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Intermolecular/interionic interactions in leucine-, NaCl-, and KCl–aqueous urea systems

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Abstract

In view of the presence of Na^+ and K^+ ions as metal complexes of proteins and nucleic acids in our body and their physiological importance, the ultrasonic velocity and its derived parameters were employed to investigate the solute–solvent and ion–solvent interactions in leucine–aqueous urea, NaCl–aqueous urea, and KCl–aqueous urea systems. The presence of short-lived clusters of water flickering among them was employed to understand the solute–solvent interactions. The successive increases in solute concentration resulted in increasing the ultrasonic velocity, specific acoustic impedance, internal pressure, and solubility parameter. Similarly, the corresponding decreases exhibited by the compressibilities and pseudo-Gruneisen parameters suggest an increase in the solute–solvent interactions. The change and the relative change in adiabatic compressibility with solute concentration suggest an almost ideal behaviour. The structure of leucine–aqueous urea may consist of a mixture of several probable zwitterionic/native leucine entities, which are associated with flickering clusters of water. The water clusters of the bulk experiencing weak influence of the latter surround these, in turn, followed by successive sheaths of a large number of hydrogen-bonded water molecules/clusters. The field of influence caused by specific interaction dies out in the successive sheaths with distance. Such a field of influence affecting the extent of interaction may increase with successive increases in solute concentration. This seems to be due to the close proximity of the interacting entities. Successive increases in temperature brings the structural entities close to each other as a result of increased thermal/kinetic motion. The structures of sodium and potassium chlorides in their solutions differ in being surrounded in their first spheres by relatively fewer or more of flickering water clusters due to their ionic size differences. Urea and KCl contribute more in disrupting the H-bonds compared to NaCl–aqueous urea in which only urea disrupts the hydrogen bonds. On the other hand, the chloride ions may be present in their probable clusters, $Cl^{-}\text{-}(H_2O)_{n=1-10}$ and swim in the bulk along with the said cationic structures.

Keywords: Intermolecular interaction; Interionic interaction; Leucine–aqueous urea; NaCl–aqueous urea; KCl–aqueous urea

1. Introduction

There has been a lot of active interest in the study of intermolecular/interionic interactions [1–7], such as solute–solute, solute–solvent, ion–ion, ion–solvent, and solvent–solvent interactions. A lot of work has been reported involving the bio-molecules. Urea is a bio-molecule, a non-electrolyte and hydrophilic water structures breaker [8–10] and is physiologically important compound. Aqueous urea and its derivatives are important solvents and have a wide range of applications [11]. It causes protein and nucleic acid denaturation. Specific interactions of urea with a molecule or changes in the solvent structure may be responsible for the denaturation process. Frank and Franks [12] considered urea as a structure breaker in its aqueous solution. According to them the properties of water–urea mixtures do not exhibit very marked deviations from ideal behaviour. The experimental results are consistent with the contention that there is no great difference between urea and water in the manner in which they interact with other water molecules.

A molecular dynamics calculation has indicated that a urea molecule can enter into the water structure without breaking it noticeably [13]. Thus, it is difficult to classify urea into a structure maker or a breaker. There remains the bulk region of water even in a solution of 7.4 mol% of urea. Singh and Ram [14] in their studies of the effects of urea,

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its concentration and temperature on water structure have attributed their results to the formation of dimer and trimer of urea molecules, the stability of which in water seems to be affected significantly by temperature.

Ions in aqueous solutions exist in hydrated forms. Ionic hydration in NaCl solutions has been reported recently [5].[1] The process of solvation of ions depends upon the ion–dipole interaction and also on the polarisability of the solvent molecules in ionic fields. The ion–dipole interactions are relatively powerful forces, especially when compared with the H-bonding that maintains the structure of water. The water molecules are so tightly held that along with the ion they become a new kinetic entity. The molecules in this solvent sheath are often referred to as immobilised or non-rotational water, because of the complete loss of freedom.

In respect of halide ions in aqueous solutions, $Cl^-(H_2O)_{n=1–4}$ clusters are reported recently [15–31]. The incremental-binding enthalpies for the clusters $I^-–(H_2O)_{n=1–10}$, as well as the hydration enthalpy and the structural property for a single iodide ion in water, were computed and compared with the available experimental data.

The hydrophobic effects considered earlier by Tanford et al. [32] while considering the solubility of amino acids and related compounds may also be viewed in the light of the recently reported [33–37] structural aspects in which the hydration shell structure for oxygen in dilute aqueous solution having a planar pentagonal $(H_2O)_5$ is evidenced. Such considerations may help in understanding the solution structure. Volume and adiabatic compressibility of aminoacids in urea–water mixtures were also studied earlier [2]. In addition, the role of metal ions in metabolic processes is well known. The alkali-metal chlorides particularly NaCl and KCl are physiologically important. Sodium and potassium ions maintain the osmotic pressure of the body fluid and protect the body from excessive fluid loss and regulate the potential across the cell membrane. The concentration of these ions also plays an important role.

The presence of several equilibria among the short-lived clusters of water [16–30] such as decamer, nanomer, octamer, hexamer, pentamer, tetramer, trimer, dimer, and monomer flickering among themselves under the varying conditions of temperature and solute (structure maker or breaker) concentration involving planar or three-dimensional entities is well known. These aspects led to select it as a solvent. Its solvation behaviour may be enhanced or diminished by the controversial role of urea in disrupting the H-bondings or weakly enhancing the network structure of water. The urea–water interactions on occasions seem similar to those of water–water interactions and exhibit an almost ideal behaviour which, otherwise, is envisaged as a non-ideal mixed solvent system because of the presence of an extensive interaction leading to self association of urea like water besides urea–water interactions. In addition, the structure-making and breaking roles of sodium and potassium ions, respectively, as well as the zwitterion formation and its interaction with the urea–water mixture led to select the NaCl/KCl/leucine–aqueous urea systems for the present investigation. Consequently, an almost ideal or weakly non-ideal behaviour in interactions may be studied. The ultrasonic velocity and its derived parameters provide fruitful information regarding the nature of intermolecular/interionic interactions. Consequently, in view of the above, an effort is being made to investigate the solute–solvent and ion–solvent interactions in leucine–aqueous urea, NaCl–aqueous urea, and KCl–aqueous urea systems.

2. Experimental

Materials and Methods: leucine (S.R.L., Bombay), sodium chloride, potassium chloride (S.D. Fine Chemicals, Boisar) and urea (Qualigens Fine Chemicals) were used. Potassium chloride was recrystallised. An extra pure sodium chloride, urea, and leucine were used. A stock solution of 0.1 M urea was prepared in triple distilled water. The ternary mixtures of several concentrations of leucine, NaCl and KCl were prepared in 0.1 M urea solution. All the solutions were prepared by weight for obtaining the concentration on the molal scale. The concentration ranged from 0.01 to 0.1 M in the case of leucine and from 0.1 to 0.9 M in those of NaCl and KCl solutions.

The pyknometer and a multifrequency ultrasonic interferometer (Mittal's model M-83; at a frequency of 4 MHz) were calibrated using triple distilled water before being used for the measurements of density and ultrasonic velocity, respectively [38]. Thermostated paraffin/water bath (Type U-10, Germany) was used to maintain a uniform temperature (±0.01°) by allowing 30 min waiting period after attaining the desired temperature prior to actual recording of data at each temperature of study. Several very close readings recorded at each temperature were averaged. The density of water at different temperatures required for calibration was obtained by using the standard equation [39]: $\rho_t = (1.000525–2) \times 10^{-5} t\,(°\mathrm{C}) - 4.72 \times 10^{-6} t^2$. The experimental values of densities of these systems have been least squares fitted to two- as well as three-parameters' equations: $\rho = a + bT$ and $\rho = a + bT + cT^2$ in which ρ is the density, T the temperature in Kelvin while a, b and c the constants for obtaining the densities at the desired temperatures. Similarly, the ultrasonic velocities were least squares fitted to the relevant equations. The uncertainties in the measurement of density and ultrasonic velocity were $\pm 0.2\,\mathrm{kg\,m^{-3}}$ and $\pm 0.2\,\mathrm{m\,s^{-1}}$, respectively.

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[1] Three sheaths of water may surround an ion. First there is a primary hydration sheath consisting of non-rotational solvent molecules that move as the ion itself moves. As the distance from the ion increases, a secondary hydration sheath surrounds the first one. There is a partial ionic and solvent structural influence in the secondary hydration sheath. Finally, the third layer is the bulk solvent itself and essentially feels no local force related to the ion.

Table 1
Density (ρ, $\times10^{-3}\,\mathrm{kg\,m^{-3}}$) of (a) leucine, (b) NaCl, and (c) KCl each in 0.1 M aqueous urea solution as functions of concentration (molality, *m*) and temperature (K)

m	*T* (K)				
	298.15	303.15	308.15	313.15	318.15
(a) Leucine					
0.00	0.9982	0.9966	0.9949	0.9931	0.9911
0.01	0.9987	0.9972	0.9955	0.9937	0.9917
0.02	0.9991	0.9976	0.9959	0.9941	0.9921
0.03	0.9994	0.9979	0.9963	0.9945	0.9925
0.04	0.9996	0.9981	0.9964	0.9946	0.9927
0.05	0.9998	0.9982	0.9965	0.9947	0.9928
0.06	1.0005	0.9991	0.9974	0.9955	0.9934
0.07	1.0007	0.9992	0.9975	0.9956	0.9935
0.08	1.0010	0.9995	0.9978	0.9959	0.9938
0.09	1.0014	0.9998	0.9981	0.9962	0.9942
0.10	1.0019	1.0004	0.9987	0.9967	0.9946
(b) NaCl					
0.10	1.0073	1.0072	1.0061	1.0043	1.0016
0.20	1.0258	1.0259	1.0250	1.0230	1.0198
0.40	1.0264	1.0265	1.0257	1.0240	1.0213
0.70	1.0381	1.0370	1.0349	1.0317	1.0275
0.80	1.0488	1.0479	1.0464	1.0441	1.0412
0.90	1.0483	1.0478	1.0464	1.0440	1.0407
(c) KCl					
0.10	1.0200	1.0204	1.0196	1.018	1.0153
0.20	1.0196	1.0196	1.0186	1.0166	1.0136
0.30	1.0249	1.0248	1.0238	1.0219	1.0190
050	1.0294	1.0312	1.0317	1.0307	1.0283
0.70	1.0420	1.0435	1.0440	1.0435	1.0419
0.90	1.0487	1.0496	1.0495	1.0486	1.0468

3. Results and discussion

Densities and ultrasonic velocities of the three systems are listed in Tables 1–4, respectively.

It is noteworthy that both of these equations to which the densities and ultrasonic velocities were fitted turn out to be equally good in reproducing the experimental results in the above three system. Such a behaviour may be attributable to dilute nature of these solutions as well as to apparently their ideal nature as discussed below.

The values of ultrasonic velocity are found to increase with increases in temperature and solute concentration. Such an increase may be attributed to an increase in the intermolecular interaction between the leucine–aqueous urea [2], NaCl–aqueous urea and KCl–aqueous urea solutions. The adiabatic compressibility, β_s and the specific acoustic impedance, Z were evaluated by using the experimental values of densities and ultrasonic velocities [40]:

$$\beta_s = \frac{1}{\rho u^2} \qquad (1)$$

$$\beta_{so} = \frac{1}{\rho_o {u_o}^2} \qquad (2)$$

$$Z = u\rho \qquad (3)$$

$$\Delta\beta = \beta_s - \beta_{so} \qquad (4)$$

$$\Delta\beta_{rel} = \frac{\Delta\beta}{\beta_{so}} \qquad (5)$$

in which u stands for the ultrasonic velocity, ρ the density, Z the specific acoustic impedance while β_s and β_{so} are the adiabatic compressibilities of solution and solvent, respectively. In the present studies β_s is taken as the adiabatic compressibility of each of the three solutions, i.e., leucine or NaCl or KCl each dissolved in 0.1 M urea solution while β_{so} as the adiabatic compressibility of 0.1 M urea solution. $\Delta\beta$ and $\Delta\beta_{rel}$ were the change and the relative change in adiabatic compressibility.

With a view to understand the ultrasonic velocity behaviour of these systems, one of the abnormal properties of water in respect of its variation with temperature may be recalled. For example, it attains a maximum value of $1557\,\mathrm{m\,s^{-1}}$ at 74 °C. The adiabatic compressibility of water shows a minimum at 64 °C. In addition, the temperature of maximum ultrasonic velocity in water is changed by the presence of ions [41–43]. Thus, from the effects of ions on the velocity and compressibility of water it is possible to obtain some information with regard to providing the ion–water interactions. These results are discussed on the basis of the dynamic structure of water around the cations. The ultrasonic velocity in the salt solutions of alkali metal chlorides has been found to decrease in the order: NaCl > LiCl > KCl > RbCl > CsCl. Also, the values of compressibility for the salt solutions are found to be lower than that of water and the order of magnitude differs in different concentrations. These values for LiCl, RbCl, and CsCl solutions do not differ markedly from one another. From these results it seems difficult to connect directly the velocity and compressibility with the structure of solutions [44,45]. However, the lower values of compressibility of aqueous electrolytic solutions found to be smaller than that of pure water may be ascribed to two effects [44]: (1) the decrease of compressibility caused by the introduction of incompressible ions, and (2) the change of water structure around the ion. According to Desnoyer and Jolicoeur [46] the strength of ion–solvent interactions decreases with increasing size of the ions, but the coordination number of the ion increases with increasing size. The x-ray and neutron scattering results indicate that the coordination number of alkali metal ions are 4 for Li^+, Na^+, and K^+ ions [47] while 8 for Cs^+ ion [48].

Since the coordination number of water molecule around sodium ion is 4, the water structure around Na^+ ion is like that of pure water. The decrease in compressibility of sodium chloride solution is mainly caused by the dilution effect. Sodium and potassium ions interact weakly with water molecules and their effects are directly opposite to each other. An ion when added to water affects the thermal motion of water molecules around it. The sodium ion is found to be a weak structure-making ion [47], i.e., no disordered water molecules exist outside the reoriented water molecules around the Na^+ ion. The K^+ ion, on the other

Table 2
Best-fit parameters for the density equations: $\rho = a_0 + a_1 t$ and $\rho = a_0 + a_1 t + a_2 t^2$

Temperature (K)	a_0	a_1	a_2	S.D.	R
(i) Leucine in 0.1 M aqueous urea solution					
$\rho = a_0 + a_1 t$					
298.15	0.99828	0.035		0.00012	0.99533
303.15	0.99675	0.03518		0.00017	0.99081
308.15	0.99507	0.035		0.00018	0.98972
313.15	0.9933	0.03318		0.00016	0.99047
318.15	0.99134	0.03209		0.00014	0.99218
$\rho = a_0 + a_1 t + a_2 t^2$					
298.15	0.99832098	0.032086247	0.029137529	0.00012	0.9956
303.15	0.99675847	0.034599068	0.0058275058	0.00018	0.99082
308.15	0.99506643	0.035116550	−0.0011655012	0.00019	0.98972
313.15	0.99326783	0.035629371	−0.24475524	0.00017	0.99068
318.15	0.99127273	0.036636364	−0.045454545	0.00014	0.99296
(ii) Sodium chloride in 0.1 M aqueous urea solution					
$\rho = a_0 + a_1 t$					
298.15	1.00886	0.04566		0.0055	0.95101
303.15	1.00907	0.04447		0.0056	0.94672
308.15	1.00825	0.04354		0.00578	0.94129
313.15	1.00656	0.04249		0.00593	0.93598
318.15	1.00378	0.04175		0.00606	0.93107
$\rho = a_0 + a_1 t + a_2 t^2$					
298.15	1.0059268	0.064355143	−0.01877272786	0.00617	0.95374
303.15	1.0061930	0.062826693	−0.018428385	0.0063	0.94948
308.15	1.0054153	0.061630729	−0.018161458	0.00652	0.94408
313.15	1.0039099	0.059402734	−0.016980469	0.0067	0.93852
318.15	1.0014252	0.056743164	−0.015048828	0.00689	0.93313
(iii) Potassium chloride in 0.1 M aqueous urea solution					
$\rho = a_0 + a_1 t$					
298.15	1.01348	0.03842		0.00242	0.98365
303.15	1.01352	0.03999		0.00233	0.98595
308.15	1.01246	0.04164		0.00242	0.9861
313.15	1.01042	0.04325		0.0027	0.98398
318.15	1.00726	0.04494		0.00298	0.98194
$\rho = a_0 + a_1 t + a_2 t^2$					
298.15	1.0168185	0.018394285	0.020132730	0.00219	0.99001
303.15	1.0161272	0.024370987	0.015701124	0.00233	0.98954
308.15	1.0143674	0.030215990	0.011486571	0.00261	0.98788
313.15	1.0121280	0.033013242	0.010293567	0.00299	0.9853
318.15	1.0090455	0.034245440	0.010747970	0.00332	0.98327

hand, is a weak structure-breaking ion. The structure breaking ions increase the thermal motion of water molecules [47]. According to Samiolov, surface density of the distribution of water molecules around the ion decreases as the ionic radius increases. Thus K^+, a structure-breaking ion causes the compressibility of the KCl in aqueous urea solution to increase in comparison to that of the NaCl in a similar aqueous urea solution. Also, the addition of incompressible ions results in decreasing the compressibility of the solution. Thus, the lowering of adiabatic compressibility of NaCl–aqueous urea solution is slightly more than that shown by KCl–aqueous solution. The standard partial molal compressibilities of sodium and potassium chlorides and bromides as well as apparent molal compressibility of NaCl were reported earlier [3–7] in their aqueous solution.

The volume and compressibility behaviour of solutes in solution can provide information concerning the solute–solvent and the solute–solute interactions. Apparent molal volume has been used to investigate the structural interactions in solutions. The concentration dependence of apparent molal volume and the partial molal volume has been used to study the solute–solute interactions. Volumetric and compressibility studies of leucine have been made by Millero et al. [49], in which the infinite dilution partial molal volume (ϕ_v^0) is reported to be 107.74 cm^3/mol. This value of ϕ_v^0 has been found to be very close to the other reported values, viz., 107.5 [50], 108 [51], and 107.75 [52]. Hakin et al. [53] calculated the standard state volume (partial molal volume) and heat capacity values by using a semi-empirical model proposed by Helgeson and coworkers (HKF model) [54]. At 298.15 K the experimental and calculated standard

Table 3
Ultrasonic velocity (u, m s^{-1}) of (a) leucine, (b) NaCl, and KCl each in 0.1 M aqueous urea solution as functions of concentration (molality, m) and temperature (K)

m	Temperature (K)				
	298.15	303.15	308.15	313.15	318.15
(a) Leucine					
0.00	1499.6	1510.9	1521.3	1531.0	1539.9
0.01	1503.0	1513.4	1521.8	1529.0	1537.4
0.02	1504.4	1514.2	1522.6	1530.4	1538.4
0.03	1505.0	1515.4	1523.8	1532.0	1539.8
0.04	1506.4	1516.4	1525.0	1534.0	1541.0
0.05	1507.8	1518.4	1527.0	1536.1	1543.0
0.06	1509.8	1520.0	1528.8	1537.4	1544.4
0.07	1511.0	1521.0	1530.0	1538.7	1545.0
0.08	1512.8	1522.2	1531.0	1540.2	1546.4
0.09	1515.0	1523.4	1531.8	1541.2	1548.3
0.10	1516.9	1524.3	1533.4	1543.2	1549.7
(b) NaCl					
0.0	1499.6	1510.9	1521.3	1531.0	1539.9
0.1	1506.7	1518.4	1528.8	1537.7	1545.3
0.2	1510.8	1520.9	1530.5	1539.6	1548.3
0.3	1511.5	1525.7	1537.9	1548.1	1556.2
0.4	1525.0	1536.9	1546.9	1555.0	1561.1
0.5	1527.5	1537.7	1546.9	1555.1	1562.2
0.6	1535.7	1544.6	1553.1	1561.2	1569.0
0.7	1542.5	1551.6	1559.7	1566.8	1572.8
0.8	1553.3	1563.7	1572.0	1578.3	1582.5
0.9	1552.3	1561.4	1569.7	1577.2	1584.0
(c) KCl					
0.0	1499.6	1510.9	1521.3	1531.0	1539.9
0.1	1512.6	1523.2	1531.3	1536.7	1539.4
0.2	1510.4	1522.5	1532.8	1541.5	1548.5
0.3	1520.4	1527.2	1535.1	1544.5	1555.2
0.5	1533.4	1540.2	1546.9	1553.5	1560.0
0.7	1543.2	1548.6	1554.8	1561.9	1569.6
0.9	1554.6	1559.5	1564.9	1570.8	1577.3

state volume are obtained as 106.81 and 105.97 cm^3/mol, respectively. In the present case of leucine–aqueous urea system, the value is around 107–108 cm^3/mol.

The results of adiabatic compressibility of the systems under investigation are displayed in Table 5. The adiabatic compressibility is found to decrease with increases in temperature and concentration. Such a decrease may be attributed to an increase in the ion–ion interaction as well as to the corresponding increase in the number of incompressible ions with an increase in solute/salt concentration. Another reason for the decrease in the adiabatic compressibility may be due to a change in the structure of water around the ions. The lowering of adiabatic compressibility of leucine–aqueous urea solution is slightly more than that shown by the NaCl–aqueous urea solution, which in turn, is slightly more than that shown by the KCl–aqueous urea solution.

The change in adiabatic compressibility is found to decrease with increase in temperature and increase with increase in concentration. At low temperature (298.15 K), weak interaction seems to be present while at other slightly higher temperatures apparently linear plots approaching in the vicinity of zero intercept value indicate an almost ideal behaviour. Even though the relative change in adiabatic compressibility, $\Delta\beta_{\text{rel}}$ follows the same pattern of behaviour as exhibited by the change in adiabatic compressibility, $\Delta\beta$; the tendency of the systems to approach/exhibit an almost ideal behaviour is somewhat improved.[2] The earlier studies on apparent molal compressibilities of sodium and potassium chlorides and bromides cited above [3–7] may be compared with the present investigation.

The values of specific acoustic impedance, Z, given in Table 6, indicate increase with increases in temperature and concentration. In the case of leucine, the increase in the value of Z may perhaps be attributed to an apparent reduction in the repulsive forces (dissociation) with increase in temperature. The trend in the behaviour of Z with variations in temperature and solute concentration is consistent with that shown by the ultrasonic velocity. This reinforces the conclusions drawn above.

The isothermal compressibility was obtained by using the relation [55]:

$$\beta_{\text{T}} = \frac{1.33 \times 10^{-8}}{(6.4 \times 10^{-4} u^{3/2} \rho)^{3/2}} \tag{6}$$

This equation was obtained by Pandey et al. [55] by combining the Mc-Gowan's relationship between β_{T} and surface tension [56] and that of Auerbach's relation between speed of sound and surface tension [57]. Using the experimental values of density and ultrasonic velocity, the isothermal compressibility of leucine, sodium, and potassium chloride solutions in 0.1 M urea have been evaluated (Table 7). The overall trend in the isothermal compressibility has been found to be decreasing with increase in concentration as well as in temperature. The decrease in the values of isother-

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[2] In view of the behaviour of changes as well as the relative changes in adiabatic compressibility, an attempt is made to examine the extent of deviation from an apparently ideal behaviour by modifying the earlier equations as follows:

$$\beta = \beta_{\text{so}} + Sm \quad \text{or} \quad \beta_{\text{s}} - \beta_{\text{so}} = Sm$$

in which β_{so}, the adiabatic compressibility of the solvent (here 0.1 M aqueous urea solution) is the intercept while S is the slope of β_{s} versus m (molality of solute) plot. Since the plots do not pass through the origin, it was modified as $\Delta\beta_{\text{s}} = Sn'm$ in which n' is an arbitrary parameter the inclusion of which eventually gave the linear plots of β_{s}versus $n'm$. Similarly, the relative change in adiabatic compressibility was obtained as follows:

$$\beta_{\text{s}} = \beta_{\text{so}} m_{\text{so}} \quad \text{or} \quad (\beta_{\text{s}}/\beta_{\text{so}}) - 1 = m_{\text{so}} - 1 = m.$$

The above may also be expressed as $(\beta_{\text{s}} - \beta_{\text{so}})/\beta_{\text{so}} = m^n$ by including n arbitrarily in order to evaluate the extent of deviation in the plots of $\Delta\beta_{\text{s}}/\beta_{\text{so}}$ against m. The values of n' and n thus obtained seem to be a measure of the extent of deviation from ideal behaviour on a pattern similar to the activity coefficient in thermodynamic studies, which, in turn, may be viewed as a measure of the extent of weak interaction in the systems under investigation.

Table 4
Best-fit parameters for the ultrasonic velocity equations: $u = u_0 + u_1 t$ and $u = u_0 + u_1 t + u_2 t^2$

Temperature (K)	u_0	u_1	u_2	S.D.	R
(i) Leucine in 0.1 M aqueous urea solution					
$u = u_0 + u_1 t$					
298.15	1500.37727	159.18182		0.63579	0.99354
303.15	1511.51818	132.54545		0.4077	0.99615
308.15	1520.50455	129.0		0.50515	0.99379
313.15	1528.65455	141.81818		1.01055	0.97985
318.15	1537.1	118.54545		1.16803	0.9625
$u = u_0 + u_1 t + u_2 t^2$					
298.15	1500.7007	137.62005	215.61772	0.63632	0.99425
303.15	1511.2105	153.05828	−205.12821	0.37666	0.99708
308.15	1520.7056	115.59674	134.03263	0.51746	0.9942
313.15	1529.2804	100.09324	417.24942	0.98089	0.98316
318.15	1538.2538	41.622378	769.23077	0.94879	0.97818
(ii) Sodium chloride in 0.1 M aqueous urea solution					
$u = u_0 + u_1 t$					
298.15	1498.28727	62.67273		3.04991	0.98871
303.15	1510.38182	59.55152		2.90796	0.98864
308.15	1521.32727	56.33939		2.87056	0.98765
313.15	1531.12545	53.05455		2.53186	0.98914
318.15	1539.78545	49.65455		1.77139	0.99389
$u = u_0 + u_1 t + u_2 t^2$					
298.15	1499.4918	53.638636	10.037879	3.14178	0.98952
303.15	1511.1182	54.028788	6.1363636	3.06272	0.98897
308.15	1521.7455	53.203030	3.4848485	3.0538	0.98777
313.15	1531.4209	50.838636	2.4621212	2.69821	0.98921
318.15	1540.1991	46.552273	3.4469697	1.86988	0.99404
(iii) Potassium chloride in 0.1 M aqueous urea solution					
$u = u_0 + u_1 t$					
298.15	1502.0793	59.12775		2.95444	0.99051
303.15	1513.45683	51.07489		2.59711	0.99018
308.15	1523.35044	45.79515		2.02519	0.99255
313.15	153189581	43.19604		0.65565	0.99911
318.15	1538.98855	43.32599		2.3757	0.98861
$u = u_0 + u_1 t + u_2 t^2$					
298.15	15013023	65.810144	−7.4577323	3.2184	0.991
303.15	1513.2515	52.841189	−1.9712380	2.897	0.99023
308.15	1523.3565	45.742638	0.58609763	2.26423	0.99255
313.15	15316898	44.968191	−1.9777748	0.70602	0.99918
318.15	1538.2219	49.919630	−7.3586829	2.55277	0.98948

mal compressibility with an increase in temperature may be associated with the loss of water molecules around the ions.

The isothermal compressibility of aqueous sodium chloride, sodium sulphate, and magnesium sulphate solutions measured at 0–45 °C [58] show a decrease with increase in concentration. If it is assumed that the size of the ion is not pressure dependent and the electrostricted water is already compressed to its maximum extent by the charge on the ions, the compressibility of a solution is mainly due to the effect of pressure on the bulk (non-hydrated) water molecules. As the concentration of the electrolyte increases and a larger portion of the water molecules are electrostricted, the amount of bulk water decreases causing the compressibility to decrease [59]. For the electrolytes with large hydration numbers such as magnesium and sodium sulphates, one would expect change in compressibility with concentration to be much more negative than electrolytes such as sodium chloride with small hydration number. This would indicate that the concentration dependence of compressibility becomes greater as the number of water molecules affected by the ions' increase. The temperature dependence of compressibility is also negative for all the solutions studied below 25 °C [59]. The compressibility of water also decreases with temperature to a minimum value near 46 °C. A number of workers [49,60–62] have postulated that this is due to the existence of two structural types of water aggregates at a given temperature (a structured form and a non-structured or less structured form). The change in compressibility with temperature for the structured form is negative, while it is positive for the less structured form. At low temperatures, the structured form is the predominant species while at higher temperatures the non-structured form predominates. The compressibility

Table 5
Adiabatic compressibility (β_s, $\times 10^{10}$ cm^2/dyne; or β_s (m^2/N)) as a function of molality, *m* of (a) leucine, (b) NaCl, and (c) KCl each in 0.1 M aqueous urea solution at several temperatures (K)

m	Temperature (K)				
	298.15	303.15	308.15	313.15	318.15
(a) Leucine					
0.00	4.4546	4.3956	4.3428	4.2958	4.2549
0.01	4.4325	4.3783	4.3388	4.3046	4.2662
0.02	4.4225	4.3720	4.3312	4.2950	4.2590
0.03	4.4176	4.3637	4.3369	4.2843	4.2495
0.04	4.4085	4.3571	4.3154	4.2727	4.2420
0.05	4.3995	4.3452	4.3037	4.2606	4.2306
0.06	4.3847	4.3315	4.2897	4.2499	4.2204
0.07	4.3769	4.3260	4.2826	4.2424	4.2167
0.08	4.3652	4.3179	4.2757	4.2328	4.2078
0.09	4.3508	4.3098	4.2699	4.2260	4.1958
0.10	4.3377	4.3021	4.2585	4.2129	4.1865
(b) NaCl					
0.00	4.4546	4.3956	4.3428	4.2958	4.2549
0.10	4.3731	4.3065	4.2527	4.2109	4.1809
0.20	4.2712	4.2142	4.1652	4.1240	4.0904
0.40	4.1894	4.1240	4.0739	4.0386	4.0175
0.70	4.0485	4.0053	3.9719	3.9483	3.9343
0.80	3.9519	3.9028	3.8673	3.8448	3.8352
0.90	3.9586	3.9146	3.8786	3.8504	3.8296
(c) KCl					
0.00	4.4546	4.3956	4.3428	4.2958	4.2549
0.10	4.2849	4.2242	4.1826	4.1596	4.1562
0.20	4.2991	4.2313	4.1783	4.1395	4.1143
0.30	4.2206	4.1841	4.1446	4.0497	4.0576
0.50	4.1315	4.0879	4.0508	4.0202	3.9959
0.70	4.0297	3.9958	3.9621	3.9282	3.8955
0.90	3.9453	3.9177	3.8909	3.8649	3.8397

Table 6
Specific acoustic impedance (Z, $\times 10^{-3}$ kg m^{-2} s^{-1}) of (a) leucine, (b) NaCl, and (c) KCl each in 0.1 M aqueous urea solution as functions of molality, *m* and temperature (K)

m	Temperature (K)				
	298.15	303.15	308.15	313.15	318.15
(a) Leucine					
0.00	1496.90	1505.70	1513.58	1520.45	1526.20
0.01	1501.00	1509.20	1514.50	1519.40	1524.60
0.02	1503.00	1510.60	1516.40	1521.40	1526.20
0.03	1504.10	1512.20	1518.20	1523.60	1528.30
0.04	1505.80	1513.50	1519.50	1525.70	1529.70
0.05	1507.50	1515.70	1521.70	1527.90	1531.90
0.06	1510.50	1518.60	1524.80	1530.50	1534.20
0.07	1512.10	1519.80	1526.20	1531.90	1534.90
0.08	1514.30	1521.40	1527.60	1533.90	1536.80
0.09	1517.10	1523.10	1528.90	1535.30	1539.30
0.10	1519.80	1524.90	1531.40	1538.10	1541.30
(b) NaCl					
0.00	1496.90	1505.70	1513.60	1520.50	1526.20
0.10	1517.70	1529.30	1538.10	1544.30	1547.80
0.20	1549.70	1560.30	1568.70	1574.90	1579.00
0.40	1565.30	1577.70	1586.70	1592.30	1594.40
0.70	1601.20	1609.10	1614.20	1616.50	1616.00
0.80	1629.00	1638.60	1644.90	1647.90	1647.60
0.90	1627.30	1636.00	1642.50	1646.70	1648.50
(c) KCl					
0.00	1496.9	1505.7	1513.6	1520.5	1526.2
0.10	1542.9	1554.2	1561.3	1564.4	1563.0
0.20	1540.0	1552.3	1561.4	1567.1	1570.0
0.30	1558.3	1565.0	1572.0	1578.3	1584.7
0.50	1578.5	1588.3	1595.9	1601.2	1604.2
0.70	1608.0	1616.0	1623.3	1629.8	1635.5
0.90	1630.4	1636.8	1642.4	1647.2	1651.1

of liquid water is expressed as sum of the two contributions: an instantaneous part of compressibility and a relaxational part of compressibility [52]. The relaxational time corresponding to relaxational contribution of compressibility is of the order of 10^{-11} s. The product of the angular frequency and the relaxation time becomes much less than one under such a situation. Thus, the effect of the said product is ignored while expressing compressibility in terms of mere two contributions, i.e., instantaneous part of compressibility and the relaxational part. With increase in temperature the instantaneous part of compressibility increases due to thermal expansion while the relaxational part decreases due to thermal rupture of the ice-like structure. Thus, the decrease of compressibility with increase in temperature is attributed to a decrease in the relaxational part of compressibility, which is dominant over the increase of instantaneous part [49].

The internal pressure can be obtained using the relation:

$$P_\mathrm{i} = \frac{\alpha T}{\beta_\mathrm{T}} - p \qquad (7)$$

where T is the temperature in Kelvin and α the thermal expansion coefficient while p is usually very small compared to the first term and consequently ignored. The overall trend in internal pressure (Table 8) has been found to be increasing with increase in temperature, which may apparently be attributed to a decrease in the repulsive forces among the components of the system. In addition, the change in the concentration of solution also brings about changes in internal pressure, even though it is not as significant as in that of temperature**.** For example, at 298.15 K the values of P_i record insignificant changes from 1.465 to 1.464 when solute concentration is increased from 0.01 to 0.09 mol/kg in the case of leucine–aqueous urea system. Similarly, the increases in the P_i values range from 1.677 to 1.734, 1.895–2.021, 2.119–2.325, and 2.357–2.631 at 303.15, 308.15, 313.15, and 318.15 K, respectively. On the other hand, the temperature variations from 298.15 to 318.15 K record comparatively significant increases in such values. These are from 1.465 to 2.357, 1.467–2.359, 1.409–2.363, 1.510–2.281, 1.592–2.243, 1.363–2.580, 1.448–2.543, 1.451–2.547, 1.575–2.422 and 1.464–2.631 for 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09 and 0.10 mol/kg, respectively. It is noteworthy that internal pressure has direct relevance in respect of the force of intermolecular interaction since it happens to be the outcome of such forces per unit area. Con-

Table 7
Isothermal compressibility (β_T, $\times 10^{10}$ cm^2/dyne) of (a) leucine, (b) NaCl, and (c) KCl each in 0.1 M aqueous urea solution as functions of concentration (molality, *m*) and temperature (K)

m	Temperature (K)				
	298.15	303.15	308.15	313.15	318.15
(a) Leucine					
0.00	5.8855	5.8014	5.7267	5.6609	5.6046
0.01	5.8516	5.7745	5.7202	5.6726	5.6201
0.02	5.8358	5.7641	5.7074	5.6575	5.6084
0.03	5.8279	5.7513	5.6939	5.6408	5.5936
0.04	5.8140	5.7410	5.6829	5.6234	5.5821
0.05	5.8001	5.7232	5.6654	5.6053	5.5650
0.06	5.7768	5.7019	5.6427	5.5879	5.5486
0.07	5.7648	5.6926	5.6319	5.5765	5.5429
0.08	5.7467	5.6799	5.6211	5.5617	5.5292
0.09	5.7246	5.6674	5.6120	5.5511	5.5106
0.10	5.7042	5.6547	5.5938	5.5308	5.4961
(b) NaCl					
0.0	5.8855	5.8014	5.7267	5.6609	5.6046
0.1	5.7449	5.6470	5.5697	5.5120	5.4732
0.2	5.5566	5.4729	5.4033	5.3472	5.3042
0.4	5.4356	5.3400	5.2688	5.2208	5.1952
0.7	5.2088	5.1478	5.1035	5.0753	5.0629
0.8	5.0495	4.9804	4.9321	4.9039	4.8951
0.9	5.0598	4.9974	4.9483	4.9119	4.8880
(c) KCl					
0.0	5.8855	5.8014	5.7267	5.6609	5.6046
0.1	5.5883	5.4987	5.4393	5.4090	5.4093
0.2	5.6099	5.5106	5.4351	5.3823	5.3514
0.3	5.4843	5.4311	5.3755	5.2410	5.2580
0.5	5.3455	5.2785	5.2239	5.1813	5.1506
0.7	5.1739	5.1221	5.0727	5.0248	4.9805
0.9	5.0399	4.9988	4.9604	4.9248	4.8918

Table 8
Internal pressure (P_i, $\times 10^{-8}$ N m^{-2}) of (a) leucine, (b) NaCl and (c) KCl each in 0.1 M aqueous urea solution as functions of concentration (molality, *m*) and temperature (K)

m	Temperature (K)				
	298.15	303.15	308.15	313.15	318.15
(a) Leucine					
0.00	1.536	1.721	1.915	2.115	2.322
0.01	1.465	1.677	1.895	2.119	2.357
0.02	1.467	1.678	1.896	2.122	2.359
0.03	1.409	1.635	1.868	2.111	2.363
0.04	1.510	1.693	1.882	2.080	2.281
0.05	1.592	1.749	1.908	2.076	2.243
0.06	1.363	1.649	1.947	2.259	2.580
0.07	1.448	1.706	1.976	2.257	2.543
0.08	1.451	1.709	1.978	2.261	2.547
0.09	1.575	1.773	1.980	2.200	2.422
0.10	1.464	1.734	2.021	2.325	2.631
(b) NaCl					
0.0	1.531	1.721	1.915	2.115	2.322
0.1	2.931	3.029	3.123	3.211	3.295
0.2	3.018	3.111	3.204	3.296	3.38
0.3	3.145	3.262	3.372	3.474	3.567
0.4	3.278	3.388	3.490	3.584	3.669
0.7	3.568	3.672	3.772	3.873	3.958
0.8	3.632	3.744	3.846	3.939	4.021
0.9	3.632	3.737	3.839	3.939	4.03
(c) KCl					
0.0	1.536	1.721	1.915	2.115	2.322
0.1	2.932	3.028	3.122	3.213	3.299
0.2	3.609	3.729	3.842	3.948	4.045
0.3	3.030	3.107	3.191	3.283	3.383
0.5	3.705	3.799	3.893	3.987	4.082
0.7	3.553	3.636	3.723	3.817	3.915
0.9	3.229	3.302	3.378	3.458	3.54

sequently, relatively close packing is envisaged with increase in temperature as evidenced by the results given above. Similar conclusions may be drawn in the cases of NaCl–aqueous urea and KCl–aqueous urea systems. These are in accord with the corresponding results. In addition, apparently linear plots of variation in the values of internal pressure with temperature and solute concentration are almost parallel to the base in both the cases and consequently, on the average, their slope values are close to zero. This may be considered as an additional support for the presence of weak intermolecular/interionic interactions in the systems under investigation. Such a conclusion reinforces an almost ideal behaviour envisaged by the equations proposed above [55] for the change and relative change in adiabatic compressibility. It seems that the increase in the values of internal pressure is closely associated with the expansivity of the system with temperature, as a consequence of which the molecular/ionic species or clusters get closer to the extent envisaged by the expansivity of the system under investigation. This will, therefore, account for the increases in the P_i values with successive increases in temperature. It is noteworthy that the coefficient of expansion/expansivity also exhibits apparently linear increases with temperature with almost the same or close slope values to those of the internal pressure versus temperature plots. Consequently, an apparent increase in internal pressure with increases in temperature and solute concentration is understandable.

The solubility parameter, δ, is obtained by taking the square root of the internal pressure. The overall trend in the behaviour of solubility parameter has been found to be increasing with increase in temperature. Such an increase may be attributed to an *increase* in the cohesive energy density. In view of the fact that the solubility parameter happens to be the square root of the internal pressure, similar trend in the variation of its values is envisaged as that in those of the P_i values. Such a contention is reinforced when a representative case of leucine–aqueous urea system is examined. For example, on increasing the temperature, from 298.15 to 318.15 K, the δ values show increases from 1.21 to 1.54 and 1.21–1.62 ($\times 10^4$ N$^{1/2}$ m^{-1}) in the respective cases of 0.01 and 0.10 mol/kg solute concentrations. Such changes are insignificant when examined at a particular temperature for variations in solute concentration. For example, at 298.15 and 303.15 K, no perceptible change is recorded in the values of δ when solute concentration is increased from 0.01 to 0.10 mol/kg unlike the insignificant changes recorded at 308.15, 313.15, and 318.15 K for such variations in the concentration of solute. Such conclusions may also be drawn in the cases of NaCl/KCl–aqueous urea systems. The structure-making and structure-breaking roles of NaCl and KCl, respectively, in affecting these parameters have already been discussed above in respect of adiabatic compressibility. Similar conclusions may also be drawn here in the cases of P_i and δ.

The pseudo-Gruneisen parameter, Γ, has been computed by using the relation [63]:

$$\Gamma = \frac{\gamma - 1}{\alpha T} \tag{8}$$

in which γ is the specific-heat ratio obtained from the relation, $\gamma = \beta_T/\beta_s$. An overall decrease in their values with increase in temperature may apparently be attributed to an increase in the kinetic energy of the system while such decreases with increase in concentration suggest an increase in the solute–solvent interactions. The behaviour of pseudo-Gruneisen parameter may also be understood in terms of expansivity of a system. In view of the fact that Γ is inversely related to the coefficient of expansion, the trend in its behaviour will be opposite of that recorded for P_i, which has direct dependence on α. Thus, the entire discussion on P_i holds good in the case of Γ when examined in view of the inverse dependence of Γ on the α values. Consequently, the results of P_i, δ, as well as of Γ are consistent and their behaviour is physically understandable. Also, the trend in their behaviour is in accord with that reported earlier in the cited literature.

The results obtained in the absence of urea and in its presence at 298.15 K are shown below.

Properties	Pure water[a]	0.1 M aqueous urea	1 M aqueous urea[a]
ρ ($\times 10^{-3}$ kg m^{-3})	0.99705[b]	0.9982	1.012857 (0.998807 M)[c]
u (m s^{-1})	1495.4	1499.6	1521.3
β_s ($\times 10^{11}$ m^2/N)	44.85 (44.77)[d]	44.55	42.69
β_T ($\times 10^{11}$ m^2/N)	59.33	58.86	55.82
Z ($\times 10^{-3}$ kg m^{-2} s^{-1})	1491.1	1496.9	1539.7
P_i ($\times 10^{-8}$ N m^{-2})	1.290	1.536	1.698
δ ($\times 10^{-4}$ N m^{-2})$^{1/2}$	1.136	1.210	1.303
Γ	4.218	3.38	3.243
α, ($\times 10^4$/K)		2.57	3.18

[a] Physico-chemical studies of multicomponent systems, Ph.D. Thesis of Qazi Javaid Ahmad, A.M.U., Aligarh, 1999.

[b] G.S. Kell, J. Chem. Eng. Data 12 (1967) 66.

[c] O. Enea, C. Jollcoeur, J. Phys. Chem. 86 (1982) 3870.

[d] Ref: [49].

Finally, an examination of the above table comparing the listed properties in pure water with those in 0.1 and 1 M aqueous urea solutions shows increases in the values of u, Z, P_i, δ, and α with successive increases in the concentration of urea. Similarly, the corresponding decreases in those of β_s, β_T, and Γ values are exhibited. Similar trend in their behaviour is also exhibited by the successive increases in solute (leucine, NaCl, and KCl) concentration in each of the three systems studied in aqueous urea solutions as evidenced by the data provided in the relevant tables.

In view of the probable presence of flickering clusters, viz., decamer, nanomer, octamer, hexamer, pentamer, tetramer, trimer, dimer, and monomer some of which occur in two or three isomeric forms with insignificant amount of inter-conversion energies among them; their structural-association with the chloride ions details of which have been given above under the halide–water interactions; structural-clustering of sodium and potassium ions with several successive sheaths of water; and also of leucine either in the form of zwitter ions or otherwise in the systems under investigation; it seems likely that these species get closer either due to the successive increases in solute (be it urea, leucine, NaCl, or KCl) concentration or that of an increase in the kinetic motion with thermal variations providing better contact of these entities as a result of their close proximity, result in an increase in the ultrasonic velocities, specific acoustic impedance, internal pressure, solubility parameter; as well as the corresponding decreases exhibited by the compressibilities and pseudo-Gruneisen parameter suggest an increase in the solute–solvent interactions with increases in temperature and solute concentration.

The structure of leucine–aqueous urea may consist of a mixture of several probable zwitterionic or even native leucine entities, which are associated with small to large flickering clusters of water through hydrogen bonding. These are, in turn, surrounded by the water clusters of the bulk experiencing weak influence of the latter followed by successive sheaths of a large number of hydrogen-bonded water molecules or clusters in three dimensions. The three-dimensional field of influence caused by the specific interionic/intermolecular interactions dies out in the successive sheaths with distance. Such a field of influence affecting the extent of interaction may increase with successive increases in the concentration of solute.

The structures of sodium and potassium chlorides in their aqueous solutions of 0.1 M urea may differ from each other in being surrounded in their first spheres by the number of water molecules/flickering water clusters. These are relatively fewer or more in numbers in the respective cases of NaCl and KCl due to the difference in their ionic sizes. It is noteworthy that urea and KCl, both being structure breakers, contribute more in disrupting the H-bonds in the system compared to the NaCl–aqueous urea system in which only urea disrupts the hydrogen bonds. Consequently, monomers or clusters of smaller sizes may surround the potassium ions in their first sphere of influence compared to the sodium ions because of the difference in their weakly structure-breaking or structure-making roles in the respective cases. However, the oxygen of water will face the cation in both the cases in a manner similar to that mentioned above. In addition, the chloride ions may be present in their probable clusters, Cl^{-}–$(H_2O)_{n=1\text{–}10}$ at the temperature of study and swim in the bulk along with the said cationic structures. It is noteworthy that the extent of intermolecular/interionic interactions increases with increase in concentration of the solute because of the close proximity of the interacting entities as mentioned above. Similar situation also arises when successive increases in temperature brings the structural entities close to each other as a result of increased thermal/kinetic motion. These conclusions are in accord with the results discussed above.

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