

Evaluation of Molar Sound Velocity and Molar Compressibility for Binary System of 1-Butanol + Hexadecane and 1- Butanol + Squalane

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Abstract

The molar sound velocity and molar compressibility of binary liquid systems of 1-Butanol + Hexadecane and 1-Butanol + Squalane have been studied over the entire range of composition at 298.15, 303.15 and 308.15 K. The nature and extent of molecular interactions for respective systems are studied by using the values of Rao constant (R) and Wada constant (W). The linearity of Rao's constant and Wada's constant is also proven.

Keywords: Molar sound velocity, molar compressibility, molecular interaction, 1-butanol, squalane, hexadecane

1. Introduction

The study of ultrasonic, volumetric and viscometric properties of liquid system is increased considerably in recent years due to extensive application owing to their ability of characterising physiochemical behavior of liquid systems. Besides such studies enable evaluation of some useful thermodynamic and transport parameters which can be used to explain the nature and extent of molecular interactions qualitatively; because the properties of pure substances are different from their mixtures. The properties of liquid systems can be altered continuously within a reasonable range by varying the concentration till an optimum value of some desired parameter is attained. The pure liquid lacks such flexibility. The studies of properties of binary liquid systems find direct application in chemical and biochemical industries [1].

In this paper, using the experimental ultrasonic velocity and density [2], we have calculated the theoretical values of molar sound velocity and molar compressibility for the binary liquid system of 1-Butanol + Hexadecane and 1-Butanol + Squalane, by using Nomoto's relation and Wada's theory at (298.15, 303.15 and 308.15) K, over the entire composition range.

From literature survey, we come to know that these parameters are used by many workers [3-10] for the acoustical studies of binary liquid systems. The previous investigation reveals that the excess thermodynamic properties of binary liquid systems of Hexadecane and squalane with hydrocarbons have been reported by several workers [11-21]. The increasing importance of the molar sound velocity and molar compressibility of binary liquid systems and the deviations from Rao's and Wada's rules have inspired us to investigate some binary liquid systems in detail.

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2. Theory

The ultrasonic studies provide a wealth of information about the state of liquids. The molar sound velocity and molar compressibility are two important parameters which are widely used for investigating the physiochemical behavior of liquid systems. Compressibility receives increasing attention in the studies on molecular interactions and on the structure of pure liquids and solutions. In 1940, Rao [22] showed empirically that the following expression hold approximately true for many liquids,

$$1/U (\partial U / \partial t) = 3 (1/\rho) (\partial \rho / \partial t)$$

And, $(M / \rho) U^{1/3} = R$

Or, $V_m U^{1/3} = R$ -----(1)

Where, U = Sound velocity, ρ = density, t = temperature (in °C), and V_m = molar volume.

Molar sound velocity or Rao Constant is denoted by R . Rao molar sound velocity relation has been extensively used and verified by a number of workers [22,23].

The Molar compressibility, W , was defined by Wada [24] as,

$$W = M / \rho \cdot \beta_s^{-1/7}$$

Or, $W = V_m \cdot \beta_s^{-1/7}$ -----(2)

Where, β_s = adiabatic compressibility. The compressibility factor depends upon the structure of the liquid.

In case of inorganic melts, the molar sound velocity can be calculated from the equation written below,

$$R = MU^{1/3} / \rho$$
 -----(3)

Employing the relation,

$$\beta_s = 1 / U^2 \rho$$

W can be written as,

$$W = M / \rho^{6/7} \cdot U^{2/7}$$

Or, $W = M^{1/7} \cdot R^{6/7}$ -----(4)

Such liquids that satisfies the relation, $R(T, P) = \text{constant}$ are called as Rao liquid or “Rao – Wada liquid”. Such liquid system represents the average liquids, organic and inorganic, except highly associated systems. In the thermodynamic and physiochemical study of binary liquid systems, the molar sound velocity (R) and molar compressibility (W) are very important parameters.

Assuming the linearity of the molar sound velocity, Nomoto [25] established the following relation for molar sound velocity in binary liquid systems:

$$R = x_1 R_1 + x_2 R_2$$
 -----(5)

Where, x_1 and x_2 are mole fractions of component 1 and 2 respectively.

R_1 and R_2 are molar sound velocity of component 1 and 2 respectively of the binary liquid system.

On the other hand molar compressibility of binary liquid system can be determined by the formula,

$$W = x_1 W_1 + x_2 W_2$$
 -----(6)

Where W_1 and W_2 are the molar compressibilities of component 1 and 2 of the binary liquid system respectively.

In the acoustical studies of binary liquid systems Nomoto has done extensive work. Whereas Rao's law has been derived thermodynamically [26] from Maxwell's equation and its molecular interpretation was given. Its experimental validity is also proven. Theoretical analysis of this relation plays a very important role in the acoustical studies of liquids.

3. Result and Discussion

Molar sound velocity (R) and molar compressibility (W) are determined by means of Nomoto's relation and Wada's theory at (298.15, 303.15 and 308.15) K for ($C_4H_9OH + C_{16}H_{34}$) and ($C_4H_9OH + C_{30}H_{62}$) are reported in Table 1 and 2 respectively.

It is evident from table 1 that in all cases, the values of both molar sound velocity and molar compressibility decreases with the increase in mole fraction of 1-Butanol in the binary liquid system of 1-Butanol and Hexadecane. Thus molecular interactions are observed, this may be due to the presence of weak forces of attractions operating in the system of unlike molecules. As the temperature increases the rate of collision increases gradually, but such change is not constant because when a particular temperature is attained then interactions becomes weaker, so we can see the variations in the values of molar sound velocity and molar compressibilities when the temperature changes from 303.15 to 308.15 K.

Table 1: Density, ρ , Speed of Sound, U, Molar Sound Velocity, R and Molar Compressibility for (x1 C₄H₉OH + x2 C₁₆H₃₄) at several temperatures

AT 298.15 K				
X1	ρ	U	R	W
0.0000	0.770456	1338.6	3.2391	2.2149
0.0899	0.770953	1332.4	3.0365	2.0771
0.1048	0.771053	1331.2	3.0029	2.0541
0.1516	0.771517	1328.2	2.8972	1.9823
0.2017	0.772074	1324.9	2.7842	1.9053
0.2494	0.772705	1321.9	2.6766	1.8321
0.3382	0.774083	1315.8	2.4763	1.6958
0.4147	0.775524	1310.6	2.3040	1.5785
0.5057	0.777651	1303.9	2.0990	1.4390
0.5845	0.779950	1297.6	1.9216	1.3183
0.6980	0.784249	1287.4	1.6662	1.1444
0.7945	0.789246	1276.8	1.4491	0.9965
0.8497	0.792847	1269.5	1.3249	0.9120
0.8963	0.796346	1262.7	1.2204	0.8408
0.9530	0.801232	1252.3	1.0934	0.7543
1.0000	0.805907	1240.5	0.9882	0.6826
AT 303.15 K				
X1	ρ	U	R	W
0.0000	0.766981	1320.0	3.2386	2.2146
0.0899	0.767402	1313.4	3.0360	2.0768
0.1048	0.767499	1312.2	3.0023	2.0538
0.1516	0.767916	1309.2	2.8969	1.9821
0.2017	0.768482	1305.8	2.7837	1.9051
0.2494	0.769093	1302.9	2.6762	1.8319
0.3382	0.770439	1296.9	2.4760	1.6957
0.4147	0.771883	1291.6	2.3036	1.5783
0.5057	0.773952	1285.5	2.0991	1.4391
0.5845	0.776223	1279.2	1.9217	1.3183
0.6980	0.780452	1269.2	1.6664	1.1445
0.7945	0.785434	1258.5	1.4491	0.9966
0.8497	0.789093	1251.4	1.3249	0.9120
0.8963	0.792717	1244.8	1.2202	0.8407
0.9530	0.797973	1235.8	1.0930	0.7541
1.0000	0.803155	1226.5	0.9879	0.6824
AT 308.15 K				
X1	ρ	U	R	W
0.0000	0.763520	1301.7	3.2382	2.2144
0.0899	0.763863	1294.9	3.0357	2.0766
0.1048	0.763961	1293.8	3.0021	2.0537
0.1516	0.764360	1290.3	2.8963	1.9817
0.2017	0.764874	1287.3	2.7835	1.9050
0.2494	0.765462	1284.4	2.6761	1.8319
0.3382	0.766796	1278.2	2.4757	1.6955
0.4147	0.768201	1273.1	2.3035	1.5783
0.5057	0.770240	1266.9	2.0990	1.4390
0.5845	0.772472	1260.9	1.9217	1.3183
0.6980	0.776353	1251.1	1.6666	1.1446
0.7945	0.781597	1240.6	1.4493	0.9967
0.8497	0.785172	1233.7	1.3252	0.9121
0.8963	0.788760	1227.4	1.2205	0.8409
0.9530	0.794054	1218.5	1.0933	0.7542
1.0000	0.799249	1209.8	0.9882	0.6825

Table 2: Density, ρ , Speed of Sound, U, Molar Sound Velocity, R and Molar Compressibility for (x1 C₄H₉OH + x2 C₃₀H₆₂) at several temperatures

AT 298.15 K

X1	ρ	U	R	W
0.0000	0.805122	1381.9	5.8496	4.0192
0.0451	0.804881	1379.5	5.6305	3.8687
0.1077	0.804649	1376.1	5.3257	3.6596
0.1346	0.804573	1374.8	5.1949	3.5698
0.1888	0.804447	1371.7	4.9308	3.3886
0.2231	0.804377	1369.7	4.7637	3.2740
0.3059	0.804273	1365.1	4.3607	2.9974
0.4052	0.804097	1358.8	3.8780	2.6661
0.5039	0.803949	1350.9	3.3979	2.3367
0.6118	0.803817	1340.5	2.8736	1.9768
0.7056	0.803732	1328.8	2.4181	1.6641
0.7998	0.803836	1312.5	1.9604	1.3499
0.8546	0.803989	1299.5	1.6942	1.1672
0.9035	0.804336	1284.3	1.4564	1.0040
0.9669	0.805126	1258.5	1.1487	0.7928
1.0000	0.805907	1240.5	0.9882	0.6826

AT 303.15 K

X1	ρ	U	R	W
0.0000	0.801912	1364.1	5.8477	4.0180
0.0451	0.801658	1361.7	5.6287	3.8677
0.1077	0.801402	1358.3	5.3242	3.6587
0.1346	0.801318	1356.5	5.1928	3.5686
0.1888	0.801160	1353.8	4.9294	3.3878
0.2231	0.801070	1351.8	4.7624	3.2732
0.3059	0.800898	1347.1	4.3598	2.9969
0.4052	0.800714	1340.8	3.8771	2.6656
0.5039	0.800528	1332.6	3.3970	2.3361
0.6118	0.800347	1322.5	2.8731	1.9765
0.7056	0.800179	1310.9	2.4179	1.6640
0.7998	0.800194	1294.8	1.9605	1.3499
0.8546	0.800335	1281.8	1.6942	1.1672
0.9035	0.800708	1266.8	1.4563	1.0040
0.9669	0.801896	1241.4	1.1481	0.7924
1.0000	0.803155	1226.5	0.9879	0.6824

AT 308.15 K

X1	ρ	U	R	W
0.0000	0.798709	1346.5	5.8458	4.0169
0.0451	0.798397	1343.0	5.6257	3.8659
0.1077	0.798084	1340.2	5.3224	3.6577
0.1346	0.797991	1338.9	5.1918	3.5680
0.1888	0.797826	1335.9	4.9281	3.3870
0.2231	0.797731	1333.9	4.7611	3.2725
0.3059	0.797543	1329.3	4.3587	2.9963
0.4052	0.797320	1322.8	3.8761	2.6650
0.5039	0.797098	1314.8	3.3963	2.3357
0.6118	0.796857	1304.6	2.8726	1.9762
0.7056	0.796621	1293.1	2.4176	1.6638
0.7998	0.796558	1277.1	1.9604	1.3499
0.8546	0.796660	1264.2	1.6942	1.1672
0.9035	0.796979	1249.1	1.4563	1.0040
0.9669	0.798060	1224.4	1.1483	0.7925
1.0000	0.799249	1209.8	0.9882	0.6825

Similarly Table 2 shows the results of molar sound velocity and molar compressibility of binary liquid system of 1-Butanol and squalane at three different temperatures. Here also the values of molar sound velocity and molar compressibility decrease with the increase in the concentration of 1-Butanol in the binary liquid system of 1-Butanol and Squalane. So, the results of the present investigation, show the molecular interactions (like dipole – dipole, dipole – induced dipole and dispersive forces) in these binary liquid systems.

Figures a, b, and c represents the variation of R and W with the mole fraction of 1-Butanol at three temperatures (298.15, 303.15 and 308.15) K respectively for the binary liquid system of 1-Butanol + Hexadecane, while figure d, e and f shows the variation of R and W with the mole fraction of 1-Butanol at three temperatures (298.15, 303.15 and 308.15) K for the binary liquid system of 1-Butanol + Squalane. It gives an idea of extent of interactions taking place between the molecules of these systems very clearly. These graphs are linear for both the system which proves the linearity of Rao's constant and Wada's constant.

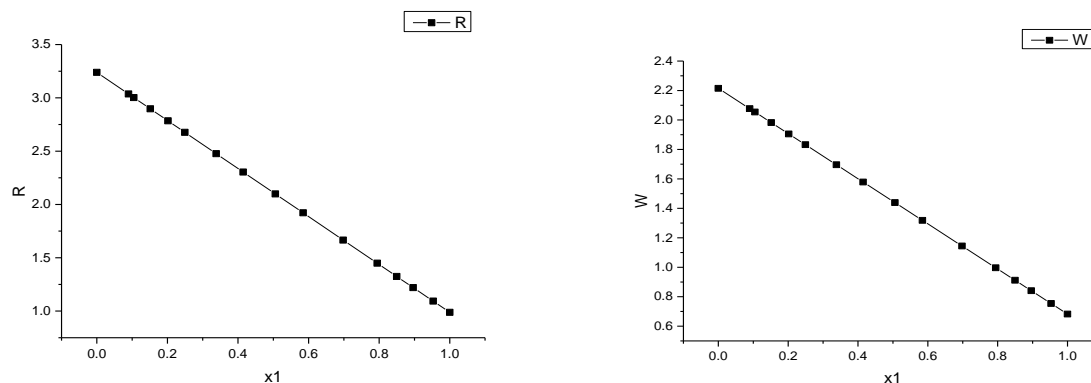


Figure 1a: Plots of molar sound velocity (R) vs x_1 and molar compressibility (W) vs x_1 for the studied system (x_1 C₄H₉OH + x_2 C₁₆H₃₄), at temperature 298.15 K.

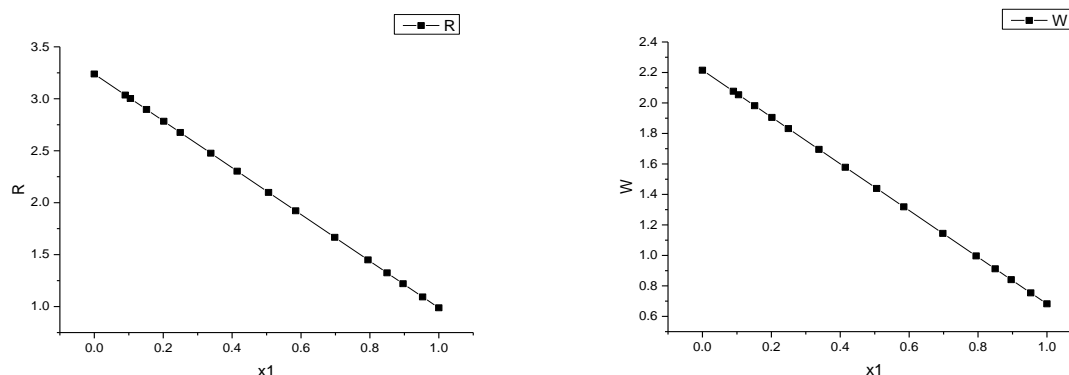


Figure 1b: Plots of molar sound velocity (R) vs x_1 and molar compressibility (W) vs x_1 for the studied system (x_1 C₄H₉OH + x_2 C₁₆H₃₄), at temperature 303.15 K.

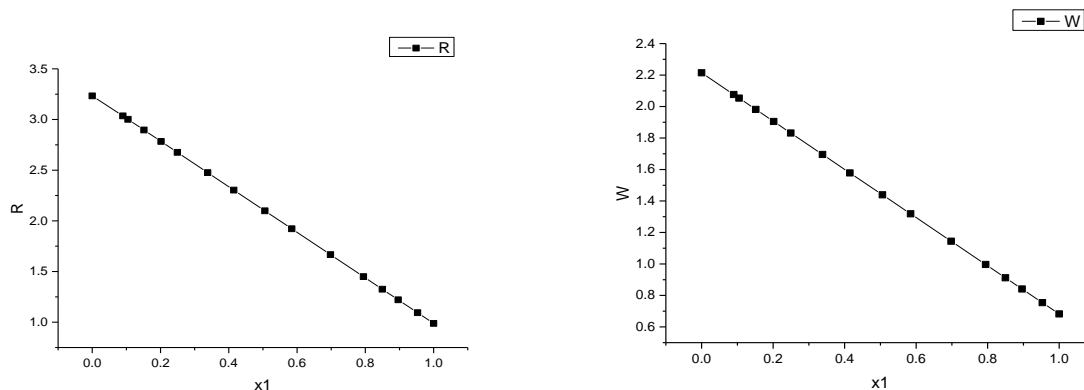


Figure 1c: Plots of molar sound velocity (R) vs x_1 and molar compressibility (W) vs x_1 for the studied system (x_1 C₄H₉OH + x_2 C₁₆H₃₄), at temperature 308.15 K.

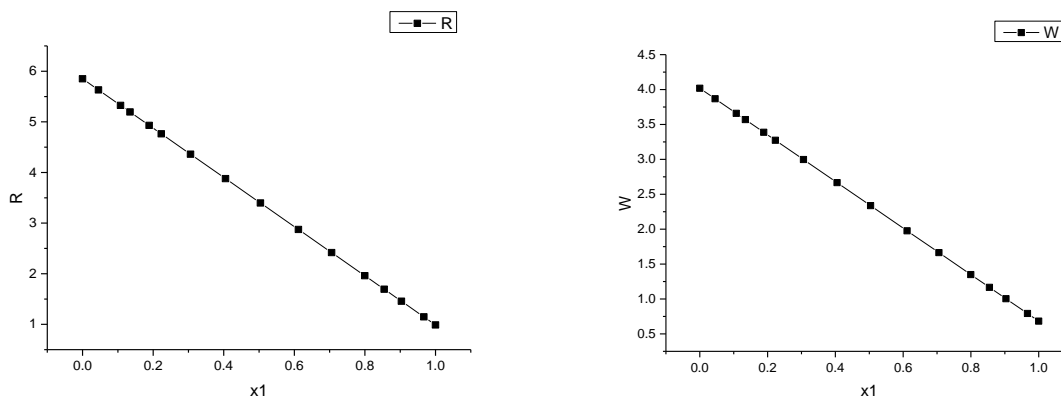


Figure 1d: Plots of molar sound velocity (R) vs x_1 and molar compressibility (W) vs x_1 for the studied system (x_1 C₄H₉OH + x_2 C₃₀H₆₂), at temperature 298.15 K.

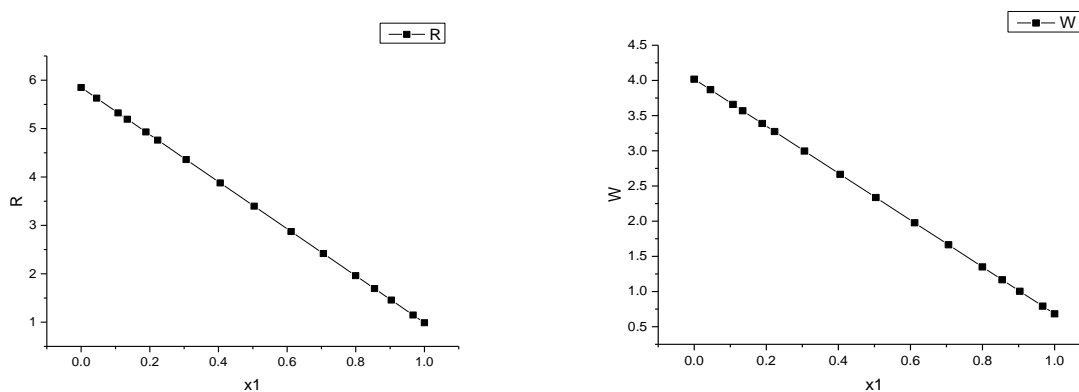


Figure 1e: Plots of molar sound velocity (R) vs x_1 and molar compressibility (W) vs x_1 for the studied system (x_1 C₄H₉OH + x_2 C₃₀H₆₂), at temperature 303.15 K.

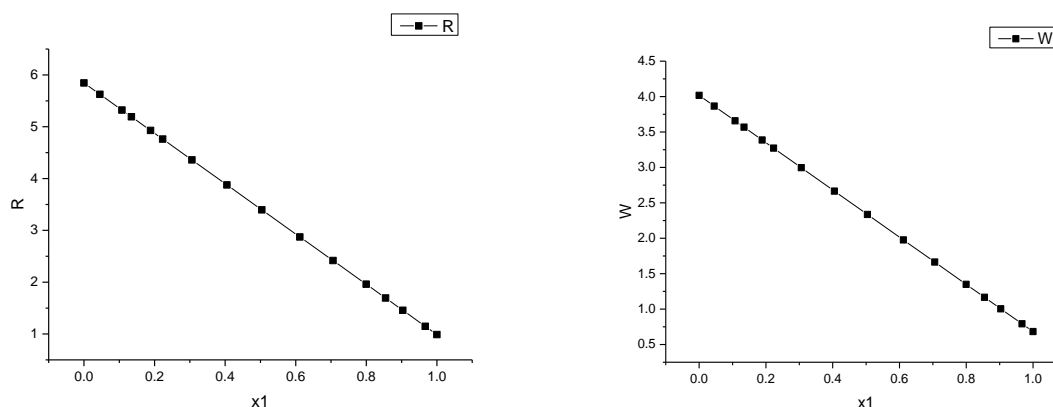


Figure 1f: Plots of molar sound velocity (R) vs x_1 and molar compressibility (W) vs x_1 for the studied system (x_1 C₄H₉OH + x_2 C₃₀H₆₂), at temperature 308.15 K

4. Conclusion

It is obvious that, there exist a molecular interaction between the components of the binary liquid systems of (C₄H₉OH + C₁₆H₃₄) and (C₄H₉OH + C₃₀H₆₂). In specific weak molecular interaction (like dipole – dipole, dipole – induced dipole and dispersive forces) are found to exist between components of respective systems. The parameters studied in this paper are discussed in the light of molecular interactions in the systems of (C₄H₉OH + C₁₆H₃₄) and (C₄H₉OH + C₃₀H₆₂). Thus the linearity of Rao's constant and Wada's constant is also proven.

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