confirms the accuracy and the reliability of the measured density data for the mineral water samples under study.

A major source of measuring uncertainties when using a density are the effect of bubbles of dissolved gases in the measuring cell. The bubbles can be formed during the filling procedure. However, the present instrument (DSA 5000 M) allows detect automatically the filling errors or bubbles forming in the sample during the cell heating.

Table 2: Experimental values of density (ρ), and speed of sound (W) as a function of temperature for mineral waters at atmospheric pressure

ES№1			ES№2		
T (K)	ρ (kg·m ⁻³)	W (m·s ⁻¹)	T (K)	ρ (kg·m ⁻³)	W (m·s ⁻¹)
278.15	1001.90	1429.99	278.15	1004.68	1433.35
283.15	1001.60	1450.52	283.14	1004.30	1453.29
293.14	1000.00	1485.00	293.13	1002.70	1487.62
303.13	997.40	1511.57	303.12	1000.10	1514.03
313.12	993.96	1531.13	313.12	996.70	1533.45
323.13	989.80	1544.63	323.12	992.30	1546.77
333.13	985.13	1552.92	333.11	987.80	1554.92
343.13	979.20	1556.94	343.12	983.10	1558.83
ES№4			ES№17		
T (K)	ρ (kg·m ⁻³)	W (m·s ⁻¹)	T (K)	ρ (kg·m ⁻³)	W (m·s ⁻¹)
278.17	1007.70	1438.23	278.17	1011.10	1442.67
283.16	1007.30	1458.28	283.16	1010.70	1462.48
293.15	1005.60	1492.02	293.15	1008.90	1495.86
303.14	1002.90	1518.00	303.13	1006.20	1521.56
313.12	999.20	1537.08	313.13	1002.60	1540.51
323.12	993.20	1550.23	323.12	997.72	1553.50
333.12	987.06	1558.30	333.12	992.20	1561.43
343.15	979.67	1562.20	343.13	984.31	1565.15

Standard uncertainties u are: (DMA4500) $u(T)=7.5$ mK; $u_r(\rho)=0.005$ %; $u_r(W)=0.05$ %; and $u_r(P)=0.05$ %.

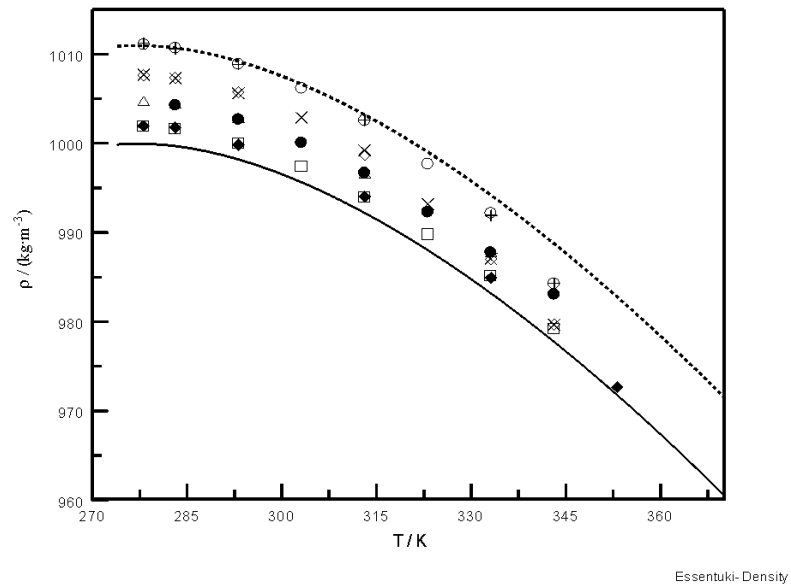


Figure 1: Measured values of density of the mineral water samples using VTD (DSA 5000 M) together with the values measured with visco-densimeter (SVM 3000) and for pure water calculated from IAPWS formulation. Solid line is pure water values calculated from the IAPWS fundamental equation of state (IAPWS, Wagner and Pruf, 2002). Dashed lines are calculated from the correlation model for the samples ESN№17. From DSA 5000 M measurements: \square – ESN№1; \bullet – ESN№2; \blacktriangleright – ESN№4; and \circ – ESN№17. From SVM 3000 visco-densimeter measurements: \blacklozenge – ESN№1; \triangle – ESN№2; \blacktriangleright – ESN№4; and \blacklozenge – ESN№17.

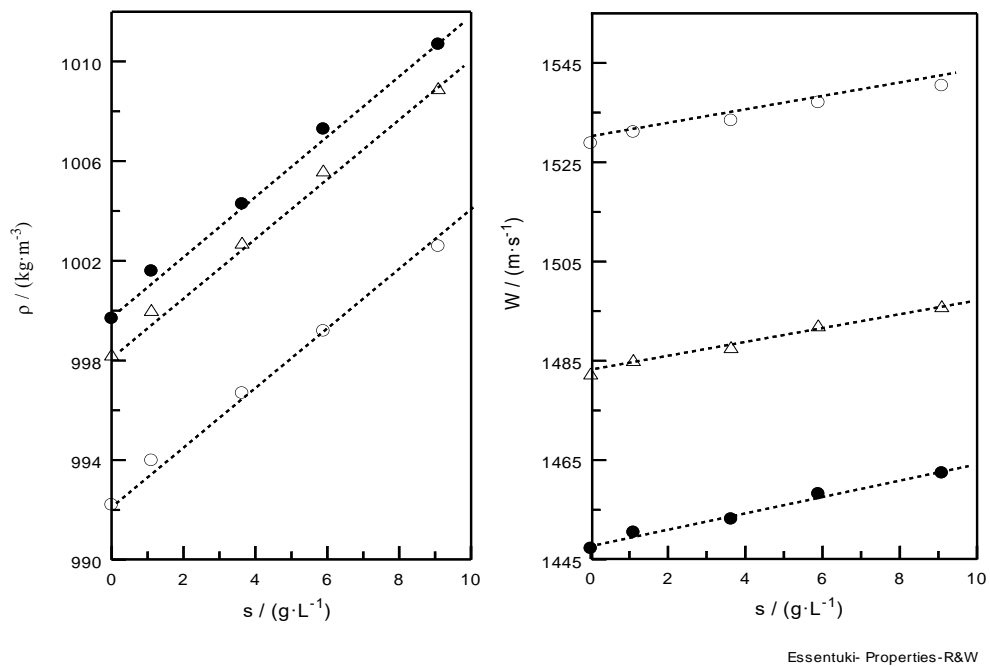


Figure 2: Measured values of density and speed of sound for various mineral waters as a functions of mineralization (TDS, S) along the selected isotherms together with the values for pure water (S=0, IAPWS, Wagner and Pruf, 2002). Dashed lines are linear interpolations. \bullet –283.15 K; \triangle –293.15 K; \circ –313.15 K.

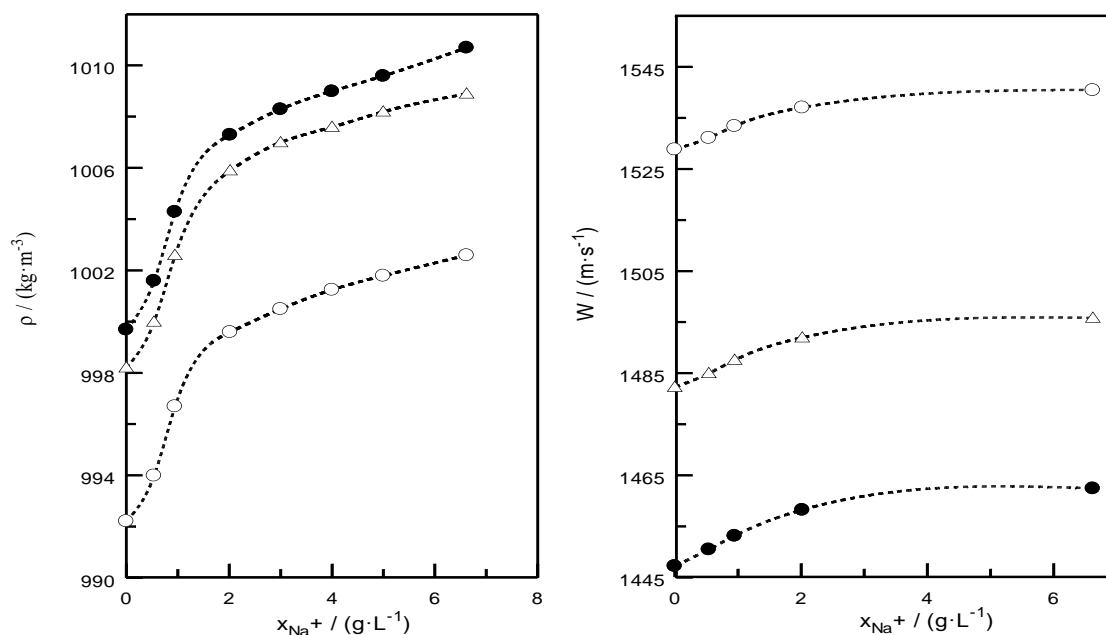


Figure 3: Measured values of density (left) and speed of sound (right) for various mineral waters as a functions of Na^+ ion concentrations (sensitivity to Na^+ concentrations) along the selected isotherms together with the values for pure water ($x_{\text{Na}^+}=0$, IAPWS, Wagner and Pruß, 2002). Dashed lines are interpolated values. ●-283.15 K; △-293.15 K; ○-313.15 K.

Also, the measuring instrument (DSA 5000 M) allows to follow the sample filling process live on screen or recall stored images later. Therefore, the instrument allows verifying the correct sample filling and measurements later, *i.e.*, alert us of potential filling or bubble forming problems. At temperatures above 323 K, we found that heating of the samples (especially high concentrated samples ESN₄ and ESN₁₇) during the measurements causes the release of the dissolved gases. Therefore, the measured data at temperatures above 323 K are affected by dissolved gases. Above the 323 K the intensity of the gas release increases. At low temperatures (below 323 K) the effect of gas release to the measured properties can be neglected. The instrument automatically detects inhomogeneity and gas bubbles forming in the whole density measuring cell by an advanced analysis of its oscillation pattern and generates a warning message in real time for any single measurement, *i.e.*, the bubbles (gas release) in the sample are detected automatically during the experiment (instrument alert us of potential gas release problems). At temperatures below 323 K we did not observed any gas release problem in our experiment (no warning messages from the instrument were observed). To study of the effect of dissolved gases in the mineral water samples at high temperatures, the measurements at high pressures are required because the solubility of gases in liquids increases with pressure increasing.

Figure 2 shows the salinity (TDS) dependence of the density (left) along the fixed temperatures. As one can see, ρ - S dependence is almost linear function. In the limit, $S \rightarrow 0$, the measured density data becomes equal to the pure water values (IAPWS, Wagner and Pruß, 2002) at each fixed temperature. The present extrapolated to zero salinity ($S \rightarrow 0$) density data and the values for pure water calculated from IAPWS formulation (Wagner and Pruß, 2002) are in good (discrepancy is AAD=0.003 %) agreement (see Fig. 4). This excellent agreement between the present extrapolated data and IAPWS (Wagner and Pruß, 2002) calculations for pure water confirms the reliability and high accuracy of the present measurements for the mineral water sample and correct operation of the measuring instrument and the procedure of measurements. The measured values of density for various mineral waters as a function of Na^+ ion concentrations (sensitivity of the measured densities to Na^+ concentrations) along the selected isotherms together with the values for pure water ($S=0$, IAPWS Wagner and Pruß,

2002) are depicted in Fig. 3 (left). As this figure shows, in the low concentration range $x_{Na^+} < 2$ g/L, rapid increase of the density along the isotherms is observing. At high concentration of Na^+ , above >2 g/L gradually increases of the measured density with almost constant slopes is observing.

III. Speed of Sound

Measurements of the speed of sound for the same natural mineral water samples were performed at atmospheric pressure as a function of temperature in the same temperature range as in density experiment, namely, from (278.15 to 343.15) K. The measured speed of sound data is presented in Table 2 and depicted in Figs. 2,3 (right), 4, and 5 in the W - T , W - ρ , and W - x_{Na^+} projections. As one can see from Figs. 4 and 5, the temperature and density behavior of the speed of sound, as a density and other properties, similar pure water behavior (Wagner and Pruß, 2002). However, speed of sound, in contrast to density, is less sensitivity to the effect of gas releases. The measured speed of sound (Fig. 2 right) of the mineral water is almost linear function of the TDS concentration like density. The sensitivity of the speed of sound data to concentration of the sodium ions (main component of the mineral waters) shown in Fig. 3 (right). As one can see, a speed of sound is smoothly increasing with x_{Na^+} . The present measured speed of sound data for mineral water samples deviates from those for pure water (IAPWS standard data, Wagner and Pruß, 2002) within (0.13 to 0.27) % for ES№1, from (0.28 to 0.42) % for ES№2, from (0.53 to 0.83) % for ES №4, and from (0.75 to 1.13) % for ES№17. At high temperatures the deviations are lower than at low temperatures.

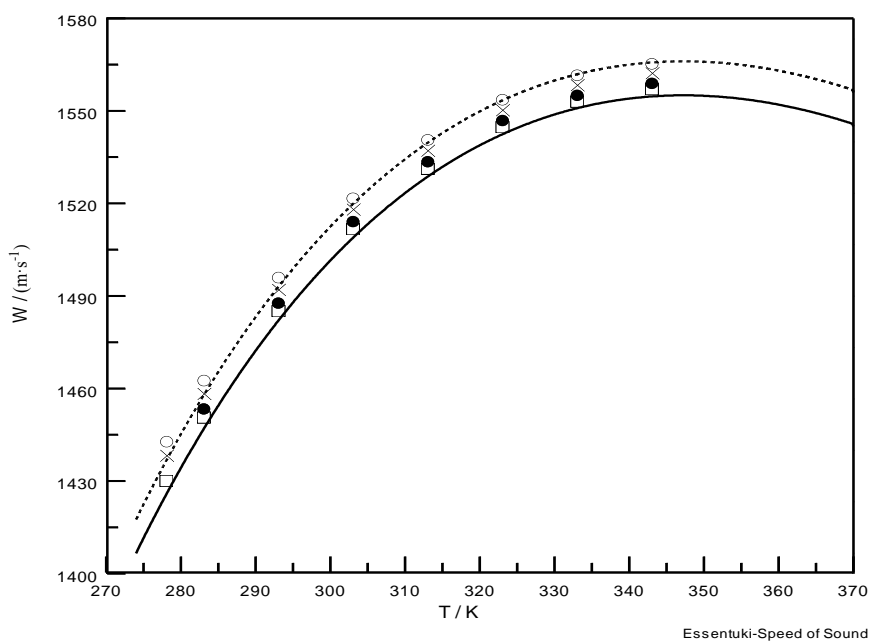


Figure 4: Measured speed of sound for various mineral waters as a function of temperature together with the values for pure water calculated from IAPWS formulation. Solid line is pure water values calculated from the IAPWS fundamental equation of state (Wagner and Pruß, 2002). Dashed lines are values calculated from the predictive correlation model for the sample ES№17. The symbols are the same as in Fig. 1.

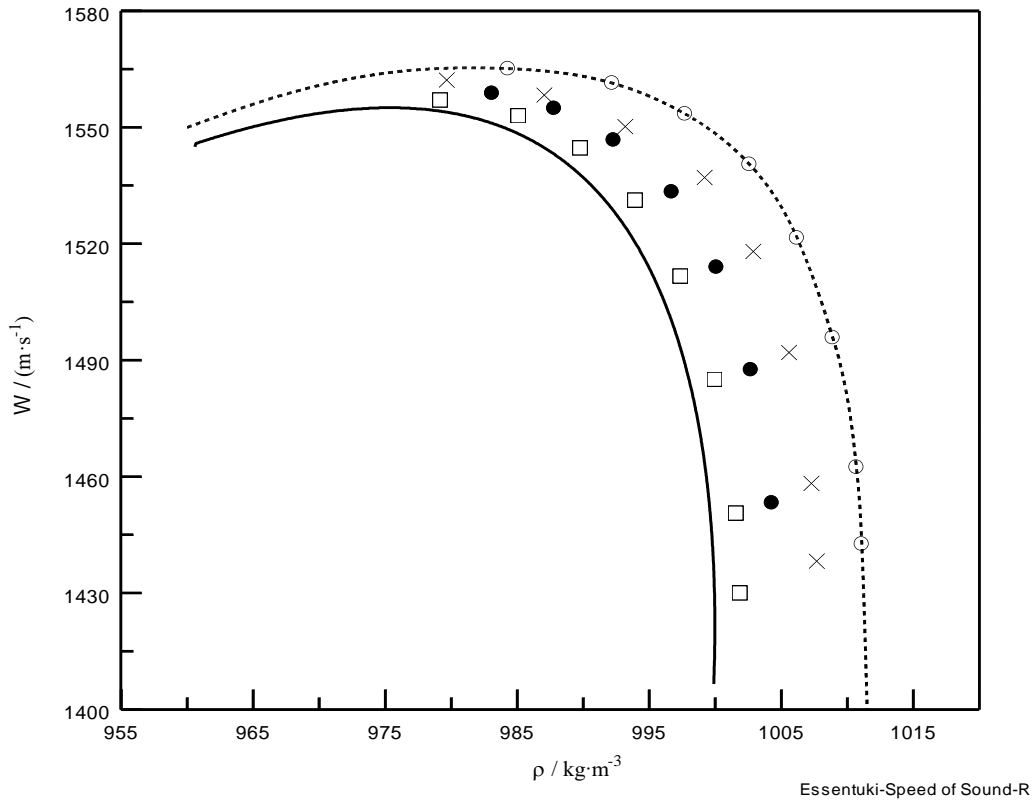


Figure 5: Measured speed of sound for various mineral waters as a function of density together with the values for pure water calculated from IAPWS formulation. Solid line is pure water values calculated from the IAPWS correlation (Wagner and Pruf, 2002). Dashed line is calculated from the prediction model. The symbols are the same as in Fig. 1.

IV. Correlation Models for Density, and Speed of Sound

Since there is no theory available for the thermodynamic (equation of state) and transport properties (temperature and concentration dependence correlation models) of multicomponent aqueous solutions, its evaluation is empirical and based solely on experimentally obtained data. Therefore, the present measured density data as a function of temperature were represented by polynomial type temperature function

$$\rho(T) = a_0 + a_1T + a_2T^2. \quad (1)$$

The derived optimal values of fitting parameters are given in Table 3. As one can see from Table 1, the AAD between measured and calculated from Eq. (1) values of density for samples ESN01, ESN02, ES N04, and ES N017 are 0.009, 0.020, 0.015, and 0.017 %, respectively.

Measured speed of sound data was fitted to the same quadratic function of temperature

$$W(T) = b_0 + b_1T + b_2T^2. \quad (2)$$

The values of derived adjustable coefficients of Eq. (2) are presented in Table 5 together with deviation statistics. As can be seen, AAD between the measured and calculated values of speed of

sound data for ESN01, ESN02, ES N04, and ES N017 is 0.062, 0.052, 0.061, and 0.058 %, respectively.

Table 3: Values of fitting parameters (a_i) of the correlation Eqs. (1), for the density of mineral water samples together with the deviation statistics

Sample	a_0	a_1	a_2	AAD, (%)	Bias, (%)	St.Dev, (%)	St.Err, (%)	Max.Dev, (%)
ES№1	705.823	2.2129	-0.004127	0.01	-0.00	0.01	0.00	0.02
ES№2	795.181	1.6478	-0.003208	0.02	-0.00	0.03	0.00	0.04
ES№4	558.613	3.2746	-0.005968	0.01	-0.00	0.02	0.01	0.04
ES№17	597.450	3.0213	-0.005517	0.02	0.00	0.02	0.01	0.05
Sample	b_0	b_1	b_2	AAD, (%)	Bias, (%)	St.Dev, (%)	St.Err (%)	Max.Dev, (%)
ES№1	-2123.8361	21.5876	-0.03166	0.06	0.00	0.07	0.03	0.09
ES№2	-1996.4817	20.8167	-0.03048	0.05	-0.00	0.06	0.02	0.06
ES№4	-2040.7540	21.1368	-0.03101	0.06	0.00	0.07	0.02	0.09
ES№17	-2008.0588	20.9698	-0.03077	0.06	-0.00	0.07	0.02	0.08

V. Concentration dependence of the density, and speed of sound

As was mentioned above, thermodynamic properties of all aqueous salt solutions, thermal and mineral waters can be represented based on pure water properties (IAPWS formulations, Wagner and Pruß, 2002), because pure water is the dominant constituent and governs aqueous systems properties, see above Figs. 3, 6, and 8. The present experimental density, and speed of sound data for the mineral waters were fitted to the Riedel's correlation equations [8].

$$\rho(T, x_i) = \rho_{H_2O}(T) \left(1 + \sum_{i=1}^n a_i x_i \right), \quad (3)$$

$$W(T, x_i) = W_{H_2O}(T) \left(1 + \sum_{i=1}^n b_i x_i \right), \quad (4)$$

where $\rho_{H_2O}(T)$, and $W_{H_2O}(T)$ are the density, speed of sound (IAPWS formulation, Wagner and Pruß, 2002) of pure water respectively at a temperature of T and at atmospheric pressure; x_i is the concentration of ions (g/l); n is the number of main components of the mineral water; a_i , b_i are the density, and speed of sound fitting coefficients (Riedel's characteristic constants of the ions) for each ion species i , which are defining the contribution of each single ion species to total measured properties. For the present mineral water samples, we have selected 8 main components (ions): Na^+ , Ca^{+2} , Mg^{+2} , K^+ , S^{+} , Si^+ , SO_4^{-2} , and Cl^{-1} which contributions to the measured properties of the mineral waters are significant. The effect of other ions to the measured properties is negligible small. As can be note, from Eq. (3), (4) the temperature dependence of the $\rho(T, x_i)$, and $W(T, x_i)$ of mineral waters is determined through the temperature behavior of pure water properties, $\rho_{H_2O}(T)$, and $W_{H_2O}(T)$, see Figs. 1, and 4. All measured $\rho(T, x_i)$, and $W(T, x_i)$ data for various temperatures and concentrations (ES№1, ES№2, ES№4, and ES№17) together were fitted to Eqs. (3) and (4). The derived values of the Riedel's characteristic constants (a_i , b_i) for 8 selected ions of Na^+ , Ca^{+2} , Mg^{+2} , K^+ , S^{+} , Si^+ , SO_4^{-2} , and Cl^{-1} are presented in Table 4.

Table 4: Characteristic constant (Riedel's characteristic constant of the ions) a_i , b_i , and c_i for density, and speed of sound correlation models Eqs. (3) and (4) for basic ions in the mineral water samples

Ions	a_i (density) (l/g)	b_i (speed of sound) (l/g)
Ca ⁺²	-0.1345	-0.1345
K ⁺	-0.0945	-0.0945
Mg ⁺²	-0.1435	-0.1435
Na ⁺	-0.0545	-0.0545
S ⁺	0.1555	0.1555
Si ⁺	-0.1245	-0.1245
Cl ⁻¹	0.3555	0.3555
SO ₄ ⁻²	0.0555	0.0555

As one can see, the values of the Riedel's characteristic constants (a_i , b_i , c_i) for density and speed of sound are the same. This means that the contribution of the same ion specie to the density and speed of sound is the same. Also, the Riedel's characteristic constants for all cations are negative (except for S⁺), while for anions are positive. Thus, using the present measured density, and speed of sound data for the mineral water samples we can separate the contribution of different ion species to the total measured properties. and natural geothermal waters.

As can be note from Eqs. (3) and (4), the Riedel's model is the linear function of the concentration of ions. However, to improve the accuracy of the experimental data representations of the Riedel's model, the next terms ($x_i^{0.5}$, $x_i^{1.5}$, x_i^2) in expansion (Eqs. 3 and 4) should be used. More experimental thermophysical property data of thermal and mineral waters from various regions over the world with various compositions are needed to improve the accuracy of prediction of the models for any natural waters over the wide range of temperature and compositions of salt ions.

IV. Conclusions

The density, and speed of sound of four natural mineral water samples from the region of south Russia (CMW filed, ES№1, ES№2, ES №4, and ES №17) have been measured over a temperature range from (278 to 345) K at atmospheric pressure. Qualitative the measured temperature dependence of the density, and speed of sound of mineral water samples is similar to pure water behavior. Quantitatively the average differences between the measured mineral waters density, and speed of sound and pure water values (IAPWS standards) are within (0.2 to 1.1) %, and (0.15 to 1.13) %, respectively, which are much higher than their experimental uncertainties. At temperatures above 323 K, we found that heating of the samples (especially high concentrated samples ES №4 and ES №17) during the measurements, causes the release of the dissolved gases, which effects on temperature behavior of the density and speed of sound. We have demonstrated that the measured (ρ, W) data at atmospheric pressure can be used to predict high-pressure and high-temperature behavior of density ($P\rho T$) and speed of sound (WPT). If the thermophysical properties of mineral water are known at reference pressure (for example, $P_0 = 0.101$ MPa) and any temperature, then their properties at high pressures at which this properties of pure water are known (IAPWS standards) maybe calculated by multiplying the properties of the mineral water at reference state, P_0 , and given temperature, T , by the ratio of the this property of pure water at the desired pressure to that at a known reference pressure, $P_0 = 0.101$ MPa. Riedel's characteristic constants of the 8 selected ions of Na⁺, Ca⁺², Mg⁺², K⁺, S⁺, Si⁺, SO₄⁻², and Cl⁻¹ for

density, and speed of sound were estimated from the present measurements. We found that the values of Riedel's characteristic constants of the ion species for the thermodynamic properties (density and speed of sound) are the same. This means that the contribution of the same ion specie to the total measured density and speed of sound is the same. Also, the Riedel's characteristic constants for the all cations are negative (except for S^{2-}), while for anions are positive.

References

- [1] Veniale F., Barberis E., Carcagiu G., Morandi N., Setti M., Tamanini M., Tessier D. (2004). Formulation of muds for pelotherapy: effects of maturation by different mineral waters, *Appl. Clay. Sci.* 25:135–148.
- [2] Misirkhan A. Talibov, Javid T. Safarov, Egon R. Hassel, and Ilmutdin M. Abdulagatov. (2018). High-pressure and high-temperature density and vapor-pressure measurements and derived thermodynamic properties of natural waters of Yardymli District of Azerbaijan. *High Temperatures-High Pressures* 47:223–255.
- [3] Misirkhan A. Talybov, Lala A. Azizova, Ilmutdin M. Abdulagatov. (2019). Experimental Vapor-Pressures and Derived Thermodynamic Properties of Geothermal Fluids from Baden-Baden Geothermal Field (Southeastern Germany). *Journal of Energy and Power Technology* 27:2-26.
- [4] Ilmutdin M. Abdulagatov, Misirkhan A. Talybov, Lala A. Azizova. (2020). Measurements of the density, speed of sound, viscosity and derived key thermodynamic properties of geothermal waters from East Turkey. *ELSEVIER, Geothermics* 88:101884.
- [5] Misirkhan A. Talybov, Ilmutdin M. Abdulagatov. (2021). High-temperature and high-pressure PVT measurements and derived thermodynamic properties of geothermal fluids from East Turkey. *ELSEVIER, Geothermics* 95:102125.
- [6] Lemmon EW, Huber ML et al. NIST Standard Reference Database 23, NIST Reference Fluid Thermodynamic and Transport Properties, REFPROP, version 10.0, Standard Reference Data Program, National Institute of Standards and Technology: Gaithersburg, MD, 2018.
- [7] Wagner W, Prüss A. (2002). New international formulation for the thermodynamic properties of ordinary water substance for general and scientific use, *J. Phys. Chem. Ref. Data* 31:387-535.
- [8] Riedel L. (1951). The heat conductivity of aqueous solutions of strong electrolytes. *Chem Ing Tech* 23:59-64.