



Ultrasonic Studies on Interionic Interactions of KSCN in 2-Ethoxyethanol + Water Mixture at Varying Temperatures

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Abstract: Density (d), ultrasonic velocity (U) and viscosity (η) of potassium thiocyanate (KSCN) at different mole fractions of 2-ethoxyethanol has been measured at 288.15, 298.15, 308.15 and 318.15K. An ultrasonic interferometer working at 2 MHz was used to measure the sound velocity. Using the experimental data, adiabatic compressibility (β_{ad}), inter molecular free length (L_f), acoustic impedance (Z), Relative association (R_A), apparent molar compressibility (ϕ_k), apparent molar volume (ϕ_v), limiting apparent molar compressibility (ϕ_k^0), limiting apparent molar volume (ϕ_v^0), association constant (S_k and S_v) and solvation number were computed. The observed variation of these parameters with respect to electrolyte concentration and temperature signifies the presence of ion- solvent and solvent-solvent interactions. Masson's and Gucker's equation has been verified. The maxima in ultrasonic velocity and minima in adiabatic compressibility are observed at $X_{2EE} = 0.0136$ elucidating complex formation in this composition. The positive S_k values suggests structure breaking property of KSCN.

Keywords: Potassium thiocyanate, 2-ethoxyethanol, ultrasonic velocity, free length and solvation number.

I. Introduction

Electrolytes plays an important role in biological sciences, engineering, Geographic's etc. [1-3]. Knowledge of the thermo acoustic properties of the electrolytes and solvents is of high interest in view of their wide applications in science and industrial process. During the last two decades, the ultrasonic velocities, density and viscosities of the solutions of mixed solvents have been extremely investigated by many workers [4-7]. The acoustic parameters are utilized in characterizing of the structure and properties of solutions. These information are proven to be very useful in obtaining the knowledge regarding various inter ionic interactions [8]. Potassium thiocyanate (KSCN) is also known as sulphocyanide or rhodamide and is soluble in water and alcohol. Since it finds a number of industrial and biological applications [9, 10] its interactions in presence of different solvent mixtures is very important. Shivakumar et al [11] reported an account of the investigation on solvation behavior of potassium thiocyanate in DMSO, DMF and their aqueous solutions at 288 – 313K temperatures. He has used ultrasonic parameters to explore ion- solvent and solvent – solvent interaction at varying conditions. More subtle effect arises with highly structured solvents like water due to strong solvation reducing the effective quantity of free solvent molecules. A good example of these effects is the hydrophobic interaction or bonding that is often evoked in aqueous biological systems. Mixed aqueous-organic or totally organic reaction media have been utilized by organic chemist to synthesize many valuable drugs and other compounds by reaction paths that involves ionic intermediate or products. 2-ethoxyethanol (1-ethoxy-2-hydroxy; ethane) is used as a co-solvent since the substituted alcohols play very important role in solvation process. It belongs to alkoxy ethanol groups, which are the perfect solvents of many substances. 2-ethoxyethanol is widely used as an ingredient in cleaning agent/disinfectants/cosmetics [12]. In literature the information available regarding the acoustic behaviour of KSCN in 2-ethoxy ethanol + water mixtures are very scanty. In this investigation we attempted to reveal the interionic interactions taking place in the system involving KSCN in 2-ethoxyethanol+water at 288.15, 298.15, 308.15 and 318.15K.

II. Experimental

2-ethoxyethanol (analytical grade, Merck) was used without further purification. Doubly distilled water was used for preparing various mole fractions (ranging from 0.0000 to 1.0000) of 2-ethoxyethanol. The recrystallized electrolyte potassium thiocyanate (Merck - AR) was dried at 100-120°C in vacuum for 24 hour prior to use. Potassium thiocyanate (KSCN) is weighed in electrical digital balance (ER-180, Afcoset Balances, Bombay) with a precision of $\pm 0.3\%$ and dissolved in solvent mixture to prepare the desired concentration. A digital multi frequency ultrasonic interferometer (M-81S, Mittal New Delhi) at 2 MHz, with a measuring frequency tolerance at 0.03% has been used for velocity measurement. A thermostat (Kumar Make, Bombay) with an accuracy of

$\pm 0.01^\circ\text{C}$ was used to maintain the temperature of the cell at 288.15, 298.15, 308.15 and 318.15 K. A pycnometer (10 cc capacity) is used to determine the density of all the solutions.

III. Results and Discussions

Thermodynamic properties such as adiabatic compressibility (β_{ad}), inter molecular free length (L_f), acoustic impedance (Z), Relative association (R_A), apparent molar compressibility (Φ_k), apparent molar volume (Φ_v), limiting apparent molar compressibility (Φ_k^0), limiting apparent molar volume (Φ_v^0) and solvation number (S_n) have been calculated for potassium thiocyanate in aqueous and mixed solvent mixture at different temperatures. The following equations were used for the calculations [13]

$$U = \lambda \times F \quad \dots\dots\dots (1)$$

$$\beta_{ad} = 1/U^2 d \quad \dots\dots\dots (2)$$

$$L_f = K \sqrt{\beta_{ad}} \quad \dots\dots\dots (3)$$

$$Z = U \times d \quad \dots\dots\dots (4)$$

$$R_A = (d/d_0) (U_0/U)^{1/3} \quad \dots\dots\dots (5)$$

$$\Phi_k = 1000(d_0 \beta_{ad} - d_l \beta_{ad}^0)/d_l d_0 + M \beta_{ad} / d_l \quad \dots\dots\dots (6)$$

$$\Phi_v = M/d_0 - 1000(d-d_0)/Cd_0 \quad \dots\dots\dots (7)$$

$$S_n = (n_1/n_2)(1 - \beta_{ad}/\beta_{ad}^0) \quad \dots\dots\dots (8)$$

where d_l , d_0 and U , U_0 are the densities and ultrasonic velocities of solution and solvent respectively. λ is the wavelength and F is the frequency of ultrasonic wave. M is the molecular weight of the solute, β_{ad}^0 and β_{ad} are the adiabatic compressibilities of solvent and solution, K is the Jacobson constant, n_1 and n_2 are the number of moles of the solvent and solute respectively.

Ultrasonic velocity (U):

The computed values of ultrasonic velocity (U) for Potassium thiocyanate in different 2-ethoxyethanol + water mixtures at 288.15, 298.15, 308.15 and 318.15 K presented in Table 1. It is observed that the variation of ultrasonic velocity with respect to concentration of KSCN depends on mole fraction of 2-ethoxyethanol. The increase in ultrasonic velocity with increase in concentration of the solute in the solution implies greater association of the molecules [14]. It is observed that the ultrasonic velocity increases initially with addition of co-solvent and found maximum at $X_{2EE} = 0.0136$ and later decreased at co-solvent rich region. This may be due to enhancement of water structure by the added co-solvent increasing the effective ionic size [15]. The maxima at $X_{2EE} = 0.0136$ have been attributed to the formation of hydrophobic aggregation resulting in labile clusters [16]. Beyond this mole fraction sound velocity decreases indicating the weak solvent-solvent interaction. Lowering of ultrasonic velocity may be due to decrease in the dielectric constant of solvent mixture. A gradual increase in the velocity with rise in temperature was observed up to $X_{2EE} = 0.0052$ as rise in the thermal energy weakens the ion-solvent interactions. However beyond this mole fraction reverse trend was observed.

Adiabatic Compressibility (β_{ad}) and density:

The change in the structural arrangement of molecules in a mixture is given by adiabatic compressibility. The variation of β_{ad} with concentration of KSCN in 2-ethoxyethanol and water mixture is presented in Table 1. The adiabatic compressibility is found to decrease with increase in concentration of KSCN in different compositions of 2-ethoxyethanol + water mixtures. This may be attributed to increasing electrostrictive compression of water around the molecules [17]. Minima in β_{ad} and maxima in ultrasound velocity was found at $X_{2EE} = 0.0136$, indicating strong solvent-solvent interaction. Density values for different concentrations of potassium thiocyanate in 2-ethoxyethanol + water mixtures at 288.15, 298.15, 308.15 and 318.15 K are presented in Table 2. Increase in density with increase in concentration of the solute suggests the presence of solute-solvent attraction through hydrogen bonding and ion-solvent interactions in the solutions [18]. On the other hand, increasing tendency of density may be interpreted as structure making tendency of the solvent due to the added solute. Decrease in density with increase in temperature indicate decline in cohesive forces. Maxima in density was observed at $X_{2EE} = 0.0052$. Further addition of co-solvent results in rise in overall volume and therefore gradual decrease in density is observed.

Inter molecular free length (L_f):

Nature of the molecular interaction are studied by intermolecular free length [19] and is calculated using the equation 3. Inter molecular free length for KSCN in 2-ethoxyethanol + water mixtures 288.15, 298.15, 308.15 and 318.15 K is calculated using the adiabatic compressibility data and presented in the Table 1. Inter molecular free length decreases linearly with increase in concentration of KSCN in different mole fractions of 2-ethoxyethanol. This may be due to decrease in compressibility with increase in concentration of the solute, which in turn indicates significant interaction between solute-solvent and solvent-solvent [20]. Lowest L_f values was found at $X_{2EE} = 0.0136$. This proves that the frame structure of solvent mixture remains stable, not affected by the added solute. As expected rise in temperature increases intermolecular distance between the surfaces of two molecules [21] weakening the ion-solvent and solvent-solvent interactions.

Specific acoustic impedance (Z):

Specific acoustic impedance [22] is the product of ultrasonic velocity (U) and density (d) and is calculated using the equation 4. The Z values computed for KSCN in 2-ethoxyethanol + water mixtures at different compositions are reported in Table 2. A gradual increase in Z value with concentration of KSCN is observed which can be attributed to the effective solute-solvent interactions [23]. It increases the intermolecular distance between the molecules which in turn enhances the impedance in the ultrasonic propagation [24] and becomes maximum at $X_{2EE} = 0.0136$ suggesting highest solvent-solvent interaction at that mole fraction. Increase in temperature effectively changes structure of the molecules causing decrease in impedance values in co-solvent rich region but opposite trend is seen in water rich region i.e., at $x_{2pr} = 0.0000$ and 0.0023.

Relative Association (R_A):

Relative association values for potassium thiocyanate in different compositions of 2-ethoxyethanol + water mixtures are computed using the equation 5 and are shown in Table 2. The increasing trend of R_A value with solute concentration shows the ion-solvent interaction [22]. There is no much effect of temperature on R_A values of KSCN in water and 2-ethoxyethanol + water system studied.

Table 1. Experimentally determined ultrasonic velocity (U: ms^{-1}), adiabatic compressibility (β_{ad} : m^2/N) and intermolecular free length (L_f : m) for KSCN in 2-ethoxyethanol + water mixtures with respect to concentration (C: Mol dm^{-3}) at different temperatures

C	TEMPERATURE											
	288.15K			298.15K			308.15K			318.15K		
	U	$10^{10}\beta_{ad}$	$10^{10}L_f$	U	$10^{10}\beta_{ad}$	$10^{10}L_f$	U	$10^{10}\beta_{ad}$	$10^{10}L_f$	U	$10^{10}\beta_{ad}$	$10^{10}L_f$
$X_{2EE} = 0.0000$												
0.01	1476	4.584	0.406	1500	4.450	0.415	1520	4.339	0.419	1538	4.261	0.428
0.02	1482	4.526	0.404	1506	4.394	0.412	1522	4.308	0.417	1540	4.239	0.426
0.03	1484	4.487	0.402	1504	4.384	0.412	1520	4.300	0.417	1540	4.218	0.425
0.04	1486	4.459	0.401	1510	4.327	0.409	1526	4.245	0.414	1544	4.176	0.423
0.05	1486	4.437	0.400	1516	4.272	0.407	1528	4.216	0.413	1544	4.154	0.422
0.06	1488	4.403	0.398	1524	4.214	0.404	1534	4.163	0.410	1546	4.120	0.420
0.07	1496	4.336	0.395	1524	4.212	0.404	1536	4.137	0.409	1548	4.100	0.419
0.08	1502	4.282	0.393	1532	4.133	0.400	1540	4.097	0.407	1550	4.067	0.418
0.09	1504	4.253	0.391	1544	4.051	0.396	1544	4.058	0.405	1552	4.039	0.416
0.1	1508	4.212	0.389	1536	4.076	0.397	1548	4.023	0.403	1558	3.999	0.414
$X_{2EE} = 0.0023$												
0.01	1528	4.270	0.392	1544	4.190	0.403	1560	4.120	0.408	1580	4.040	0.416
0.02	1532	4.220	0.390	1550	4.140	0.400	1564	4.080	0.406	1582	4.010	0.415
0.03	1534	4.200	0.389	1550	4.120	0.399	1566	4.050	0.405	1584	3.980	0.413
0.04	1536	4.170	0.387	1554	4.080	0.397	1568	4.020	0.403	1584	3.960	0.412
0.05	1540	4.130	0.386	1558	4.060	0.396	1574	3.970	0.401	1590	3.910	0.410
0.06	1544	4.080	0.383	1562	4.010	0.394	1578	3.930	0.399	1590	3.890	0.409
0.07	1552	4.020	0.380	1566	3.970	0.392	1584	3.890	0.397	1592	3.870	0.407
0.08	1560	3.960	0.378	1568	3.940	0.390	1588	3.850	0.395	1600	3.810	0.404
0.09	1560	3.540	0.377	1576	3.880	0.387	1590	3.830	0.394	1600	3.800	0.404
0.1	1568	3.890	0.374	1580	3.850	0.386	1590	3.100	0.354	1608	3.750	0.401
$X_{2EE} = 0.0052$												
0.01	1602	3.897	0.375	1608	3.867	0.387	1612	3.848	0.395	1620	3.810	0.404
0.02	1602	3.897	0.375	1610	3.858	0.386	1614	3.839	0.394	1620	3.810	0.404
0.03	1608	3.867	0.373	1612	3.848	0.386	1616	3.829	0.394	1622	3.801	0.404
0.04	1608	3.867	0.373	1614	3.839	0.385	1618	3.820	0.393	1622	3.801	0.404
0.05	1614	3.839	0.372	1616	3.829	0.385	1620	3.810	0.393	1624	3.792	0.403
0.06	1614	3.839	0.372	1618	3.820	0.384	1620	3.810	0.393	1624	3.792	0.403
0.07	1616	3.829	0.371	1620	3.810	0.384	1620	3.810	0.393	1626	3.782	0.403
0.08	1620	3.810	0.370	1622	3.801	0.384	1623	3.796	0.392	1632	3.755	0.401
0.09	1620	3.810	0.370	1624	3.792	0.383	1624	3.792	0.392	1634	3.745	0.401
0.1	1622	3.801	0.370	1624	3.792	0.383	1628	3.773	0.391	1636	3.736	0.400
$X_{2EE} = 0.0136$												
0.01	1660	3.604	0.360	1642	3.704	0.379	1616	3.844	0.394	1600	3.950	0.412
0.02	1662	3.586	0.359	1644	3.680	0.377	1616	3.829	0.394	1604	3.917	0.410
0.03	1662	3.577	0.359	1650	3.637	0.375	1620	3.792	0.392	1608	3.883	0.408
0.04	1664	3.546	0.357	1654	3.605	0.373	1622	3.767	0.390	1608	3.866	0.407
0.05	1664	3.524	0.356	1652	3.600	0.373	1624	3.744	0.389	1614	3.820	0.405
0.06	1666	3.502	0.355	1652	3.586	0.373	1626	3.719	0.388	1614	3.803	0.404
0.07	1668	3.481	0.354	1656	3.553	0.371	1628	3.694	0.387	1618	3.771	0.402
0.08	1672	3.449	0.352	1656	3.536	0.370	1632	3.658	0.385	1620	3.744	0.401
0.09	1674	3.427	0.351	1658	3.515	0.369	1634	3.637	0.384	1620	3.732	0.400
0.1	1676	3.404	0.350	1658	3.502	0.368	1634	3.620	0.383	1620	3.713	0.399
$X_{2EE} = 0.0301$												
0.01	1598	3.920	0.376	1572	4.080	0.397	1556	4.190	0.412	1524	4.410	0.435
0.02	1600	3.900	0.375	1576	4.040	0.395	1556	4.180	0.411	1524	4.420	0.435
0.03	1604	3.860	0.373	1580	4.010	0.394	1558	4.150	0.410	1530	4.340	0.432
0.04	1604	3.840	0.372	1582	3.980	0.392	1560	4.120	0.408	1532	4.310	0.430
0.05	1608	3.810	0.370	1586	3.940	0.390	1560	4.100	0.407	1532	4.290	0.429
0.06	1610	3.780	0.369	1586	3.930	0.390	1560	4.080	0.406	1532	4.280	0.429

0.07	1612	3.760	0.368	1588	3.900	0.388	1560	4.070	0.406	1536	4.230	0.426
0.08	1616	3.720	0.366	1594	3.850	0.386	1562	4.040	0.404	1540	4.200	0.424
0.09	1620	3.690	0.364	1594	3.840	0.385	1566	4.000	0.402	1542	4.170	0.423
0.1	1624	3.660	0.363	1594	3.820	0.384	1574	3.950	0.400	1546	4.130	0.421
X_{2FE} = 0.0765												
0.01	1496	4.580	0.406	1470	4.770	0.430	1438	5.030	0.451	1400	5.350	0.479
0.02	1498	4.540	0.404	1476	4.710	0.427	1444	4.970	0.448	1402	5.320	0.478
0.03	1506	4.470	0.401	1476	4.690	0.426	1448	4.910	0.446	1412	5.220	0.473
0.04	1508	4.430	0.399	1480	4.640	0.424	1452	4.860	0.443	1420	5.130	0.469
0.05	1508	4.410	0.398	1480	4.620	0.423	1458	4.810	0.441	1422	5.090	0.467
0.06	1510	4.380	0.397	1484	4.570	0.421	1460	4.770	0.439	1426	5.040	0.465
0.07	1510	4.360	0.396	1488	4.530	0.419	1460	4.740	0.438	1434	4.960	0.461
0.08	1526	4.250	0.391	1488	4.500	0.417	146	4.720	0.437	1436	4.920	0.459
0.09	1528	4.220	0.390	1492	4.460	0.415	1468	4.650	0.434	1446	4.830	0.455
0.1	1530	4.190	0.388	1496	4.420	0.414	1472	4.600	0.431	1448	4.800	0.454
X_{2FE} = 1.0000												
0.01	1332	5.890	0.460	1314	6.190	0.489	1304	6.340	0.506	1268	6.760	0.539
0.02	1360	5.700	0.453	1330	6.010	0.482	1306	6.290	0.504	1268	6.730	0.537
0.03	1362	5.650	0.451	1332	5.960	0.480	1308	6.230	0.502	1272	6.650	0.396
0.04	1380	5.470	0.444	1334	5.900	0.478	1308	6.190	0.500	1278	6.550	0.530
0.05	1388	5.390	0.440	1336	5.860	0.476	1312	6.120	0.498	1284	6.440	0.526
0.06	1390	5.330	0.438	1354	5.660	0.468	1326	5.950	0.491	1298	6.270	0.519
0.07	1392	5.290	0.436	1360	5.580	0.465	1330	5.850	0.486	1300	6.210	0.516
0.08	1398	5.210	0.433	1368	5.480	0.460	1336	5.800	0.484	1300	6.180	0.515
0.09	1404	5.140	0.430	1374	5.400	0.457	1340	5.730	0.481	1306	6.080	0.511
0.1	1408	5.080	0.428	1376	5.360	0.455	1344	5.660	0.478	1312	5.990	0.507

4.74

Table 2. Experimentally determined density (d : kg.m⁻³), specific acoustic impedance (Z : kgm⁻²s⁻¹) and relative association (R_A : mol/dm³) for KSCN in 2-ethoxyethanol + water mixtures with respect to concentration (C) at different temperatures.

C	TEMPERATURE											
	288.15K			298.15K			308.15K			318.15K		
	10 ⁻³ d	10 ⁻⁵ Z	R _A	10 ⁻³ d	10 ⁻⁵ Z	R _A	10 ⁻³ d	10 ⁻⁵ Z	R _A	10 ⁻³ d	10 ⁻⁵ Z	R _A
X_{2FE} = 0.0000												
0.01	1.0013	14.83	1.0008	0.9987	15.02	1.0008	0.9976	15.16	1.0050	0.9922	15.27	1.0016
0.02	1.0060	14.95	1.0041	1.0034	15.15	1.0041	1.0020	15.27	1.0087	0.9948	15.36	1.0038
0.03	1.0120	15.03	1.0097	1.0085	15.2	1.0097	1.0066	15.32	1.0136	0.9996	15.44	1.0086
0.04	1.0157	15.13	1.0129	1.0136	15.32	1.0129	1.0115	15.43	1.0170	1.0044	15.54	1.0126
0.05	1.0207	15.20	1.0179	1.0185	15.45	1.0179	1.0159	15.53	1.0208	1.0099	15.63	1.0181
0.06	1.0258	15.33	1.0225	1.0217	15.59	1.0225	1.0209	15.66	1.0243	1.0156	15.67	1.0234
0.07	1.0306	15.46	1.0255	1.0223	15.67	1.0255	1.0246	15.73	1.0274	1.0178	15.79	1.0252
0.08	1.0351	15.59	1.0286	1.0309	15.83	1.0286	1.0291	15.84	1.0307	1.0234	15.87	1.0304
0.09	1.0395	15.67	1.0325	1.0355	16.02	1.0325	1.0336	15.97	1.0341	1.0278	15.96	1.0344
0.1	1.0440	15.76	1.0360	1.0399	15.98	1.0360	1.0373	16.08	1.0366	1.0302	16.08	1.0355
X_{2FE} = 0.0023												
0.01	1.0040	15.34	1.0051	1.0002	15.44	1.0044	0.9980	15.57	1.0024	0.9926	15.68	1.0001
0.02	1.0088	15.45	1.0090	1.0046	15.57	1.0075	1.0027	15.68	1.0063	0.9955	15.75	1.0026
0.03	1.0124	15.53	1.0122	1.0095	15.65	1.0124	1.0073	15.77	1.0105	1.0023	15.88	1.0091
0.04	1.0163	15.61	1.0157	1.0144	15.76	1.0165	1.0117	15.86	1.0144	1.0064	15.94	1.0132
0.05	1.0221	15.74	1.0206	1.0187	15.87	1.0199	1.0160	15.99	1.0175	1.0107	16.07	1.0162
0.06	1.0292	15.89	1.0268	1.0233	15.98	1.0236	1.0207	16.10	1.0213	1.0163	16.16	1.0219
0.07	1.0327	16.03	1.0285	1.0279	16.09	1.0273	1.0252	16.24	1.0245	1.0189	16.22	1.0241
0.08	1.0378	16.18	1.0318	1.0327	16.18	1.0317	1.0299	16.36	1.0283	1.0240	16.38	1.0275
0.09	1.0422	16.26	1.0362	1.0367	16.33	1.0339	1.0339	16.44	1.0319	1.0284	16.45	1.0319
0.1	1.0458	16.39	1.0380	1.0404	16.43	1.0368	1.0377	16.50	1.0357	1.0316	16.59	1.0334
X_{2FE} = 0.0052												
0.01	1.0074	16.14	0.9951	1.0020	16.11	0.9931	0.9991	16.11	0.9982	0.9933	16.09	0.9956
0.02	1.0115	16.20	0.9992	1.0063	16.20	0.9974	1.0030	16.19	1.0017	0.9961	16.14	0.9984
0.03	1.0156	16.33	1.0020	1.0111	16.30	1.0021	1.0078	16.29	1.0061	1.0043	16.29	1.0063
0.04	1.0208	16.41	1.0071	1.0150	16.38	1.0060	1.0120	16.37	1.0099	1.0075	16.34	1.0095
0.05	1.0261	16.56	1.0111	1.0200	16.48	1.0109	1.0163	16.46	1.0137	1.0134	16.46	1.0150
0.06	1.0299	16.62	1.0148	1.0246	16.58	1.0151	1.0209	16.54	1.0183	1.0165	16.51	1.0181
0.07	1.0338	16.71	1.0182	1.0286	16.66	1.0182	1.0259	16.62	1.0233	1.0193	16.57	1.0204
0.08	1.0384	16.82	1.0219	1.0330	16.76	1.0221	1.0307	16.72	1.0277	1.0275	16.77	1.0274
0.09	1.0422	16.88	1.0257	1.0371	16.84	1.0262	1.0347	16.80	1.0312	1.0298	16.83	1.0293
0.1	1.0463	16.97	1.0293	1.0418	16.92	1.0308	1.0385	16.91	1.0342	1.0332	16.90	1.0322
X_{2FE} = 0.0136												
0.01	1.0068	16.72	1.0038	1.0013	16.44	1.0031	0.9961	16.09	1.0000	0.9888	15.82	0.9947
0.02	1.0095	16.82	1.0061	1.0054	16.53	1.0068	1.0002	16.16	1.0042	0.9922	15.91	0.9972
0.03	1.0122	16.89	1.0088	1.0098	16.66	1.0099	1.0049	16.28	1.0080	0.9961	16.02	1.0003

15.76

0.04	1.0185	16.99	1.0146	1.014	16.77	1.0133	1.009	16.37	1.0117	1.0005	16.09	1.0048
0.05	1.0249	17.06	1.0210	1.0179	16.82	1.0176	1.0127	16.45	1.0150	1.005	16.22	1.0080
0.06	1.0288	17.16	1.0245	1.0217	16.88	1.0214	1.017	16.54	1.0189	1.0095	16.29	1.0125
0.07	1.0326	17.23	1.0279	1.0263	17.00	1.0252	1.0213	16.62	1.0228	1.013	16.39	1.0152
0.08	1.037	17.35	1.0314	1.0312	17.08	1.0301	1.0263	16.75	1.0270	1.0177	16.49	1.0195
0.09	1.0412	17.44	1.0352	1.0348	17.16	1.0333	1.0297	16.83	1.0300	1.0209	16.54	1.0227
0.1	1.0459	17.53	1.0394	1.0388	17.22	1.0373	1.0345	16.90	1.0348	1.0263	16.63	1.0281
X_{2EE} = 0.0301												
0.01	0.9977	15.94	1.0011	0.9916	15.59	1.0038	0.9865	15.34	1.0045	0.9764	14.88	1.0035
0.02	1.0021	16.03	1.0050	0.9957	15.69	1.0071	0.9887	15.38	1.0068	0.9752	14.86	1.0022
0.03	1.0067	16.15	1.0088	0.9999	15.80	1.0105	0.9926	15.47	1.0103	0.9835	15.05	1.0094
0.04	1.0122	16.24	1.0143	1.0039	15.88	1.0141	0.9979	15.58	1.0153	0.9876	15.13	1.0132
0.05	1.0162	16.34	1.0175	1.0088	16.00	1.0182	1.0012	15.62	1.0187	0.9924	15.20	1.0181
0.06	1.0206	16.34	1.0215	1.0128	16.06	1.0222	1.0063	15.7	1.0238	0.9954	15.25	1.0212
0.07	1.0239	16.50	1.0243	1.0178	16.16	1.0268	1.0104	15.76	1.0280	1.0013	15.30	1.0264
0.08	1.0283	16.62	1.0279	1.0217	16.29	1.0295	1.0145	15.84	1.0317	1.0047	15.47	1.0289
0.09	1.0324	16.73	1.0312	1.0250	16.34	1.0329	1.0193	15.96	1.0357	1.0094	15.56	1.0333
0.1	1.0362	16.83	1.0341	1.0301	16.42	1.0379	1.0228	16.09	1.0375	1.0129	15.65	1.0360
X_{2EE} = 0.0765												
0.01	0.9762	14.60	1.0015	0.9699	14.26	1.0021	0.9605	13.81	1.0002	0.9529	13.34	0.9996
0.02	0.9818	14.71	1.0068	0.9747	14.39	1.0058	0.9657	13.94	1.0042	0.9560	13.40	1.0024
0.03	0.9864	14.85	1.0097	0.9794	14.46	1.0106	0.9713	14.06	1.0091	0.9606	13.56	1.0048
0.04	0.9926	14.97	1.0156	0.9838	14.56	1.0142	0.9757	14.16	1.0127	0.9658	13.71	1.0084
0.05	0.9973	15.04	1.0204	0.9888	14.63	1.0194	0.9777	14.25	1.0134	0.9714	13.71	1.0137
0.06	1.0016	15.12	1.0243	0.9932	14.73	1.0230	0.9833	14.36	1.0188	0.9766	13.92	1.0182
0.07	1.0055	15.18	1.0283	0.9980	14.85	1.0270	0.9891	14.44	1.0248	0.9810	14.06	1.0209
0.08	1.0111	15.43	1.0304	1.0029	14.92	1.0320	0.9939	14.51	2.2186	0.9861	14.16	1.0257
0.09	1.0158	15.52	1.0348	1.0083	15.04	1.0367	0.9985	14.68	1.0326	0.9905	14.32	1.0279
0.1	1.0202	15.61	1.0389	1.0119	15.13	1.0394	1.0039	14.77	1.0373	0.9944	14.39	1.0315
X_{2EE} = 1.0000												
0.01	0.9419	13.49	1.0002	1.0397	13.66	1.0034	0.9276	12.09	1.0045	0.9203	11.67	1.0058
0.02	0.9481	12.89	1.0023	0.9411	12.54	1.0080	0.9320	12.17	1.0082	0.9239	11.71	1.0087
0.03	0.9541	12.99	1.0082	0.9460	12.60	1.0138	0.9380	12.26	1.0152	0.9293	11.82	1.0145
0.04	0.9594	13.23	1.0094	0.9522	12.70	1.0194	0.9445	12.35	1.0206	0.9349	11.95	1.0212
0.05	0.9637	13.38	1.0119	0.9585	12.80	1.0246	0.9496	12.46	1.0256	0.9414	12.09	1.0300
0.06	0.9710	13.49	1.0191	0.9642	13.06	1.0312	0.9551	12.66	1.0310	0.9471	12.29	1.0351
0.07	0.9761	13.59	1.0240	0.9695	13.19	1.0369	0.9605	12.77	1.0363	0.9522	12.38	1.0407
0.08	0.9813	13.71	1.0280	0.9752	13.34	1.0440	0.9662	12.90	1.0425	0.9575	12.45	1.0453
0.09	0.9878	13.87	1.0333	0.9802	13.47	1.0494	0.9725	13.03	1.0498	0.9636	12.58	1.0509
0.1	0.9938	13.99	1.0386	0.9862	13.57	1.0547	0.9782	13.15	1.0554	0.9698	12.72	1.0565

Apparent Molar Compressibility (ϕ_k):

Apparent molar compressibility was calculated using the equation (6) is a function of concentration as suggested by Gucker [25] as follows

$$\phi_k = \phi_k^0 + S_k \sqrt{C} \quad (9)$$

Where ϕ_k^0 is the limiting apparent molar compressibility and S_k is obtained from the intercept of the linear plot (Fig. 1) of ϕ_k versus $\sqrt{C}$, and association constant S_k is the experimental slope. The limiting apparent compressibility (ϕ_k^0) and related constant S_k values obtained are provided in Table 3. Most of the negative values of ϕ_k^0 strengthen the view that there exist solute-solvent interactions in the system and the loss of compressibility of solvent due to electrostrictive solvation [22]. The positive S_k values signify the existence of ion-ion interaction of the system and also structure breaking property of the electrolyte.

Table 3. Computed limiting apparent molar compressibility (ϕ_k^0 ; $\text{m}^2 \text{mol}^{-1}$) and the slope S_k for KSCN in 2 - ethoxyethanol + water mixtures at different temperatures.

X_{2EE}	TEMPERATURE							
	288.15K		298.15K		308.15K		318.15K	
	10¹⁵ ϕ_k^0	10¹⁵ S_k	10¹⁵ ϕ_k^0	10¹⁵ S_k	10¹⁵ ϕ_k^0	10¹⁵ S_k	10¹⁵ ϕ_k^0	10¹⁵ S_k
0.0000	-223.00	47.50	-518.20	309.00	-339.50	279.00	-94.55	68.10
0.0023	-609.30	442.30	-530.20	431.20	644.80	-880.00	-122.90	37.98
0.0052	-1022.00	927.80	-902.20	847.10	-401.40	446.00	-376.30	401.90
0.0136	2989.00	-2503.00	-929.00	856.10	975.00	-959.00	1021.00	-994.90
0.0301	-455.20	357.20	102.40	-131.50	-973.00	816.70	150.20	-140.00
0.0765	-103.20	-41.75	-234.70	140.40	-842.00	729.80	-609.30	326.30
1.0000	-1664.00	150.90	-2249.00	416.10	-2391.00	444.40	-1829.00	-53.16

Apparent Molar Volume (ϕ_v)

The apparent molar volume ϕ_v is calculated using the equation 7. The relation between apparent molar compressibility and $\sqrt{C}$ is given by least squares method as,

$$\phi_v = \phi_v^0 + S_v \sqrt{C} \quad (10)$$

The linear plot of apparent molar volume (ϕ_v) versus $\sqrt{C}$ is shown in Fig. 2. The intercept and slope obtained from this gives limiting apparent molar volume (ϕ_v^0) and its related constant S_v . Computed molar volume (ϕ_v^0) and S_v values are presented in Table 4. The preferential solvation of the ions by different species in the solvent system and type of interaction between solvent molecules are due to change in partial molar volume with respect to change in compositions of solvent mixtures. The positive ϕ_v^0 in all the compositions of solvent strengthens the strong ion-solvent interactions. Negative S_v values are interpreted as a sign of weak ion-ion interaction and also gives information about inter ionic penetration of the ions in the solvent structure [26]. Relatively lower ϕ_v^0 values for potassium thiocyanate in solvent mixture were found at $X_{2EE}=0.0052$, implying strong solvent-solvent interaction. In the present work, larger ϕ_v^0 values substantiate strong ion-solvent interactions.

Table 4. Computed limiting apparent molar volume ($(\phi_v^0; \text{m}^3 \text{mol}^{-1})$) and the slope S_v for KSCN in 2-ethoxyethanol + water mixtures at different temperatures

X_{2EE}	TEMPERATURE							
	288.15K		298.15K		308.15K		318.15K	
	$10^6 \phi_v^0$	$10^6 S_v$	$10^6 \phi_v^0$	$10^6 S_v$	$10^6 \phi_v^0$	$10^6 S_v$	$10^6 \phi_v^0$	$10^6 S_v$
0.0000	61.45	-928.00	61.38	-7.33	31.87	-9.69	86.13	-33.43
0.0023	63.64	-41.19	61.78	-25.58	61.90	-23.84	64.48	-26.29
0.0052	44.84	26.02	62.16	-29.89	72.17	-61.89	63.07	-21.98
0.0136	71.85	-60.05	69.34	-40.87	86.15	-83.83	111.40	-153.00
0.0301	56.36	-9.17	66.25	-33.48	48.65	18.62	64.91	-24.12
0.0765	64.25	-41.58	51.57	1.23	57.81	-13.65	80.39	-89.38
1.0000	324.90	-124.40	285.60	3.86	304.00	-49.33	302.90	-31.44

Solvation Number (S_n):

Solvation number (S_n) of an ion is the number of solvent molecules surrounded to that ion which loses entire translational degree of freedom and always moves along with the ion. The theory proposed by Passynski [27] was used for calculating solvation numbers (equation 8). The computed values of S_n values for KSCN in 2-ethoxyethanol+water mixture at 298.15K are presented in Table 5. The S_n values are found to initially increase followed by a later decrease as the amount of 2-ethoxyethanol is increased in the mixture. Strong solute-solvent interaction is observed at $X_{2EE} = 0.0052$ since the highest S_n values were found at this composition.

Table 5. Calculated solvation number (S_n) for KSCN in 2-ethoxyethanol + water mixtures at different temperatures

C	X_{2EE}						
	0.0000	0.0023	0.0052	0.0136	0.0301	0.0765	1.0000
0.1	-2.0	-5.1	24.7	-1.0	-0.6	2.1	2.3
0.2	2.5	0.6	12.9	0.7	1.1	2.3	2.7
0.3	2.1	1.2	9.0	1.9	1.5	1.8	2.1
0.4	3.4	2.1	7.0	2.3	1.6	1.9	1.9
0.5	4.1	2.2	5.8	1.9	1.9	1.7	1.6
0.6	4.6	2.4	5.0	1.8	1.7	1.7	1.9
0.7	4.0	3.2	4.5	2.1	1.7	1.7	1.9
0.8	4.7	3.2	4.0	2.0	2.0	1.7	1.8
0.9	5.3	3.7	3.7	2.0	1.8	1.7	1.8
1.0	4.5	3.7	3.3	2.0	1.8	1.7	1.7

VI. Conclusions

Various ultrasonic parameters calculated have been effectively used to explain the ion-ion, ion-solvent and solvent-solvent interactions in the system comprising of potassium thiocyanate, 2-ethoxyethanol and water. Ultrasonic studies revealed that the ternary system involves strong solvent-solvent interactions at $X_{2EE} = 0.0136$ as a result of formation of hydrophobic aggregations. The positive S_k values specify the structure breaking nature of KSCN in 2-ethoxyethanol+water media. Highest solvation number was observed at $X_{2EE} = 0.0052$ indicating strong solute-solvent interactions for KSCN in 2-ethoxyethanol + water system at 298.15K.

Figure 1. Plot of ϕ_k ($\text{m}^2 \text{mol}^{-1}$) Vs $\sqrt{C}$ ($\text{mol}^{1/2} \text{dm}^{-3/2}$) for KSCN in 2-ethoxyethanol + water mixture at different Temperatures

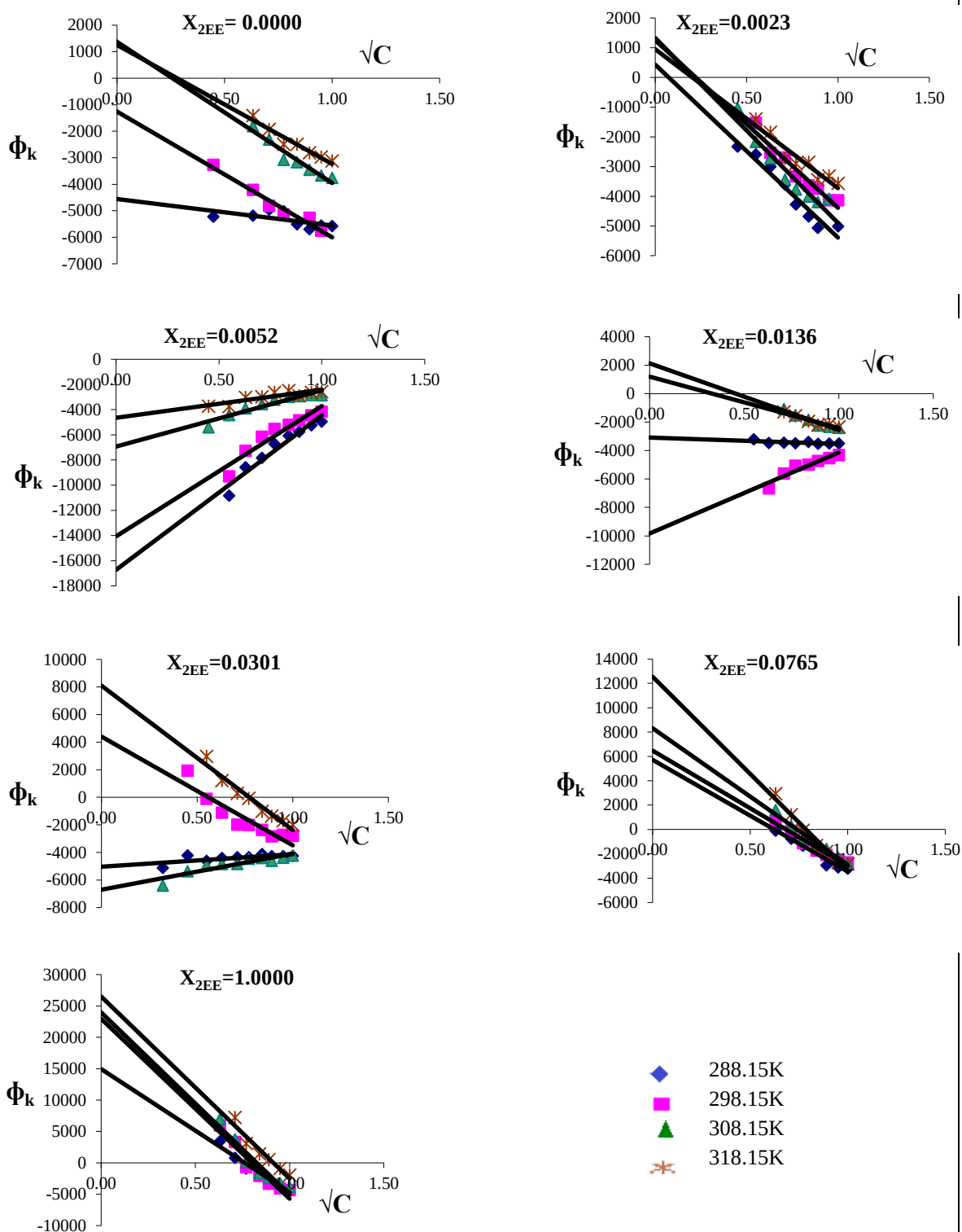
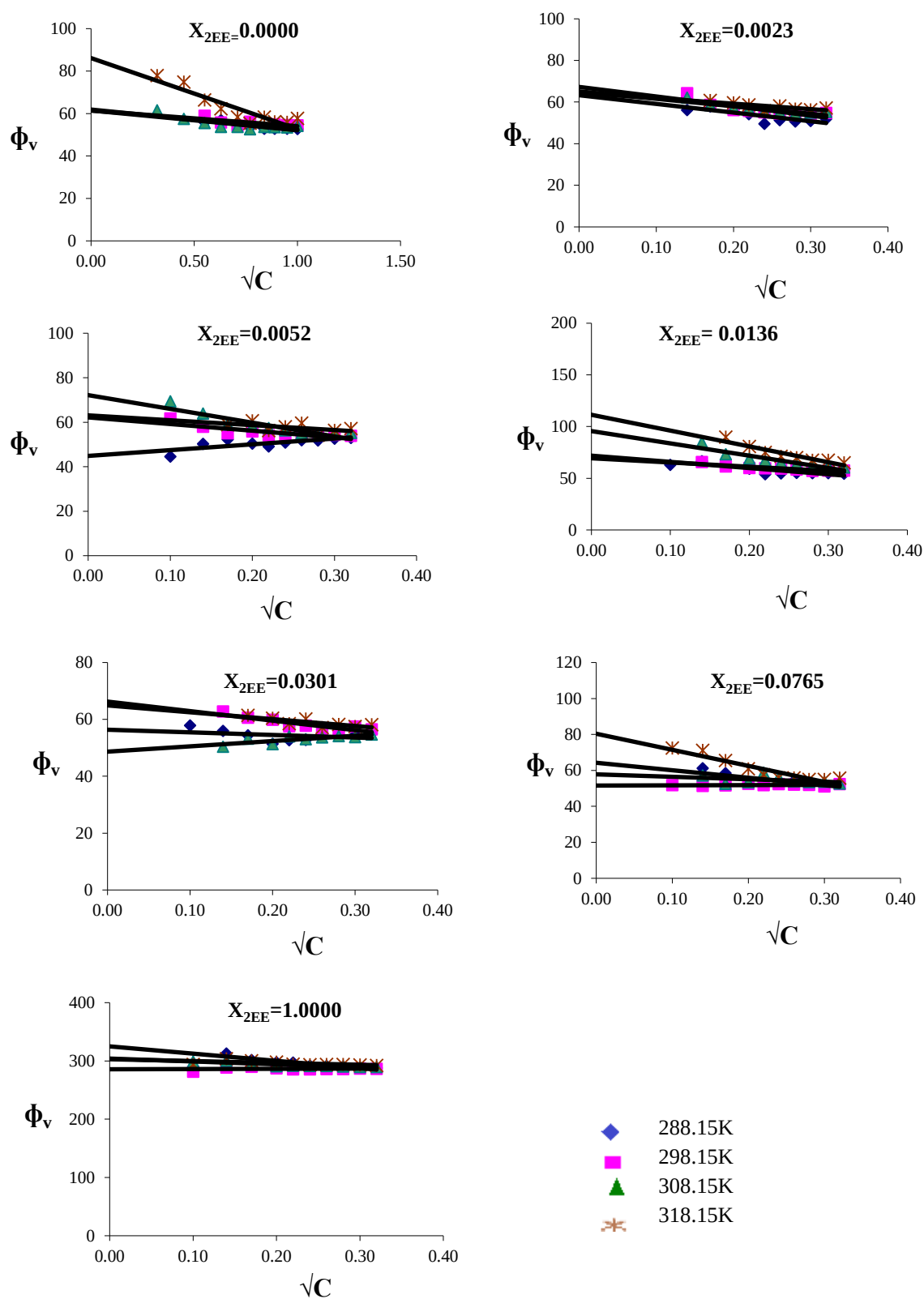


Figure2. Plot of ϕ_v ($\text{m}^3 \text{mol}^{-1}$) Vs $\sqrt{C}$ ($\text{mol}^{1/2} \text{dm}^{-3/2}$) for KSCN in 2-ethoxyethanol + water mixture at different Temperatures



V. References

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