

## Densities and Speeds of Sound in L-Leucine/L-Isoleucine + Aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> Systems at (298.15 to 323.15) K

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**ABSTRACT:** Density ( $\rho$ ) and speed of sound ( $u$ ) values have been measured of L-leucine + 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> and L-isoleucine + 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> systems for several molal concentrations of L-leucine/L-isoleucine at different temperatures  $T = (298.15, 303.15, 308.15, 313.15, 318.15, \text{ and } 323.15)$  K. Using the experimental values of  $\rho$  and  $u$ , the apparent molar volumes, partial molar volumes, transfer partial molar volumes, isentropic compressibilities, apparent molar isentropic compressibilities, partial molar isentropic compressibilities, and transfer partial molar isentropic compressibilities have been calculated. The measured and calculated thermodynamic parameters have been discussed in terms of zwitterion–ion, zwitterion–water dipole, ion–ion, and ion–water dipole interactions.

### ■ INTRODUCTION

Metal ions are essential for the biological function of many proteins. At least one-third of all proteins encoded in the human genome appear to contain metal ions which perform a wide range of specific functions.<sup>1</sup> Salt-induced precipitation is an extensively used method as an initial step to purify proteins because of its selectivity and low cost. Thus, the study of the interactions of ions and proteins is useful to understand the physiological systems and in the separation and purification processes of proteins.<sup>2–6</sup> However, proteins are complex molecules, and their behavior in solutions is governed by a combination of a number of specific interactions. One approach that reduces the degree of complexity in the study of these interactions and requires less complex measurement techniques is to study the interactions in systems containing smaller biomolecules, such as amino acids. As amino acids are the building blocks of the proteins, their study provides important information which can be related to the behavior of larger biomolecules such as proteins. Amino acids also play a significant role in metabolism and in many neurochemical response mechanisms, such as memory, appetite control, and pain transmission.<sup>7,8</sup> They are also used as food additives and have many applications in the pharmaceutical industries. Studies of the effect of concentration of salt and temperature on the thermodynamic properties of aqueous amino acid solutions have been proven to be very useful in elucidating the various interactions that occur in these solutions.<sup>9–17</sup> The volumetric and compressibility studies of amino acids in aqueous salt solutions have been employed to understand the nature of interactions operative in solutions.<sup>10,14,16,18–28</sup> K<sub>2</sub>SO<sub>4</sub> influences the unfolding of protein, RNase Sa.<sup>29</sup> KNO<sub>3</sub> affects the nucleic acid synthesis in the greening cucumber cotyledons<sup>30</sup> and the stability of tropomyosin.<sup>31</sup> Thus, the study of interactions in amino acid/ aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> systems is significant with a view to understanding the interactions in protein–aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> systems.

This study focuses on the measurements of density ( $\rho$ ) and speed of sound ( $u$ ) values of L-leucine or L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub> or 0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub>

solution as functions of molal concentration of L-leucine/ L-isoleucine and  $T = (298.15, 303.15, 308.15, 313.15, 318.15, \text{ and } 323.15)$  K. The measured density and speed of sound data have been used to compute the apparent molar volume ( $\phi_v$ ), partial molar volume ( $\phi_v^0$ ), transfer partial molar volume ( $\Delta_{tr}\phi_v^0$ ), isentropic compressibility ( $\kappa_s$ ), apparent molar isentropic compressibility ( $\phi_{\kappa}$ ), partial molar isentropic compressibility ( $\phi_{\kappa}^0$ ), and transfer partial molar isentropic compressibility ( $\Delta_{tr}\phi_{\kappa}^0$ ) values with the view to understanding the zwitterion–ion, zwitterion–water dipole, ion–ion, and ion–water dipole interactions operative in the solutions.

### ■ MATERIALS AND METHODS

The amino acids L-leucine and L-isoleucine and the salts potassium sulfate and potassium nitrate of high purity ( $\geq 99\%$  by mass fraction), used in the present studies, were purchased from SRL (India) and E. Merck (India), respectively. The amino acids were recrystallized twice in (ethanol + water) mixtures, dried at  $T = 383.15$  K, and kept in vacuum desiccator over P<sub>2</sub>O<sub>5</sub> for at least 72 h before use. The salts were recrystallized in triply distilled water, dried at  $T = 423.15$  K for at least 3 h, and then kept over P<sub>2</sub>O<sub>5</sub> in a vacuum desiccator at room temperature for a minimum of 48 h prior to their use. Stock solutions of 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub> and 0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> were prepared at 298.15 K in triply distilled water and were used as solvents for the preparation of L-leucine and L-isoleucine solutions. The molalities of 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub> and 0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solutions were found to be 0.512 mol·kg<sup>-1</sup> and 0.512 mol·kg<sup>-1</sup>, respectively. All of the solutions were stored in special airtight bottles to prevent the exposure of solutions to air and evaporation. The density and speed of sound values of the solutions were measured at different temperatures with a density and sound velocity meter (Anton Paar DSA 5000 M, Austria). The uncertainties in density and speed of

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**Table 1. Density,  $\rho \cdot 10^{-3}/(\text{kg} \cdot \text{m}^{-3})$ , as a Function of Molal Concentration of L-Leucine/L-Isoleucine at Different Temperatures**

$m^a$ mol·kg <sup>-1</sup>	T/K					
	298.15	303.15	308.15	313.15	318.15	323.15
L-Leucine in 0.512 mol·kg <sup>-1</sup> Aqueous K <sub>2</sub> SO <sub>4</sub>						
0.0000	1.063810	1.062020	1.060060	1.057740	1.055140	1.052950
0.0188	1.064067	1.062275	1.060313	1.057993	1.055393	1.053202
0.0378	1.064312	1.062517	1.060553	1.058232	1.055629	1.053436
0.0568	1.064603	1.062806	1.060840	1.058518	1.055922	1.053721
0.0759	1.064844	1.063045	1.061078	1.058754	1.056150	1.053955
0.0957	1.064954	1.063154	1.061186	1.058861	1.056259	1.054066
0.1143	1.065148	1.063343	1.061373	1.059048	1.056446	1.054249
L-Leucine in 0.512 mol·kg <sup>-1</sup> Aqueous KNO <sub>3</sub>						
0.0000	1.027984	1.026225	1.024102	1.022050	1.020200	1.018200
0.0195	1.028359	1.026598	1.024472	1.022437	1.020496	1.018507
0.0398	1.028741	1.026977	1.024840	1.022809	1.020860	1.018858
0.0588	1.029102	1.027335	1.025207	1.023169	1.021217	1.019227
0.0786	1.029453	1.027683	1.025547	1.023511	1.021562	1.019561
0.0984	1.029788	1.028016	1.025883	1.023841	1.021891	1.019897
0.1183	1.030161	1.028387	1.026257	1.024208	1.022257	1.020262
L-Isoleucine in 0.512 mol·kg <sup>-1</sup> Aqueous K <sub>2</sub> SO <sub>4</sub>						
0.0000	1.063810	1.062020	1.060060	1.057740	1.055140	1.052950
0.0188	1.064146	1.062350	1.060379	1.058065	1.055461	1.053268
0.0377	1.064469	1.062666	1.060695	1.058372	1.055774	1.053577
0.0567	1.064839	1.063035	1.061063	1.058736	1.056132	1.053934
0.0758	1.065123	1.063322	1.061350	1.059021	1.056411	1.054210
0.0952	1.065418	1.063611	1.061634	1.059289	1.056679	1.054477
0.1142	1.065753	1.063838	1.061858	1.059525	1.056897	1.054622
L-Isoleucine in 0.512 mol·kg <sup>-1</sup> Aqueous KNO <sub>3</sub>						
0.0000	1.027984	1.026225	1.024102	1.022050	1.020200	1.018200
0.0194	1.028435	1.026672	1.024545	1.022665	1.020722	1.018774
0.0397	1.028876	1.027112	1.024985	1.023103	1.021155	1.019152
0.0587	1.029303	1.027536	1.025407	1.023517	1.021564	1.019628
0.0785	1.029758	1.027989	1.025855	1.023967	1.022017	1.020066
0.0983	1.030172	1.028398	1.026264	1.024379	1.022429	1.020479
0.1182	1.030577	1.028801	1.026651	1.024747	1.022787	1.020825

<sup>a</sup> Solvent = (water + K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub>).

sound measurements were within  $\pm 5 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$  and  $\pm 0.5 \text{ m} \cdot \text{s}^{-1}$ , respectively, under the most favorable conditions. The reproducibility of the density and speed of sound values were found to be within  $1.10^{-3} \text{ kg} \cdot \text{m}^{-3}$  and  $0.1 \text{ m} \cdot \text{s}^{-1}$ , respectively. The uncertainties in the derived parameters,  $\phi_v^0$ ,  $\Delta_{\text{tr}}\phi_v^0$ ,  $K_{\text{sv}}$ ,  $\phi_{\text{K}}^0$ , and  $\Delta_{\text{tr}}\phi_{\text{K}}^0$  are  $\pm 0.05 \cdot 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ ,  $\pm 0.05 \cdot 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ ,  $\pm 0.5 \cdot 10^{-11} \text{ m}^2 \cdot \text{N}^{-1}$ ,  $\pm 0.5 \cdot 10^{-11} \text{ bar}^{-1}$ ,  $\text{m}^3 \cdot \text{mol}^{-1}$ , and  $\pm 0.5 \cdot 10^{-11} \text{ bar}^{-1} \cdot \text{m}^3 \cdot \text{mol}^{-1}$ , respectively.

## RESULTS AND DISCUSSION

The density and speed of sound values of L-leucine + 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> and L-isoleucine + 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> systems have been measured as a function of molal concentration of L-leucine/L-isoleucine at temperatures,  $T = (298.15, 303.15, 308.15, 313.15, 318.15, \text{ and } 323.15) \text{ K}$ . The measured values

**Table 2. Speed of Sound,  $u/(\text{m} \cdot \text{s}^{-1})$ , as a Function of Molal Concentration of L-Leucine/L-Isoleucine at Different Temperatures**

$m$ mol·kg <sup>-1</sup>	T/K					
	298.15	303.15	308.15	313.15	318.15	323.15
L-Leucine in 0.512 mol·kg <sup>-1</sup> Aqueous K <sub>2</sub> SO <sub>4</sub>						
0.0000	1563.6	1571.6	1580.3	1587.6	1593.5	1598.3
0.0188	1564.7	1574.0	1582.5	1589.7	1595.6	1600.2
0.0378	1566.3	1576.2	1584.5	1591.6	1597.4	1602.1
0.0568	1568.3	1578.3	1586.5	1593.6	1599.5	1604.1
0.0759	1570.9	1580.6	1588.9	1595.5	1601.5	1605.9
0.0957	1573.3	1582.8	1590.9	1597.7	1603.2	1607.4
0.1143	1576.0	1585.3	1593.2	1599.9	1605.2	1609.4
L-Leucine in 0.512 mol·kg <sup>-1</sup> Aqueous KNO <sub>3</sub>						
0.0000	1517.8	1526.8	1536.3	1544.4	1551.1	1556.6
0.0195	1518.9	1528.7	1538.1	1546.2	1553.2	1558.4
0.0398	1520.0	1530.9	1540.1	1548.1	1554.8	1559.9
0.0588	1522.3	1533.0	1542.2	1550.1	1556.5	1561.5
0.0786	1524.8	1535.2	1544.3	1551.9	1558.2	1563.3
0.0984	1526.9	1537.2	1546.2	1553.8	1559.9	1564.9
0.1183	1528.9	1539.4	1548.3	1555.8	1561.9	1566.2
L-Isoleucine in 0.512 mol·kg <sup>-1</sup> Aqueous K <sub>2</sub> SO <sub>4</sub>						
0.0000	1563.6	1571.6	1580.3	1587.6	1593.5	1598.3
0.0188	1565.2	1573.4	1582.6	1589.8	1595.7	1600.3
0.0377	1567.2	1575.3	1585.2	1591.9	1597.8	1602.6
0.0567	1569.3	1577.2	1587.3	1593.9	1599.9	1604.5
0.0758	1571.3	1579.8	1589.2	1595.9	1601.7	1606.8
0.0952	1573.4	1581.4	1591.4	1598.0	1603.7	1608.7
0.1142	1575.7	1583.2	1593.1	1599.8	1605.5	1610.9
L-Isoleucine in 0.512 mol·kg <sup>-1</sup> Aqueous KNO <sub>3</sub>						
0.0000	1517.8	1526.8	1536.3	1544.4	1551.1	1556.6
0.0194	1519.2	1530.1	1538.4	1546.6	1553.3	1558.6
0.0397	1520.9	1532.7	1540.7	1548.5	1555.6	1560.6
0.0587	1523.1	1534.6	1542.5	1550.2	1557.6	1562.8
0.0785	1525.2	1536.7	1544.6	1552.2	1559.5	1564.6
0.0983	1527.3	1538.6	1546.5	1554.6	1561.3	1566.3
0.1182	1529.4	1540.4	1548.7	1556.2	1563.3	1568.2

of  $\rho$  and  $u$  have been listed in Tables 1 and 2. The  $\rho$  and  $u$  of L-leucine in 2 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> and 1.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solutions have been measured in our laboratory earlier.<sup>24,25</sup> Similarly, the  $\rho$  and  $u$  of L-isoleucine in 1 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solution have been measured in our laboratory earlier.<sup>26</sup> The observed  $\rho$  of L-leucine in 0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solution at 298.15 K is 1.028359 (10<sup>3</sup>/kg·m<sup>-3</sup>), whereas the reported  $\rho$  of L-leucine in 2 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solution and in 1.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solution from our laboratory are 1.1230 (10<sup>3</sup>/kg·m<sup>-3</sup>)<sup>24</sup> and 1.0872 (10<sup>3</sup>/kg·m<sup>-3</sup>),<sup>25</sup> respectively. The observed  $\rho$  of L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solution at 303.15 K is 1.026672 (10<sup>3</sup>/kg·m<sup>-3</sup>), whereas the reported  $\rho$  of L-isoleucine in 1 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solution from our laboratory is 1.0534 (10<sup>3</sup>/kg·m<sup>-3</sup>).<sup>26</sup> The density values of the studied systems exhibit an usual increase with an increase of the molal concentration of L-leucine/L-isoleucine in aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> solutions and decrease with an increase in temperature. All of the systems seem

to exhibit almost linear behavior in their variation of  $\rho$  with the increase in L-leucine/L-isoleucine concentration as well as with temperature. The observed  $u$  of L-leucine in 0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solution at 298.15 K is 1518.9/(m·s<sup>-1</sup>), whereas the reported  $u$  from our laboratory of L-leucine in 2 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solution is 1566.4/(m·s<sup>-1</sup>).<sup>24</sup> The observed  $u$  of L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub> and 0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solutions at 303.15 K are 1573.4 and 1530.1/(m·s<sup>-1</sup>), respectively, whereas the reported  $u$  from our laboratory of L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub> and in 1 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solutions are 1573.8 and 1542.6/(m·s<sup>-1</sup>),<sup>26</sup> respectively. The speed of sound values increase with an increase in molal concentration of L-leucine/L-isoleucine in aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> solutions as well as with temperature in all of the systems under investigation.

Using the measured values of density of solvent and solution, the apparent molar volume values have been calculated by the following equation:

$$\phi_v = (M/\rho) - \{(\rho - \rho_0)/m\rho\rho_0\} \quad (1)$$

where  $m$  is the molality of the solution,  $M$  is the molar mass of the solute (kg·mol<sup>-1</sup>), and  $\rho_0$  and  $\rho$  are the density values (kg·m<sup>-3</sup>) of solvent and solution, respectively. The apparent molar volume values have been fitted by least-squares method to the equation:<sup>32</sup>

$$\phi_v = \phi_v^0 + S_v m \quad (2)$$

where  $\phi_v^0$  is the apparent molar volume at infinite dilution that is also referred to as the partial molar volume of the solute and  $S_v$  is the volumetric pairwise interaction coefficient.<sup>28,33</sup> The  $\phi_v^0$ ,  $S_v$ , and  $\sigma_v$  (standard deviation) values of L-leucine/L-isoleucine in 0.5 mol·L<sup>-1</sup> K<sub>2</sub>SO<sub>4</sub>/0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solutions have been listed in Table 3. The observed  $\phi_v^0$  values of L-leucine/L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> solutions could not be compared with the literature values as these values are not available. The observed  $\phi_v^0$  value of L-leucine in aqueous medium at 298.15 K is 107.32 (10<sup>-6</sup> m<sup>3</sup>·mol<sup>-1</sup>), whereas the corresponding literature values are 107.74,<sup>34</sup> 107.83,<sup>35</sup> 107.69,<sup>36</sup> 107.76,<sup>37</sup> and 107.72 (10<sup>-6</sup> m<sup>3</sup>·mol<sup>-1</sup>).<sup>38</sup> The observed  $\phi_v^0$  value of L-isoleucine in aqueous medium at 298.15 K is 105.37 (10<sup>-6</sup> m<sup>3</sup>·mol<sup>-1</sup>). The literature values of  $\phi_v^0$  of L-isoleucine in aqueous medium at 298.15 K are 105.80,<sup>35</sup> 105.71,<sup>36</sup> 105.73,<sup>37</sup> and 105.79 (10<sup>-6</sup> m<sup>3</sup>·mol<sup>-1</sup>).<sup>39</sup> The observed  $\phi_v^0$  of L-leucine in 0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> at 298.15 K is 109.07 (10<sup>-6</sup> m<sup>3</sup>·mol<sup>-1</sup>). The reported  $\phi_v^0$  of L-leucine in 2 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solution from our laboratory is 112.84 (10<sup>-6</sup> m<sup>3</sup>·mol<sup>-1</sup>).<sup>24</sup> The observed values of  $\phi_v^0$  of L-leucine and L-isoleucine in aqueous medium are quite close to literature values. The  $\phi_v^0$  values of L-leucine and L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous solutions of K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> solutions are higher than corresponding values in aqueous medium at all temperatures of study. The  $\phi_v^0$  values of L-leucine and L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous solutions of K<sub>2</sub>SO<sub>4</sub> and KNO<sub>3</sub> show an increase with an increase in temperature. In neutral solutions, the amino acid molecules exist as zwitterions.<sup>40–43</sup> The electrostriction of water molecules occurs near the terminal groups of zwitterions, NH<sub>3</sub><sup>+</sup> and COO<sup>-</sup>. The presence of K<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup> furnished by K<sub>2</sub>SO<sub>4</sub> and KNO<sub>3</sub> seems to affect the hydration spheres of charged terminal groups of zwitterions. As a result of K<sup>+</sup>–COO<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>–NH<sub>3</sub><sup>+</sup>, and NO<sub>3</sub><sup>-</sup>–NH<sub>3</sub><sup>+</sup> interactions, the hydrated zwitterions may relax some water molecules to the bulk water which, in turn, may cause an increase in the volume. The increase in  $\phi_v^0$  value with an

**Table 3. Partial Molar Volume,  $\phi_v^0 \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$ , Slope,  $S_v \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-2} \cdot \text{kg})$ , and Standard Deviation,  $\sigma_v \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$ , of L-Leucine/L-Isoleucine at Different Temperatures**

T/K	$\phi_v^0$	$S_v$	$\sigma_v$
L-Leucine in 0.512 mol·kg <sup>-1</sup> Aqueous K <sub>2</sub> SO <sub>4</sub>			
298.15	110.53(0.54)	17.11(0.73)	0.5
303.15	110.68(0.63)	21.40(0.85)	0.6
308.15	111.06(0.54)	17.26(0.73)	0.5
313.15	111.33(0.55)	17.68(0.75)	0.5
318.15	111.84(0.65)	13.30(0.88)	0.7
323.15	112.04(0.50)	14.15(0.67)	0.5
L-Leucine in 0.512 mol·kg <sup>-1</sup> Aqueous KNO <sub>3</sub>			
298.15	109.07(0.31)	8.47(3.42)	0.1
303.15	109.36(0.31)	8.41(3.44)	0.1
308.15	109.65(0.41)	7.56(4.56)	0.2
313.15	109.94(0.36)	11.34(3.96)	0.2
318.15	110.34(0.21)	-2.47(2.32)	0.1
323.15	110.99(0.24)	-0.91(2.61)	0.1
L-Isoleucine in 0.512 mol·kg <sup>-1</sup> Aqueous K <sub>2</sub> SO <sub>4</sub>			
298.15	107.24(0.28)	7.67(3.83)	0.3
303.15	107.45(0.39)	12.13(5.29)	0.4
308.15	107.77(0.42)	12.25(5.45)	0.4
313.15	108.12(0.44)	12.12(5.92)	0.4
318.15	108.37(0.41)	13.49(5.61)	0.4
323.15	108.54(0.56)	17.22(7.58)	0.6
L-Isoleucine in 0.512 mol·kg <sup>-1</sup> Aqueous KNO <sub>3</sub>			
298.15	106.05(0.24)	3.53(2.94)	0.2
303.15	106.30(0.27)	3.34(3.24)	0.2
308.15	106.43(0.23)	5.52(2.71)	0.2
313.15	106.53(0.37)	40.22(4.47)	0.3
318.15	107.34(0.36)	21.45(3.68)	0.2
323.15	107.66(0.55)	20.80(6.62)	0.4

increase in temperature may be attributed to the volume expansion of hydrated zwitterions or reduction in electrostriction. The observed higher  $\phi_v^0$  values for L-leucine/L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solutions as compared with their values in aqueous medium suggest the domination of zwitterion–ion interactions than zwitterion–water dipole interactions in solutions. The higher values of  $\phi_v^0$  of amino acid molecules in presence of sodium acetate, sodium propionate, and sodium butyrate than in aqueous medium have been also reported in literature.<sup>44</sup> The  $S_v$  values are experimental slopes.

The partial molar volume of transfer of L-leucine/L-isoleucine from water to 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solutions ( $\Delta_{tr}\phi_v^0$ ) at a temperature is defined as,

$$\Delta_{tr}\phi_v^0 = \phi_v^0(0.5 \text{ mol}\cdot\text{L}^{-1} \text{ aqueous K}_2\text{SO}_4/0.5 \text{ mol}\cdot\text{L}^{-1} \text{ aqueous KNO}_3 \text{ solution}) - \phi_v^0(\text{water}) \quad (3)$$

The  $\Delta_{tr}\phi_v^0$  values of L-leucine/L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solution at different temperatures have been listed in Table 4. The  $\Delta_{tr}\phi_v^0$  values of L-leucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub> or 0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> are higher than those of L-isoleucine at a given

**Table 4. Transfer Partial Molar Volumes,  $\Delta_{tr}\phi_v^0 \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$ , of L-Leucine/L-Isoleucine from Water to 0.512 mol·kg<sup>-1</sup> Aqueous K<sub>2</sub>SO<sub>4</sub>/0.512 mol·kg<sup>-1</sup> Aqueous KNO<sub>3</sub> at Different Temperatures**

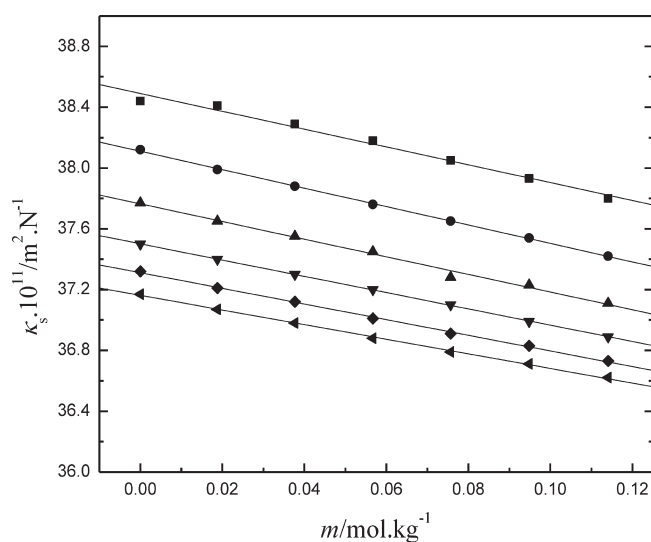
T/K =	$\Delta_{tr}\phi_v^0$				
	298.15	303.15	308.15	313.15	318.15
	L-Leucine in 0.512 mol·kg <sup>-1</sup> Aqueous K <sub>2</sub> SO <sub>4</sub>				
3.21	3.25	3.51	3.63	4.02	4.12
	L-Leucine in 0.512 mol·kg <sup>-1</sup> Aqueous KNO <sub>3</sub>				
1.75	1.93	2.10	2.24	2.52	3.07
	L-Isoleucine in 0.512 mol·kg <sup>-1</sup> Aqueous K <sub>2</sub> SO <sub>4</sub>				
1.87	2.02	2.29	2.57	2.72	2.82
	L-Isoleucine in 0.512 mol·kg <sup>-1</sup> Aqueous KNO <sub>3</sub>				
0.68	0.87	0.95	0.98	1.69	1.94

temperature. The  $\Delta_{tr}\phi_v^0$  for L-leucine/L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> systems increase with an increase in temperature. The higher  $\Delta_{tr}\phi_v^0$  values of L-leucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> solution than the corresponding values of L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> solution further reinforce the view that the COO<sup>-</sup>-K<sup>+</sup>, NH<sub>3</sub><sup>+</sup>-SO<sub>4</sub><sup>2-</sup>, and NH<sub>3</sub><sup>+</sup>-NO<sub>3</sub><sup>-</sup> interactions are stronger in L-leucine + 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> systems than those in L-isoleucine + 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> systems. Furthermore, the increase of  $\Delta_{tr}\phi_v^0$  values with an increase in temperature for all of the systems under investigation suggests the corresponding reduction of electrostricted water molecules.

The isentropic compressibility values of L-leucine/L-isoleucine + 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> systems have been calculated using the Newton–Laplace equation:<sup>45</sup>

$$\kappa_s = 1/\rho u^2 \quad (4)$$

The isentropic compressibility values of L-leucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub> solution as a function of molal concentration of L-leucine at T = (298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K have been plotted in Figure 1 as a representative case. The  $\kappa_s$  values for all of the systems under investigation exhibit similar trends of variation with variations in molal concentration of L-leucine or L-isoleucine and temperature. The  $\kappa_s$  values of 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub> and 0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solutions decrease with an increase in molal concentration of L-leucine or L-isoleucine in the solutions. This decreasing trend of  $\kappa_s$  values may be attributed to a corresponding increase in cohesive forces in (L-leucine/L-isoleucine + aqueous salt) solutions at all temperatures of study. The  $\kappa_s$  values of (L-leucine + 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>) are less than those of (L-leucine + 0.5 mol·L<sup>-1</sup> KNO<sub>3</sub>) solutions at all temperatures of study. This trend may be ascribed to stronger zwitterion–SO<sub>4</sub><sup>2-</sup> interactions than zwitterion–NO<sub>3</sub><sup>-</sup> interactions due to stronger polar nature of SO<sub>4</sub><sup>2-</sup> in comparison with NO<sub>3</sub><sup>-</sup>. Moreover, each K<sub>2</sub>SO<sub>4</sub> molecule furnishes two K<sup>+</sup> ions, whereas KNO<sub>3</sub> molecules provide one K<sup>+</sup> ion in solutions. Thus, the presence of twice number of K<sup>+</sup> ions in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub> solution leads to a higher magnitude of cohesive forces in solution. Similarly, the  $\kappa_s$  values of (L-isoleucine + 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>) solution are less than those of (L-isoleucine + 0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub>) solutions at all temperatures of study. The decrease in isentropic



**Figure 1.**  $\kappa_s$  values versus molal concentration of L-leucine in 0.5 M aqueous K<sub>2</sub>SO<sub>4</sub> solution. ■, T = 298.15 K; ●, T = 303.15 K; ▲, T = 308.15 K; ▼, T = 313.15 K; ◆, T = 318.15 K; ◀, T = 323.15 K.

compressibility values with an increase in temperature may be ascribed to changes occurring in the structure of water clusters around zwitterions and ions (K<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>) in aqueous solutions.<sup>34,46–49</sup> The thermal rupture of water clusters with an increase in temperature may cause the formation of smaller clusters of water molecules, which in turn may form the compact clusters at higher temperatures.<sup>50</sup>

The apparent molar isentropic compressibilities have been calculated using the equation:<sup>51,52</sup>

$$\phi_\kappa = \{(\kappa_s - \kappa_0)/m\rho_0\} + \kappa_s\phi_v \quad (5)$$

In the above-mentioned eq 5,  $m$  is the molality of the solution (mol·kg<sup>-1</sup>),  $\rho_0$  is the density of the solvent (kg·m<sup>-3</sup>), and  $\kappa_s$  ( $= 1/\rho u^2$ ) and  $\kappa_0$  ( $= 1/\rho_0 u_0^2$ ) are the isentropic compressibilities of the solution and solvent (m<sup>2</sup>·N<sup>-1</sup>), respectively. The values of  $\phi_\kappa$  have been fitted by the least-squares method to the linear equation:

$$\phi_\kappa = \phi_\kappa^0 + S_\kappa m \quad (6)$$

where  $\phi_\kappa^0$  is the apparent molar isentropic compressibility at infinite dilution, which is also referred to as the partial molar isentropic compressibility, and is a measure of solute–solvent interactions. The  $\phi_\kappa^0$ ,  $S_\kappa$ , and standard deviation  $\sigma_\kappa$  values of linear regression of eq 6 have been listed in Table 5. The  $\phi_\kappa^0$  values for L-leucine/L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> solution are negative except for the L-leucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub> and 0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> systems at 298.15 K. The observed  $\phi_\kappa^0$  of L-leucine in 0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> at 298.15 K is 1.28 (10<sup>-11</sup> bar<sup>-1</sup>·m<sup>3</sup>·mol<sup>-1</sup>). The reported  $\phi_\kappa^0$  of L-leucine in 2 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> from our laboratory is -5.56 (10<sup>-11</sup> bar<sup>-1</sup>·m<sup>3</sup>·mol<sup>-1</sup>).<sup>24</sup> The negative values of  $\phi_\kappa^0$  (loss of compressibility of the medium) indicate that the water molecules surrounding the L-leucine/L-isoleucine molecules present a greater resistance to compression than the bulk. On the other hand, positive values of  $\phi_\kappa^0$  indicate that the water molecules around the L-leucine/L-isoleucine molecules are more compressible than the water molecules in the bulk



**Table 5.** Partial Molar Isentropic Compressibility,  $\phi_{\kappa}^0 \cdot 10^{11}/(\text{bar}^{-1} \cdot \text{m}^3 \cdot \text{mol}^{-1})$ , Slope,  $S_{\kappa} \cdot 10^{11}/(\text{bar}^{-1} \cdot \text{m}^3 \cdot \text{mol}^{-2} \cdot \text{mol}^{-2} \cdot \text{kg})$ , and Standard Deviation,  $\sigma_{\kappa} \cdot 10^{11}/(\text{bar}^{-1} \cdot \text{m}^3 \cdot \text{mol}^{-1})$  of L-Leucine/L-Isoleucine at Different Temperatures

T/K	$\phi_{\kappa}^0$	$S_{\kappa}$	$\sigma_{\kappa}$
L-Leucine in 0.512 mol·kg <sup>-1</sup> Aqueous K <sub>2</sub> SO <sub>4</sub>			
298.15	1.99(0.92)	-31.12(12.46)	0.9
303.15	-1.90(0.05)	3.73(0.77)	0.5
308.15	-1.30(0.39)	-0.55(4.19)	0.3
313.15	-1.18(0.09)	2.85(1.27)	0.1
318.15	-1.05(0.13)	3.17(1.74)	0.1
323.15	-0.93(0.08)	4.21(1.14)	0.9
L-Leucine in 0.512 mol·kg <sup>-1</sup> Aqueous KNO <sub>3</sub>			
298.15	1.28(0.34)	-23.40(4.47)	0.4
303.15	-1.46(0.18)	-3.57(1.42)	0.1
308.15	-1.18(0.16)	-3.83(1.39)	0.1
313.15	-0.97(0.07)	-1.93(0.88)	0.7
318.15	-0.87(0.07)	0.85(0.95)	0.7
323.15	-0.75(0.15)	4.07(2.02)	0.2
L-Isoleucine in 0.512 mol·kg <sup>-1</sup> Aqueous K <sub>2</sub> SO <sub>4</sub>			
298.15	-0.24(0.29)	-10.99(3.93)	0.3
303.15	-0.76(0.07)	-3.47(0.95)	0.7
308.15	-2.23(0.12)	5.86(1.63)	0.1
313.15	-1.80(0.03)	5.22(0.35)	0.2
318.15	-1.70(0.08)	5.46(1.05)	0.8
323.15	-1.55(0.17)	3.39(0.44)	0.1
L-Isoleucine in 0.512 mol·kg <sup>-1</sup> Aqueous KNO <sub>3</sub>			
298.15	-0.32(0.17)	-12.74(2.26)	0.2
303.15	-2.78(0.39)	-19.46(5.06)	0.4
308.15	-2.35(0.13)	4.06(1.53)	0.9
313.15	-2.11(0.32)	12.92(4.18)	0.3
318.15	-1.86(0.07)	9.53(0.89)	0.7
323.15	-1.47(0.17)	7.91(2.22)	0.2

solution. The observed values of  $\phi_{\kappa}^0$  of L-leucine/L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> systems could not be compared with the reported values as these are not available in the literature. The reported  $\phi_{\kappa}^0$  values of L-leucine in aqueous systems at 298.15 K are -3.178<sup>34</sup> and -3.159 (10<sup>-11</sup> bar<sup>-1</sup>·m<sup>3</sup>·mol<sup>-1</sup>),<sup>37</sup> whereas our value is -2.334 (10<sup>-11</sup> bar<sup>-1</sup>·m<sup>3</sup>·mol<sup>-1</sup>). The reported  $\phi_{\kappa}^0$  value of L-isoleucine in aqueous systems at 298.15 K is -3.21 (10<sup>-11</sup> bar<sup>-1</sup>·m<sup>3</sup>·mol<sup>-1</sup>),<sup>37</sup> whereas our value is -2.954 (10<sup>-11</sup> bar<sup>-1</sup>·m<sup>3</sup>·mol<sup>-1</sup>). Thus, our  $\phi_{\kappa}^0$  values are quite close to the literature values. The  $S_{\kappa}$  values are the experimental slope.

The partial molar isentropic compressibilities of transfer,  $\Delta_{\text{tr}}\phi_{\kappa}^0$ , of L-leucine/L-isoleucine from water to 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub> or 0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solution at a temperature have been calculated using the following equation:

$$\Delta_{\text{tr}}\phi_{\kappa}^0 = \phi_{\kappa}^0(0.5 \text{ mol}\cdot\text{L}^{-1} \text{ aqueous K}_2\text{SO}_4/0.5 \text{ mol}\cdot\text{L}^{-1} \text{ aqueous KNO}_3 \text{ solution}) - \phi_{\kappa}^0(\text{water}) \quad (7)$$

The computed  $\Delta_{\text{tr}}\phi_{\kappa}^0$  values of L-leucine and L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> solutions have been listed in Table 6. The  $\Delta_{\text{tr}}\phi_{\kappa}^0$  values of L-leucine in 0.5 mol·L<sup>-1</sup> aqueous

**Table 6.** Transfer Partial Molar Isentropic Compressibility,  $\Delta_{\text{tr}}\phi_{\kappa}^0 \cdot 10^{11}/(\text{bar}^{-1} \cdot \text{m}^3 \cdot \text{mol}^{-1})$ , of L-Leucine/L-Isoleucine from Water to 0.512 mol·kg<sup>-1</sup> Aqueous K<sub>2</sub>SO<sub>4</sub>/0.512 mol·kg<sup>-1</sup> KNO<sub>3</sub> at Different Temperatures

T/K = 298.15	$\Delta_{\text{tr}}\phi_{\kappa}^0$				
	303.15	308.15	313.15	318.15	323.15
L-Leucine in 0.512 mol·kg <sup>-1</sup> Aqueous K <sub>2</sub> SO <sub>4</sub>					
4.33	4.91	5.94	6.41	7.26	8.18
L-Leucine in 0.512 mol·kg <sup>-1</sup> Aqueous KNO <sub>3</sub>					
3.61	2.33	3.70	4.59	5.00	6.43
L-Isoleucine in 0.512 mol·kg <sup>-1</sup> Aqueous K <sub>2</sub> SO <sub>4</sub>					
2.71	5.97	6.78	7.66	8.93	10.05
L-Isoleucine in 0.512 mol·kg <sup>-1</sup> Aqueous KNO <sub>3</sub>					
2.64	3.90	6.66	7.34	8.85	10.12

K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> solution is higher than the  $\Delta_{\text{tr}}\phi_{\kappa}^0$  values of L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> at a particular temperature. The  $\Delta_{\text{tr}}\phi_{\kappa}^0$  values of L-leucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub> solution are higher than the corresponding values of L-leucine in 0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solution. Similarly, the  $\Delta_{\text{tr}}\phi_{\kappa}^0$  values of L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub> solution are higher than the corresponding values of L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solution. The  $\Delta_{\text{tr}}\phi_{\kappa}^0$  values for L-leucine/L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/KNO<sub>3</sub> solution increase with an increase in temperature. These trends of variations of  $\Delta_{\text{tr}}\phi_{\kappa}^0$  are consistent with the trends of variation of  $\Delta_{\text{tr}}\phi_{\nu}^0$ . The positive values of  $\Delta_{\text{tr}}\phi_{\kappa}^0$  may be attributed to the interactions occurring between K<sup>+</sup> and COO<sup>-</sup>/SO<sub>4</sub><sup>2-</sup> and between NO<sub>3</sub><sup>-</sup> and NH<sub>3</sub><sup>+</sup> ions. Due to these interactions, the electrostriction of neighboring water molecules around the charged centers of L-leucine/L-isoleucine will be reduced in the presence of K<sub>2</sub>SO<sub>4</sub> and KNO<sub>3</sub>. Therefore, the electrostricted water goes out of the hydration spheres of these ions and enters into the bulk which is more compressible,<sup>22,53,54</sup> which makes a positive contribution to  $\Delta_{\text{tr}}\phi_{\kappa}^0$ .

## CONCLUSIONS

The observed higher  $\phi_{\nu}^0$  values for L-leucine/L-isoleucine in 0.5 mol·L<sup>-1</sup> aqueous solution of K<sub>2</sub>SO<sub>4</sub> and 0.5 mol·L<sup>-1</sup> aqueous solution of KNO<sub>3</sub> as compared with their values in water suggest the domination of zwitterion-ion interactions than zwitterion-water dipole interactions in solutions. The  $\kappa_s$  values of (L-leucine + 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>) are lesser than those of (L-leucine + 0.5 mol·L<sup>-1</sup> KNO<sub>3</sub>) solutions at all temperatures of study which may be ascribed to stronger zwitterion-SO<sub>4</sub><sup>2-</sup> interactions than zwitterion-NO<sub>3</sub><sup>-</sup> interactions due to the stronger polar nature of SO<sub>4</sub><sup>2-</sup> in comparison with NO<sub>3</sub><sup>-</sup>. The decrease in isentropic compressibility values with an increase in temperature may be due to thermal rupture of water clusters which may cause the formation of a smaller cluster of water molecules leading to the compact clusters at higher temperatures. The negative  $\phi_{\kappa}^0$  may be due to the hydration of the charged centers of the amino acids as the hydrated water molecules appear to be less compressible than the bulk water. The higher values of  $\Delta_{\text{tr}}\phi_{\nu}^0$  of L-leucine in 0.5 mol·L<sup>-1</sup> aqueous K<sub>2</sub>SO<sub>4</sub>/0.5 mol·L<sup>-1</sup> aqueous KNO<sub>3</sub> solution than

corresponding values of L-isoleucine in  $0.5 \text{ mol} \cdot \text{L}^{-1}$  aqueous  $\text{K}_2\text{SO}_4/0.5 \text{ mol} \cdot \text{L}^{-1}$  aqueous  $\text{KNO}_3$  solution may be attributed to strong interactions in (L-leucine + aqueous salt) systems.

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