Volumetric Properties of Potassium Dihydrogen Citrate and Tripotassium Citrate in Water and in Aqueous Solutions of Alanine at T = (283.15 to 308.15) K

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Volumetric Properties of Potassium Dihydrogen Citrate and Tripotassium Citrate in Water and in Aqueous Solutions of Alanine at $T = $ (283.15 to 308.15) K

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Densities and sound velocities for solutions of potassium dihydrogen citrate (KH_2Cit) and tripotassium citrate (K_3Cit) in aqueous solutions of (0.00, 0.23, 0.47, and 0.72) $mol \cdot kg^{-1}$ of alanine have been determined experimentally at $T = $ (283.15, 288.15, 293.15, 298.15, 303.15, and 308.15) K at atmospheric pressure. From these experimental data, the apparent molar volume and isentropic compressibility values have been evaluated and fitted to a Redlich−Mayer-type equation. The results show positive transfer volumes at infinite dilution for electrolytes from water to aqueous alanine solutions, and these values increase with the concentration of alanine. The apparent molar isentropic compressibility of both KH_2Cit and K_3Cit in aqueous alanine solutions is negative, which implies that the water molecules around these salts are less compressible than the water molecules in the bulk solutions. It was found that the effect of alanine concentration on the apparent molar volume and isentropic compressibility of K_3Cit is more than those of KH_2Cit.

Introduction

Electrolytes are known to influence the stability of biologically important molecules such as proteins.[1,2] Because proteins are complex molecules and their behavior in solutions is governed by a combination of many more specific interactions, direct study of electrolyte−protein interactions is difficult. Therefore, to obtain more insight into the hydration of proteins and noncovalent forces stabilizing their native structure, it is necessary to determine the effects of salts on the model compounds of proteins such as amino acids and peptides. Although the volumetric behavior of amino acids in aqueous electrolyte solutions has been extensively studied by many research groups,[3–22] experimental data on the volumetric behavior of electrolytes in aqueous amino acid solutions are relatively scarce. Furthermore, regarding the volumetric behavior of aqueous electrolyte solutions, much less attention has been directed to organic salts which have significant biological and industrial importance. Among the organic salts, citrates are of considerable significance in many biochemical and chemical processes, and these salts are produced in large quantities and used in food, cosmetic, pharmaceutical, and chemical industries.[23–26] The present work, which is a continuation of our studies of volumetric behavior of aqueous solutions of organic salts,[27,28] presents experimental data on the density and sound velocity of potassium dihydrogen citrate (KH_2Cit) and tripotassium citrate (K_3Cit) in aqueous solutions of (0.00, 0.23, 0.47, and 0.72) $mol \cdot kg^{-1}$ of alanine at $T = $ (283.15, 288.15, 293.15, 298.15, 303.15, and 308.15) K, and the values of apparent molar volume, V_φ, and apparent molar isentropic compressibility, K_φ were then calculated from the measured data. Although there are some reports on the volumetric properties of aqueous tripotassium citrate solutions,[28,29] there are not any experimental data on the density or ultrasonic velocity of aqueous solutions of KH_2Cit in the literature.

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Experimental Section

Materials. Alanine (S-(+)-alanine) and potassium dihydrogen citrate ($C_6H_7KO_7$) were obtained from Merck. Tripotassium citrate ($C_6H_5K_3O_7 \cdot H_2O$) was obtained from Fluka. The amino acid and salts were used without further purification, and double distilled, deionized water was used.

Apparatus and Procedures. All the solutions were prepared by mass on a Sartorius CP124S balance precise to within ± 0.0001 g. The density and sound velocity of the mixtures were measured at different temperatures with a digital vibrating-tube analyzer (Anton Paar DSA 5000, Austria) with proportional temperature control that kept the samples at working temperature within ± 10^{-3} K. The apparatus was calibrated with double distilled, deionized, and degassed water and dry air at atmospheric pressure according to the instrument catalog. Densities and ultrasonic velocities can be measured to ± 10^{-6} $g \cdot cm^{-3}$ and ± 10^{-2} $m \cdot s^{-1}$, respectively, under the most favorable conditions. The uncertainties of density and ultrasonic velocity measurements were ± $3 \cdot 10^{-6}$ $g \cdot cm^{-3}$ and ± 10^{-1} $m \cdot s^{-1}$, respectively.

Results and Discussion

Experimental data of density (d) and sound velocity (u) for various potassium dihydrogen citrate and tripotassium citrate solutions determined at $T = $ (283.15, 288.15, 293.15, 298.15, 303.15, and 308.15) K are given in Tables 1 and 2, respectively. The experimental density and ultrasonic velocity data have been fitted to the following equation

$$F = P_1 \exp\left(\frac{P_2 + P_3 w_s + P_4 w_s^{1.5}}{T - P_5}\right) + P_6 w_a \qquad (1)$$

where w_s and w_a are the weight fraction of the salt and amino acid, respectively; T is the absolute temperature; and P_1, P_2, P_3, P_4, P_5, and P_6 are the curve-fit coefficients. The curve-fit coefficients and the absolute relative deviations (ARD) for density and sound velocity of investigated systems are given in Table 3. On the basis of the obtained ARD values, we conclude that eq 1 can be successfully used for the correlation of the investigated physical

Table 1. Experimental Density d/(g·cm^{-3}) and Ultrasonic Velocity u/(m·s^{-1}) of KH$_2$Cit in Aqueous Amino Acid Solutions at Different Temperatures

m_s	$T = 283.15$ K		$T = 288.15$ K		$T = 293.15$ K		$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K	
mol·kg^{-1}	d	u	d	u	d	u	d	u	d	u	d	u
					$m_a = 0.00$ mol·kg^{-1}							
0.0000	0.999699	1447.59	0.999099	1466.25	0.998203	1482.66	0.997043	1497.00	0.995645	1509.44	0.994029	1520.12
0.0063	1.000472	1448.79	0.999861	1466.92	0.998956	1483.11	0.997788	1497.32	0.996385	1509.69	0.994762	1520.35
0.0186	1.001971	1450.10	1.001338	1468.23	1.000414	1484.32	0.999232	1498.46	0.997809	1510.74	0.996176	1521.33
0.0314	1.003529	1451.49	1.002874	1469.53	1.001931	1485.54	1.000729	1499.59	0.999297	1511.79	0.997649	1522.32
0.0407	1.004651	1452.55	1.003984	1470.40	1.003026	1486.36	1.001815	1500.36	1.000370	1512.53	0.998709	1523.01
0.0561	1.006516	1454.17	1.005822	1472.02	1.004843	1487.86	1.003610	1501.76	1.002147	1513.83	1.000472	1524.23
0.0574	1.006666	1454.33	1.005968	1472.12	1.004987	1487.95	1.003753	1501.86	1.002289	1513.93	1.000612	1524.32
0.0868	1.010190	1457.20	1.009446	1475.03	1.008423	1490.67	1.007152	1504.37	1.005655	1516.28	1.003950	1526.53
0.0905	1.010651	1457.87	1.009899	1475.39	1.008870	1491.02	1.007595	1504.69	1.006094	1516.59	1.004385	1526.80
0.1399	1.016401	1462.88	1.015575	1480.14	1.014480	1495.46	1.013146	1508.83	1.011593	1520.47	1.009837	1530.44
0.1655	1.019362	1465.42	1.018497	1482.51	1.017370	1497.68	1.016004	1510.90	1.014426	1522.42	1.012648	1532.27
0.2840	1.032786	1477.02	1.031761	1493.42	1.030491	1507.85	1.029000	1520.45	1.027306	1531.38	1.025424	1540.67
0.3960	1.044960	1487.37	1.043803	1503.11	1.042412	1516.97	1.040810	1529.04	1.039020	1539.43	1.037047	1548.24
0.4766	1.053369	1494.58	1.052126	1509.81	1.050655	1523.31	1.048983	1534.98	1.047125	1545.03	1.045096	1553.52
0.5861	1.064692	1504.06	1.063335	1518.86	1.061762	1531.83	1.059998	1543.01	1.058060	1552.60	1.055951	1560.69
0.5922	1.065268	1504.67	1.063904	1519.37	1.062326	1532.32	1.060556	1543.47	1.058614	1553.03	1.056504	1561.11
0.7578	1.081711	1518.53	1.080195	1532.54	1.078480	1544.73	1.076586	1555.24	1.074528	1564.18	1.072311	1571.63
					$m_a = 0.23$ mol·kg^{-1}							
0.0000	1.006295	1464.37	1.005608	1482.04	1.004641	1497.71	1.003426	1511.40	1.001982	1523.35	1.000329	1533.61
0.0100	1.007517	1465.69	1.006815	1483.15	1.005835	1498.73	1.004606	1512.36	1.003152	1524.23	1.001487	1534.42
0.0397	1.011089	1468.81	1.010337	1486.06	1.009314	1501.43	1.008049	1514.85	1.006558	1526.56	1.004867	1536.59
0.0586	1.013353	1470.73	1.012573	1487.92	1.011523	1503.16	1.010234	1516.49	1.008722	1528.08	1.007013	1538.02
0.1000	1.018250	1475.26	1.017406	1492.24	1.016302	1507.23	1.014962	1520.33	1.013407	1531.76	1.011658	1541.48
0.1475	1.023712	1479.57	1.022800	1496.24	1.021633	1510.91	1.020242	1523.77	1.018640	1534.90	1.016844	1544.39
0.2010	1.029873	1484.97	1.028887	1501.23	1.027658	1515.59	1.026205	1528.12	1.024551	1538.97	1.022708	1548.20
0.2855	1.039292	1493.07	1.038201	1508.74	1.036873	1522.64	1.035334	1534.71	1.033603	1545.13	1.031690	1554.00
0.3944	1.051073	1502.82	1.049853	1518.00	1.048411	1531.34	1.046772	1542.87	1.044946	1552.80	1.042949	1561.22
0.5999	1.072368	1520.81	1.070941	1534.88	1.069312	1547.23	1.067499	1557.90	1.065518	1566.98	1.063378	1574.58
0.7854	1.090428	1535.76	1.088842	1548.98	1.087066	1560.58	1.085121	1570.47	1.083017	1578.84	1.080764	1585.79
					$m_a = 0.47$ mol·kg^{-1}							
0.0000	1.012689	1480.42	1.011923	1497.41	1.010890	1512.44	1.009620	1525.64	1.008131	1537.07	1.006443	1546.87
0.0410	1.017618	1484.80	1.016787	1501.43	1.015698	1516.19	1.014379	1529.13	1.012844	1540.33	1.011118	1549.90
0.0609	1.019957	1486.86	1.019099	1503.39	1.017983	1518.02	1.016638	1530.81	1.015086	1541.89	1.013338	1551.38
0.1011	1.024706	1490.91	1.023787	1507.13	1.022621	1521.52	1.021230	1534.08	1.019633	1544.94	1.017849	1554.21
0.1014	1.024752	1490.83	1.023832	1507.07	1.022665	1521.45	1.021273	1534.00	1.019679	1544.86	1.017891	1554.13
0.1500	1.030309	1495.10	1.029324	1511.01	1.028097	1525.10	1.026653	1537.35	1.025009	1547.96	1.023182	1557.00
0.1501	1.030388	1495.58	1.029400	1511.55	1.028173	1525.68	1.026727	1537.95	1.025083	1548.58	1.023256	1557.62
0.1996	1.035904	1500.45	1.034852	1516.08	1.033566	1529.90	1.032072	1541.90	1.030382	1552.27	1.028510	1561.11
0.3015	1.047233	1509.65	1.046059	1524.7	1.044662	1537.93	1.043067	1549.42	1.041285	1559.32	1.039332	1567.70
0.3975	1.057504	1518.27	1.056225	1532.8	1.054732	1545.54	1.053048	1556.58	1.051188	1566.05	1.049163	1574.00
0.6004	1.078224	1535.49	1.076747	1549.02	1.075076	1560.86	1.073229	1570.99	1.071219	1579.61	1.069058	1586.80
0.8065	1.098105	1552.10	1.096457	1564.73	1.094629	1575.67	1.092640	1584.99	1.090498	1592.85	1.088213	1599.34
					$m_a = 0.72$ mol·kg^{-1}							
0.0000	1.019089	1496.71	1.018244	1513.02	1.017145	1527.48	1.015823	1540.10	1.014291	1551.04	1.012566	1560.41
0.0202	1.021512	1498.82	1.020635	1514.97	1.019511	1529.30	1.018165	1541.78	1.016612	1552.60	1.014868	1561.85
0.0604	1.026264	1502.92	1.025329	1518.80	1.024153	1532.86	1.022759	1545.10	1.021164	1555.71	1.019383	1564.76
0.1008	1.030957	1506.72	1.029967	1522.34	1.028740	1536.13	1.027302	1548.16	1.025668	1558.58	1.023850	1567.42
0.1474	1.036323	1511.21	1.035273	1526.55	1.033990	1540.05	1.032503	1551.80	1.030823	1561.99	1.028966	1570.62
0.2013	1.042326	1516.27	1.041207	1531.23	1.039866	1544.44	1.038324	1555.94	1.036595	1565.86	1.034693	1574.21
0.3053	1.053761	1525.73	1.052520	1540.13	1.051070	1552.78	1.049429	1563.78	1.047611	1573.17	1.045626	1581.09
0.3984	1.063740	1535.25	1.062400	1549.19	1.060860	1561.19	1.059135	1571.73	1.057242	1580.70	1.055189	1588.23
0.6005	1.084229	1550.72	1.082703	1563.66	1.080988	1574.91	1.079107	1584.56	1.077069	1592.73	1.074885	1599.52
0.7882	1.102308	1565.60	1.100630	1577.69	1.098777	1588.17	1.096767	1597.07	1.094612	1604.56	1.092316	1610.69

properties at different temperatures and concentrations. In fact, for each property and for each salt, one set of parameters successfully has been used to correlate all experimental data measured at six temperatures and four amino acid molalities.

The apparent molar volumes of the electrolytes V_φ in aqueous amino acid solutions were computed from the density of the solution by using the following equation[30]

$$V_\varphi = \frac{1000}{m_s d d_0}(d_0 - d) + \frac{M_s}{d} \tag{2}$$

where M_s is the molar mass of the salt; m_s is the molality of the salt; and d and d_0 are the densities of the solution and

solvent, respectively. For ternary systems, amino + water is considered as the solvent.

The Redlich−Mayer-type equation[31,32] in the form

$$V_\varphi = V_\varphi^0 + S_v m_s^{0.5} + B_v m_s \tag{3}$$

was used to obtain V_φ^0, the limiting apparent molar volume of KH$_2$Cit or K$_3$Cit at different temperatures and different amino acid concentrations. In this equation, S_v and B_v are the empirical parameters which depend on solute, solvent, and temperature. In this work, the temperature dependence of V_φ^0, S_v, and B_v was

Table 2. Experimental Density $d/(\text{g}\cdot\text{cm}^{-3})$ and Ultrasonic Velocity $u/(\text{m}\cdot\text{s}^{-1})$ of K₃Cit in Aqueous Amino Acid Solutions at Different Temperatures

m_s	$T = 283.15$ K		$T = 288.15$ K		$T = 293.15$ K		$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K	
$\text{mol}\cdot\text{kg}^{-1}$	d	u	d	u	d	u	d	u	d	u	d	u
					$m_a = 0.23 \text{ mol}\cdot\text{kg}^{-1}$							
0.0000	1.006338	1464.06	1.005647	1481.75	1.004677	1497.44	1.003459	1511.12	1.002013	1523.08	1.000357	1533.33
0.0278	1.012105	1470.95	1.011357	1488.38	1.010337	1503.83	1.009077	1517.33	1.007596	1529.12	1.005910	1539.23
0.0392	1.014446	1473.07	1.013676	1490.43	1.012638	1505.77	1.011361	1519.20	1.009868	1530.91	1.008171	1540.92
0.0394	1.014452	1473.43	1.013681	1490.79	1.012642	1506.14	1.011365	1519.60	1.009872	1531.29	1.008175	1541.32
0.0469	1.015977	1474.57	1.015191	1491.96	1.014141	1507.26	1.012854	1520.66	1.011351	1532.32	1.009647	1542.29
0.0628	1.019202	1478.09	1.018385	1495.27	1.017310	1510.44	1.016002	1523.74	1.014481	1535.28	1.012763	1545.18
0.0936	1.025322	1484.52	1.024451	1501.45	1.023330	1516.41	1.021982	1529.51	1.020426	1540.87	1.018680	1550.62
0.1286	1.032144	1491.97	1.031215	1508.58	1.030042	1523.33	1.028653	1536.21	1.027062	1547.41	1.025284	1557.00
0.1552	1.037349	1497.56	1.036376	1513.99	1.035166	1528.58	1.033745	1541.30	1.032127	1552.34	1.030328	1561.79
0.1860	1.043224	1503.66	1.042202	1519.86	1.040953	1534.23	1.039497	1546.74	1.037848	1557.63	1.036022	1566.93
0.2438	1.053987	1515.12	1.052881	1530.93	1.051559	1544.89	1.050040	1557.09	1.048341	1567.65	1.046473	1576.64
0.3215	1.068308	1530.47	1.067097	1545.79	1.065685	1559.29	1.064090	1571.03	1.062324	1581.19	1.060400	1589.83
0.4163	1.085150	1549.02	1.083824	1563.63	1.082314	1576.48	1.080632	1587.67	1.078797	1597.33	1.076810	1605.54
0.4965	1.098838	1564.29	1.097427	1578.33	1.095839	1590.69	1.094097	1601.43	1.092202	1610.66	1.090168	1618.50
0.6035	1.116323	1584.22	1.114808	1597.45	1.113131	1609.15	1.111309	1619.27	1.109348	1627.99	1.107257	1635.36
0.6986	1.131531	1602.78	1.129933	1615.49	1.128184	1626.68	1.126300	1636.33	1.124285	1644.63	1.122148	1651.61
0.7586	1.141083	1612.92	1.139435	1625.23	1.137644	1636.04	1.135725	1645.35	1.133679	1653.34	1.131515	1660.02
					$m_a = 0.47 \text{ mol}\cdot\text{kg}^{-1}$							
0.0000	1.012738	1480.49	1.011964	1497.56	1.010930	1512.60	1.009657	1525.79	1.008167	1537.24	1.006475	1547.04
0.0093	1.014684	1482.80	1.013891	1499.80	1.012839	1514.79	1.011551	1527.90	1.010047	1539.28	1.008346	1549.01
0.0186	1.016591	1484.96	1.015782	1501.81	1.014714	1516.71	1.013412	1529.81	1.011899	1541.10	1.010187	1550.78
0.0280	1.018497	1486.90	1.017670	1503.74	1.016586	1518.62	1.015272	1531.64	1.013747	1542.89	1.012028	1552.52
0.0476	1.022474	1491.15	1.021611	1507.73	1.020496	1522.52	1.019157	1535.36	1.017609	1546.49	1.015871	1556.05
0.0628	1.025528	1494.40	1.024639	1510.90	1.023502	1525.54	1.022141	1538.28	1.020579	1549.36	1.018824	1558.84
0.0959	1.032084	1501.34	1.031139	1517.62	1.029954	1532.02	1.028554	1544.57	1.026956	1555.45	1.025174	1564.76
0.1284	1.038281	1507.88	1.037284	1523.94	1.036056	1538.09	1.034617	1550.45	1.032987	1561.17	1.031180	1570.32
0.1303	1.038635	1508.31	1.037636	1524.36	1.036403	1538.50	1.034963	1550.88	1.033332	1561.58	1.031519	1570.72
0.1527	1.042945	1512.76	1.041912	1528.63	1.040650	1542.62	1.039187	1554.85	1.037534	1565.45	1.035702	1574.45
0.1858	1.049366	1519.52	1.048280	1535.13	1.046977	1548.90	1.045475	1560.94	1.043790	1571.35	1.041934	1580.18
0.2483	1.06102	1531.92	1.059847	1547.08	1.058469	1560.49	1.056902	1572.13	1.055164	1582.18	1.053262	1590.72
0.3198	1.074022	1545.94	1.072758	1560.64	1.071301	1573.54	1.069668	1584.77	1.067872	1594.47	1.065923	1602.67
0.4196	1.091333	1564.93	1.089957	1578.93	1.088403	1591.25	1.086685	1601.93	1.084817	1611.11	1.082803	1618.86
0.4948	1.104246	1579.27	1.102790	1592.75	1.101167	1604.60	1.099391	1614.83	1.097473	1623.62	1.095416	1631.05
0.5974	1.121327	1598.53	1.119771	1611.30	1.118065	1622.52	1.116218	1632.20	1.114235	1640.51	1.112127	1647.47
0.7036	1.137728	1617.65	1.136088	1629.75	1.134308	1640.34	1.132394	1649.47	1.130357	1657.25	1.128199	1663.77
0.7569	1.145910	1627.36	1.144231	1639.09	1.142415	1649.37	1.140471	1658.20	1.138407	1665.76	1.136227	1672.04
					$m_a = 0.72 \text{ mol}\cdot\text{kg}^{-1}$							
0.0000	1.018714	1495.79	1.017869	1512.17	1.016772	1526.68	1.015448	1539.36	1.013917	1550.32	1.012194	1559.72
0.0123	1.021240	1498.60	1.020371	1514.88	1.019251	1529.30	1.017910	1541.88	1.016363	1552.78	1.014626	1562.11
0.0187	1.022545	1500.02	1.021665	1516.26	1.020537	1530.63	1.019186	1543.17	1.017632	1554.04	1.015888	1563.33
0.0398	1.026829	1504.49	1.02591	1520.63	1.024749	1534.84	1.023372	1547.28	1.021795	1558.03	1.020031	1567.21
0.0629	1.031393	1509.38	1.030435	1525.32	1.029243	1539.38	1.027836	1551.62	1.026235	1562.26	1.024450	1571.31
0.0951	1.037756	1516.08	1.036747	1531.77	1.035510	1545.61	1.034066	1557.69	1.032432	1568.14	1.030620	1577.01
0.1274	1.044054	1522.74	1.042992	1538.19	1.041710	1551.81	1.040232	1563.68	1.038567	1573.95	1.036728	1582.66
0.1512	1.048551	1527.43	1.047458	1542.67	1.046146	1556.16	1.044640	1567.92	1.042952	1578.04	1.041095	1586.65
0.1872	1.055294	1534.54	1.05415	1549.58	1.052795	1562.83	1.051252	1574.34	1.049532	1584.28	1.047647	1592.73
0.2586	1.068444	1548.71	1.067205	1563.27	1.065771	1576.05	1.064159	1587.18	1.062382	1596.78	1.060445	1604.91
0.3222	1.079965	1560.98	1.078648	1575.05	1.077148	1587.44	1.075477	1598.20	1.073649	1607.43	1.071674	1615.21
0.4153	1.096250	1578.83	1.094831	1592.28	1.093241	1604.09	1.091496	1614.29	1.089602	1623.05	1.087569	1630.42
0.4952	1.109674	1593.88	1.108177	1606.74	1.106519	1618.06	1.104714	1627.84	1.102769	1636.22	1.100695	1643.23
0.6124	1.129049	1615.63	1.127444	1627.79	1.125694	1638.42	1.123811	1647.58	1.121798	1655.36	1.119665	1661.86
0.7035	1.143269	1632.03	1.141595	1643.56	1.139783	1653.65	1.137846	1662.32	1.135786	1669.69	1.133612	1675.83
0.7557	1.151377	1641.42	1.149664	1652.67	1.147818	1662.48	1.145853	1670.91	1.143766	1678.06	1.141571	1683.97

expressed in polynomial form with $(T - 283.15)$ K as a variable, as follows

$$V_\varphi^0 = A^0 + A^1(T - 283.15) + A^2(T - 283.15)^2 \quad (4)$$

$$S_v = S_v^0 + S_v^1(T - 283.15) + S_v^2(T - 283.15)^2 \quad (5)$$

$$B_v = B_v^0 + B_v^1(T - 283.15) + B_v^2(T - 283.15)^2 \quad (6)$$

The coefficients of these equations for V_φ at each amino acid concentration are given in Table 4. The values of V_φ^0 at different temperatures and amino acid concentrations calcu-

lated from eq 4 are given in Table 5. The values of the infinite dilution apparent molar volume are an important property. At infinite dilution, each ion is surrounded only by the solvent molecules and is infinitely distant from other ions. It follows, therefore, that V_φ^0 is unaffected by ion–ion interaction, and it is a measure only of the ion–solvent interaction.[33,34] As an example, in Figures 1 and 2, the temperature and concentration dependence of V_φ have been given, respectively, for KH₂Cit in water and K₃Cit in aqueous solutions of 0.72 mol·kg⁻¹ of alanine. A similar behavior has been obtained for other systems studied in this work. Figures 1

and 2 show that the apparent molar volumes of investigated electrolytes in water and in aqueous alanine solutions increased by increasing the salt molality. For the low concentrations of the salt, the small volume is attributed to the strong attractive interactions due to the hydration of ions. By increasing the salt concentration, the ion–ion interaction increases and the positive initial slope of V_φ against salt concentration is attributed to these interactions. In the electrolyte solutions, the solute–solute interactions are characterized by positive slopes of V_φ vs concentration plots.[33] This is attributed to the phenomenon, described in terms of destructive overlap of cospheres,[35,36] resulting in a net decrease of solvation, thereby increasing the solute volume. The effect of temperature on the V_φ^0 of the salts in aqueous alanine solutions has been shown in Figure 3. As can be seen from Figure 3, the infinite dilution apparent molar volume of investigated salts in aqueous alanine solutions increases with increasing temperature and alanine concentration, and also at each temperature the infinite dilution apparent molar volumes of KH_2Cit are larger than those of K_3Cit. In fact, the infinite dilution apparent molar volume is equal to the infinite dilution partial molar volume, and therefore, due to the additivity principle at infinite dilution, we have

$$V_\varphi^0(K_3Cit) = 3V_\varphi^0(K^+) + V_\varphi^0(Cit^{3-}), \quad V_\varphi^0(KH_2Cit)$$
$$= V_\varphi^0(K^+) + V_\varphi^0(H_2Cit^{1-}) \qquad (7)$$

The infinite dilution apparent molar volume of ions can be expressed as the sum of two contributions[37]

$$V_\varphi^0(ion) = V_\varphi^0(int) + V_\varphi^0(elect) \qquad (8)$$

where $V_\varphi^0(int)$ is the intrinsic (related to the size of the ions and to packing effects) apparent molar volume and $V_\varphi^0(elect)$ is the electrostriction apparent molar volume related to ion–solvent interactions (i.e., the decrease in volume due to hydration). Table 5 and Figure 3 show that the values of V_φ^0 for KH_2Cit are larger than those for K_3Cit. This is because the triply charged Cit^{3-} ions are more hydrated than the singly charged H_2Cit^{1-} ions, and therefore the values of $V_\varphi^0(elect)$ for K_3Cit are more negative than those for KH_2Cit. The term $\partial V_\varphi^0(int)/\partial T$ contributes negligibly to the overall temperature dependence of $V_\varphi^0(ion)$, and therefore, an increase in the V_φ^0 by increasing temperature occurs with loss of hydration. Also, as can be seen from Figures 1 and 2, the initial slopes of V_φ against molality of salts are positive, whose magnitudes increase by decreasing temperature. This is because at higher temperatures ion–solvent interactions are weakened.

Table 3. Fitting Parameters of Equation 1 along with the Corresponding Absolute Relative Deviation, ARD, for Density and Ultrasonic Velocity of the Investigated Systems

	Density					
	parameters					
system	P_1	P_2	P_3	P_4	P_5	P_6
K_3Cit + alanine + H_2O	0.7106	439.4408	867.1751	−0.0931	−1001.0159	0.3163
KH_2Cit + alanine + H_2O	0.8300	134.4907	383.6506	−0.0926	−437.9846	0.3239

	Sound Velocity					
	parameters					
system	P_1	P_2	P_3	P_4	P_5	P_6
K_3Cit + alanine + H_2O	1830.621	−23.6276	54.0298	0.0286	181.7592	751.2232
KH_2Cit + alanine + H_2O	1691.4212	−9.0110	19.2198	−0.1024	224.8175	757.1022

	$ARD^a \cdot 10^5$ (for Density)					
	temperature					
system	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
K_3Cit + alanine (0.00 m) + H_2O^b	–	23.09	24.64	28.44	23.55	21.56
K_3Cit + alanine (0.23 m) + H_2O	43.12	12.39	31.64	36.63	24.10	10.63
K_3Cit + alanine (0.47 m) + H_2O	26.57	16.46	37.17	38.68	21.96	15.04
K_3Cit + alanine (0.72 m) + H_2O	39.88	16.56	17.29	16.86	24.86	52.13
KH_2Cit + alanine (0.00 m) + H_2O	55.06	18.62	34.62	38.70	30.46	24.70
KH_2Cit + alanine (0.23 m) + H_2O	27.81	20.77	43.65	43.25	21.17	21.09
KH_2Cit + alanine (0.47 m) + H_2O	23.93	19.64	36.78	31.78	6.99	39.11
KH_2Cit + alanine (0.72 m) + H_2O	28.25	24.12	34.92	25.85	23.34	55.16

	$ARD^a \cdot 10^2$ (for Sound Velocity)					
	temperature					
system	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
K_3Cit + alanine (0.00 m) + H_2O^b	–	0.12	0.10	0.10	0.09	0.07
K_3Cit + alanine (0.23 m) + H_2O	0.16	0.07	0.07	0.08	0.06	0.06
K_3Cit + alanine (0.47 m) + H_2O	0.06	0.06	0.08	0.07	0.04	0.10
K_3Cit + alanine (0.72 m) + H_2O	0.05	0.06	0.07	0.05	0.10	0.19
KH_2Cit + alanine (0.00 m) + H_2O	0.12	0.08	0.02	0.04	0.07	0.08
KH_2Cit + alanine (0.23 m) + H_2O	0.03	0.02	0.01	0.03	0.04	0.02
KH_2Cit + alanine (0.47 m) + H_2O	0.06	0.02	0.02	0.03	0.05	0.08
KH_2Cit + alanine (0.72 m) + H_2O	0.16	0.08	0.04	0.06	0.08	0.14

^{a} $ARD = 1 / NP\Sigma[d_{exptl} − d_{calcd} / d_{exptl}]$. ^{b} Experimental data taken from ref 28.

Table 4. Fitting Parameters of Equations 4, 5, and 6 for V_φ and Equations 14, 15, and 16 for $10^4 K_\varphi$ along with the Corresponding Absolute Relative Deviation

	V_φ									
	parameters									
system	A^0	A^1	A^2	S_v^0	S_v^1	S_v^2	B_v^0	B_v^1	B_v^2	$10^2 \cdot$ ARD
K_3Cit + alanine (0.00 m) + H_2O^a	90.1462	0.4257	−0.0058	34.5338	−0.1993	0.0050	−11.0222	−0.0008	−0.0023	0.39
K_3Cit + alanine (0.23 m) + H_2O	95.5972	0.4545	−0.0059	21.5356	−0.2455	0.0028	−0.6744	−0.0007	0.0007	0.20
K_3Cit + alanine (0.47 m) + H_2O	96.7703	0.4297	−0.0050	24.3879	−0.2363	0.0006	−3.6646	−0.0006	0.0025	0.30
K_3Cit + alanine (0.72 m) + H_2O	99.4232	0.3978	−0.0044	20.7796	−0.2123	0.0003	−1.7793	−0.0005	0.0023	0.13
KH_2Cit + alanine (0.00 m) + H_2O	106.7227	0.3762	−0.0046	5.1997	−0.1392	0.0066	2.2536	−0.0011	−0.0046	0.11
KH_2Cit + alanine (0.23 m) + H_2O	107.8105	0.341	−0.0033	5.4822	−0.1077	0.0033	1.0033	−0.0010	−0.0023	0.08
KH_2Cit + alanine (0.47 m) + H_2O	108.6518	0.3388	−0.0034	4.5956	−0.1182	0.0028	2.1113	−0.0117	−0.0010	0.13
KH_2Cit + alanine (0.72 m) + H_2O	109.5779	0.3107	−0.0030	4.7904	−0.0771	0.0020	1.3641	−0.0377	−0.0004	0.09

	K_φ									
	parameters									
system	A^0	A^1	A^2	S_k^0	S_k^1	S_k^2	B_k^0	B_k^1	B_k^2	$10^2 \cdot$ ARD
K_3Cit + alanine (0.00 m) + H_2O^a	−2.5264	0.0660	−0.0012	2.0948	−0.1367	0.0030	−0.8897	0.0966	−0.0022	0.76
K_3Cit + alanine (0.23 m) + H_2O	−2.1812	0.0306	−0.0004	1.3421	−0.0211	0.0003	−0.3664	0.0054	−0.0001	0.99
K_3Cit + alanine (0.47 m) + H_2O	−2.0415	0.0257	−0.0003	1.2693	−0.0119	−0.0001	−0.3709	−0.0003	0.0002	1.29
K_3Cit + alanine (0.72 m) + H_2O	−1.8296	0.0235	−0.0003	0.8374	−0.0115	0.0001	−0.0591	0.0003	0.0000	0.70
KH_2Cit + alanine (0.00 m) + H_2O	−1.2182	0.0882	−0.0021	1.7370	−0.2773	0.0074	−1.2020	0.2349	−0.0064	5.88
KH_2Cit + alanine (0.23 m) + H_2O	−0.8945	0.0292	−0.0005	0.6719	−0.0460	0.0011	−0.2729	0.0307	−0.0008	1.80
KH_2Cit + alanine (0.47 m) + H_2O	−0.7298	0.0178	−0.0002	0.2961	−0.0083	0.0001	0.0105	−0.0001	0.0000	0.97
KH_2Cit + alanine (0.72 m) + H_2O	−0.6468	0.0160	−0.0002	0.1897	−0.0073	0.0001	0.072	0.0002	0.0000	1.94

^{a} Experimental data taken from ref 28.

Table 5. Values of $V_\varphi^0/(cm^3 \cdot mol^{-1})$ and $E_\varphi^0/(cm^3 \cdot mol^{-1} \cdot K^{-1})$ of Investigated Electrolytes at Different Temperatures and Alanine Concentrations

	temperature					
system	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
	V_φ^0					
K_3Cit + alanine (0.00 m) + H_2O	90.146	92.130	93.823	95.227	96.340	97.164
K_3Cit + alanine (0.23 m) + H_2O	95.597	97.722	99.552	101.087	102.327	103.272
K_3Cit + alanine (0.47 m) + H_2O	96.770	98.794	100.567	102.091	103.364	104.388
K_3Cit + alanine (0.72 m) + H_2O	99.423	101.302	102.961	104.400	105.619	106.618
KH_2Cit + alanine (0.00 m) + H_2O	106.723	108.489	110.025	111.331	112.407	113.253
KH_2Cit + alanine (0.23 m) + H_2O	107.811	109.433	110.891	112.183	113.311	114.273
KH_2Cit + alanine (0.47 m) + H_2O	108.652	110.261	111.700	112.969	114.068	114.997
KH_2Cit + alanine (0.72 m) + H_2O	109.578	111.056	112.385	113.563	114.592	115.470
	E_φ^0					
K_3Cit + alanine (0.00 m) + H_2O	0.426	0.368	0.310	0.252	0.194	0.136
K_3Cit + alanine (0.23 m) + H_2O	0.4545	0.3955	0.3365	0.2775	0.2185	0.1595
K_3Cit + alanine (0.47 m) + H_2O	0.4297	0.3797	0.3297	0.2797	0.2297	0.1797
K_2Cit + alanine (0.72 m) + H_2O	0.3978	0.3538	0.3098	0.2658	0.2218	0.1778
KH_2Cit + alanine (0.00 m) + H_2O	0.3762	0.3302	0.2842	0.2382	0.1922	0.1462
KH_2Cit + alanine (0.23 m) + H_2O	0.3410	0.3080	0.2750	0.2420	0.2090	0.1760
KH_2Cit + alanine (0.47 m) + H_2O	0.3388	0.3048	0.2708	0.2368	0.2028	0.1688
KH_2Cit + alanine (0.72 m) + H_2O	0.3107	0.2807	0.2507	0.2207	0.1907	0.1607

The infinite dilution apparent molar expansibility can be obtained by differentiating eq 4 with respect to temperature

$$E_\varphi^0 = \left(\frac{\partial V_\varphi^0}{\partial T}\right)_P = A^1 + 2A^2(T - 283.15) \quad (9)$$

The E_φ^0 values of the investigated salts at different temperatures and alanine concentrations are also given in Table 5. As mentioned above, $E_\varphi^0 = \left(\partial V_\varphi^0(\text{elect}) / \partial T\right)_P$.

From Table 5, we note that at each temperature E_φ^0 values have a positive value and decrease by increasing temperature. On heating, some water molecules may be released from the hydration layers. This would increase the solution volume a little more rapidly than that of the solvent (aqueous alanine solutions).

Figure 4 shows the effect of alanine concentration on the apparent molar volume of the KH_2Cit and K_3Cit at 298.15 K. Figure 4 shows that the initial slope of V_φ against molality of the salt for K_3Cit is larger than those for KH_2Cit. This behavior can be attributed to the fact that the interactions between Cit^{3-} (produced from the dissociation of K_3Cit) and water are stronger than the interactions between H_2Cit^{1-} (produced from the dissociation of KH_2Cit) and water and also, by increasing the salt concentration, the increase in ion–ion interactions for K_3Cit is more than those for KH_2Cit. This Figure also shows a positive transfer volume of the salts from an aqueous solution to an aqueous alanine solution. This indicates that the ions in aqueous alanine solutions are larger than those in aqueous solutions, and the value of V_φ increases as the concentration of alanine increases. The apparent molar volumes of transfer, $\Delta_t V_\varphi^0$, at infinite dilution for the investigated salts from water to aqueous alanine solutions are listed in Table 6 at each temperature. Table 6 shows that $\Delta_t V_\varphi^0$ have positive values for both electrolytes investigated in this work. This effect can be attributed to the fact that the amino and carboxyl groups of alanine become, respectively, negatively and positively charged or dipolar species ($^+NH_3-(CH_3CH)-COO^-$) in aqueous solutions. In fact, the neutral dipolar species or zwitterions are the predominant species
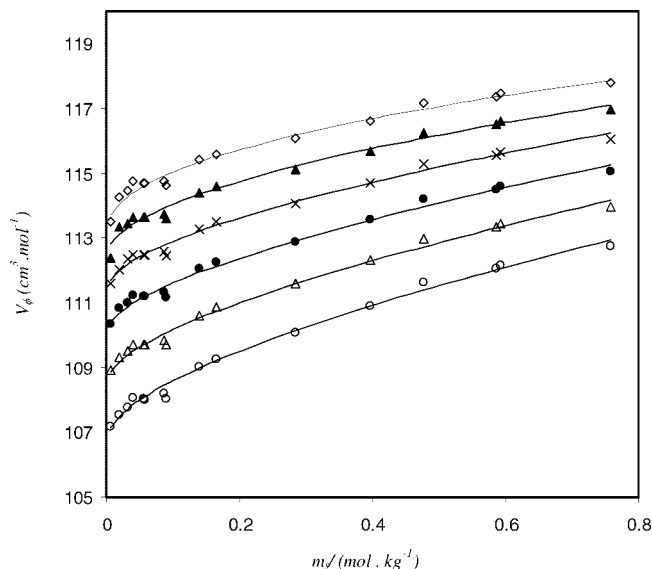
Figure 1. Plot of the apparent molar volume of KH_2Cit, V_φ, in water against molality of the salt, m_s, at different temperatures: $\bigcirc$, $T = 283.15$ K; $\triangle$, $T = 288.15$ K; $\bullet$, $T = 293.15$ K; $\times$, $T = 298.15$ K; $\blacktriangle$, $T = 303.15$ K; $\Diamond$, $T = 308.15$ K; —, calculated by eqs 3 to 6.
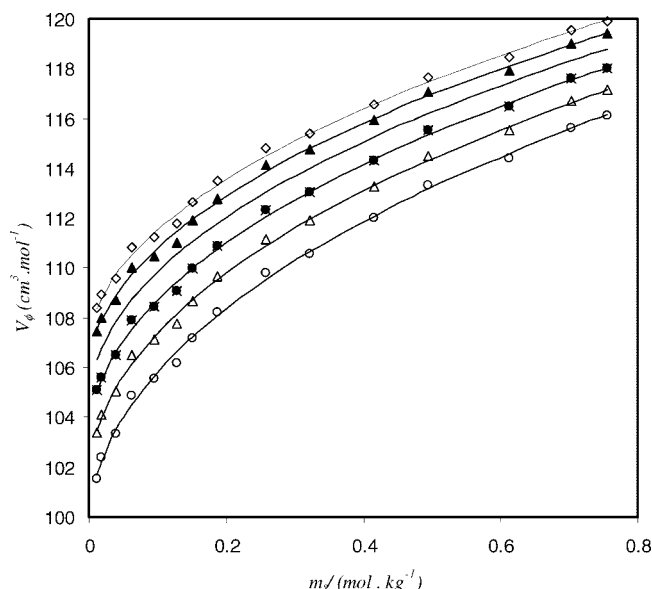

Figure 3. Plot of infinite dilution apparent molar volume of the investigated electrolytes, V_φ^0, against temperature: $\bigcirc$, KH_2Cit in water; $\triangle$, KH_2Cit in aqueous solution of 0.23 m alanine; $\times$, KH_2Cit in aqueous solution of 0.47 m alanine; $\times$, KH_2Cit in aqueous solution of 0.72 m alanine; $\bullet$, K_3Cit in water; $\blacktriangle$, K_3Cit in aqueous solution of 0.23 m alanine; $\blacklozenge$, K_3Cit in aqueous solution of 0.47 m alanine; $\blacksquare$, K_3Cit in aqueous solution of 0.72 m alanine.

Figure 2. Plot of apparent molar volume of K_3Cit, V_φ, in aqueous solution of 0.72 m alanine against molality of the salt, m_s, at different temperatures: $\bigcirc$, $T = 283.15$ K; $\triangle$, $T = 288.15$ K; $\bullet$, $T = 293.15$ K; $\times$, $T = 298.15$ K; $\blacktriangle$, $T = 303.15$ K; $\Diamond$, $T = 308.15$ K; —, calculated by eqs 3 to 6.
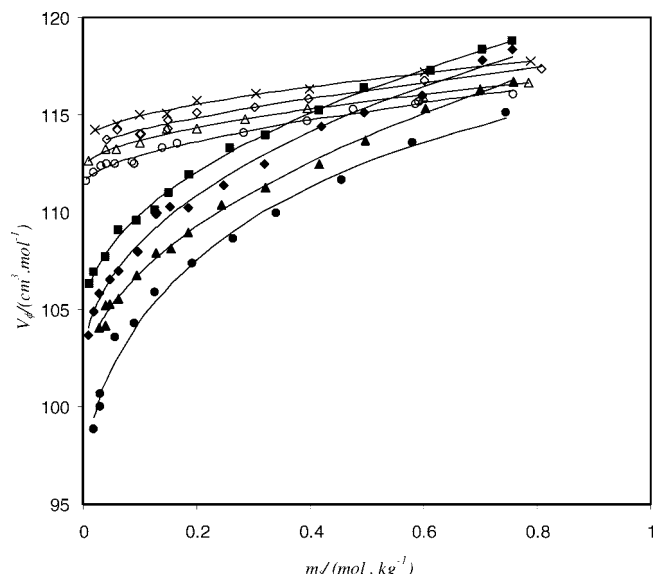

Figure 4. Plot of apparent molar volume of the investigated electrolytes, V_φ, against molality of the salt, m_s, at $T = 298.15$ K: $\bigcirc$, KH_2Cit in water; $\triangle$, KH_2Cit in aqueous solution of 0.23 m alanine; $\Diamond$, KH_2Cit in aqueous solution of 0.47 m alanine; $\times$, KH_2Cit in aqueous solution of 0.72 m alanine; $\bullet$, K_3Cit in water (data taken from ref 28); $\blacktriangle$, K_3Cit in aqueous solution of 0.23 m alanine; $\blacklozenge$, K_3Cit in aqueous solution of 0.47 m alanine; $\blacksquare$, K_3Cit in aqueous solution of 0.72 m alanine; —, calculated by eqs 3 to 6.

in the isoelectric solution of amino acids. At acidic solutions, cationic amino acid species ($^+NH_3-(CH_3CH)-COOH$) become predominant, while anionic amino acid species ($NH_2-(CH_3CH)-COO^-$) become predominant at the basic solutions. The positive transfer volume of electrolytes from an aqueous solution to an aqueous alanine solution suggests that the ions are less hydrated in solutions containing alanine because the alanines tend to take more water molecules to hydrate themselves, leaving ions with less water molecules. In other words, the strong attractive interactions between the zwitterionic alanine species and water molecules induce the dehydration of ions and therefore increase the V_φ. Also, because of the charged group−ion interactions occurring between COO^- groups of amino acids and K^+ ions of salts and between NH^{3+} groups of amino acid and anions (Cit^{3-} and H_2Cit^{1-}) of salts, the water

molecules are allowed to relax to the bulk state and therefore increase the V_φ.

Table 6 and Figure 4 show that the values of $\Delta_t V_\varphi^0$ and $\Delta_t V\varphi$ for K_3Cit are larger than those for KH_2Cit. KH_2Cit is an acidic salt. Therefore, as mentioned above, in the aqueous solutions of KH_2Cit, the cationic form of alanine ($^+NH_3-(CH_3CH)-COOH$) becomes predominant, while the neutral dipolar form of alanine ($^+NH_3-(CH_3CH)-COO^-$) is predominant in the aqueous solutions of K_3Cit. In fact, the neutral dipolar form of alanine ($^+NH_3-(CH_3CH)-COO^-$) has a better ability to dehydrate ions than the cationic form of alanine ($^+NH_3-(CH_3CH)-COOH$). This is because the neutral dipolar

Table 6. Values of $\Delta_t V_\varphi^0/(cm^3 \cdot mol^{-1})$ for Investigated Electrolytes from Water to Aqueous Alanine Solutions at Different Temperatures

| | $\Delta_t V_\varphi^0$ | | | | | |
| | temperature | | | | | |
system	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
K_3Cit + alanine (0.23 m) + H_2O	5.451	5.592	5.729	5.860	5.987	6.108
K_3Cit + alanine (0.47 m) + H_2O	6.624	6.664	6.744	6.864	7.024	7.224
K_3Cit + alanine (0.72 m) + H_2O	9.277	9.172	9.138	9.173	9.279	9.454
KH_2Cit + alanine (0.23 m) + H_2O	1.088	0.944	0.866	0.852	0.904	1.020
KH_2Cit + alanine (0.47 m) + H_2O	1.929	1.772	1.675	1.638	1.661	1.744
KH_2Cit + alanine (0.72 m) + H_2O	2.855	2.567	2.360	2.232	2.185	2.217

forms, which have two polar groups, are more hydrated than the cationic forms, which have one polar group.

On the basis of the sound velocity and density values, the isentropic compressibility, κ_s (kPa)$^{-1}$, values were calculated for the investigated mixtures from the Laplace−Newton equation

$$\kappa_s = d^{-1}u^{-2} \tag{10}$$

where u (m·s^{-1}) is sound velocity. The isentropic compressibility of all the solutions decreases with increasing concentration. As an example, in Figures 5 and 6, the temperature and concentration dependence of the isentropic compressibilities have been given, respectively, for KH_2Cit in water and K_3Cit in aqueous solutions of 0.72 mol·kg^{-1} of alanine. From Figures 5 and 6, we note that at each working temperature as the concentration of electrolyte is increased κ_s is decreased. If we assume that the size of the ion is not pressure dependent and the electrostricted water is already compressed to its maximum extend by the charge on the ions,[37] we can assume that the compressibility of a solution is mainly due to the effect of pressure on the bulk (unhydrated) water molecules. As the concentration of the electrolyte increases and a large portion of the water molecule are electrostricted, the amount of bulk water decreases causing the compressibility to decrease. Also, Figures 5 and 6 show that the concentration dependence of κ_s becomes greater as temperature decreases. This is because at higher temperatures ion–solvent interactions are weakened, and therefore the number of water molecules affected by the ions decreases. It has been shown that[37] for electrolytes with large

hydration numbers, such as $MgSO_4$ and Na_2SO_4, the concentration dependence of κ_s is more negative than electrolytes such as NaCl with small hydration numbers. The temperature dependence of κ_s, $\partial\kappa_s/\partial T$, is also negative for all the solutions studied in this work. It has been shown that[38] the compressibility of pure water also decreases with temperature to a minimum κ_s value near 319.15 K. It has been postulated[38] that this is due to the existence of two structural types of water aggregates at a given temperature. The $\partial\kappa_s/\partial T$ term for the structured form is negative, while it is positive for the less-structured form. At temperatures below 319.15 K, the structured form is the predominant species, while at high temperatures, the nonstructured form predominates. As can be seen from Figures 5 and 6, the value of $\partial\kappa_s/\partial T$ is much less negative in dilute electrolyte solution than in water, and as the concentration of electrolyte increases, $\partial\kappa_s/\partial T$ becomes less negative. The isentropic compressibility isotherms of other aqueous solutions investigated in this work have a form similar to those shown in Figures 5 and 6. In Figure 7 the values of κ_s are plotted as a function of salt concentration at various alanine concentrations at 298.15 K, for KH_2Cit and K_3Cit. This figure shows that at each temperature at a constant salt concentration the values of κ_s for K_3Cit solutions is smaller than those for KH_2Cit solutions. A similar behavior has been observed for other temperatures studied in this work. This effect can be attributed to the strong attractive interactions due to the hydration of K_3Cit ions, therefore decreasing the amount of bulk water. Figure 7 also show that at each temperature at a constant salt concentration the values of κ_s decrease as the concentration of alanine increases. This effect can be attributed to the strong attractive
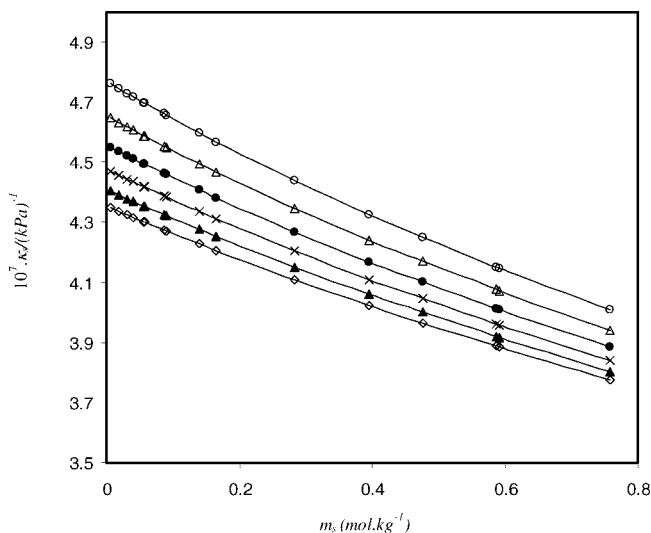
Figure 5. Plot of isentropic compressibility κ_s of KH_2Cit + water against molality of the salt, m_s, at different temperatures: ○, T = 283.15 K; Δ, T = 288.15 K; •, T = 293.15 K; ×, T = 298.15 K; ▲, T = 303.15 K; •, T = 308.15 K.
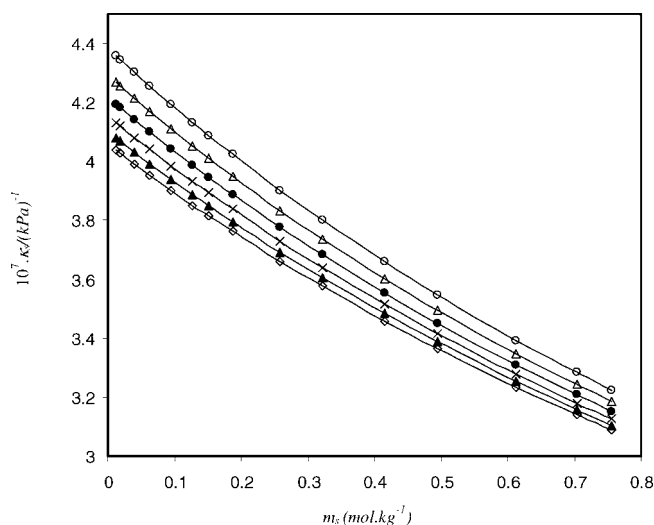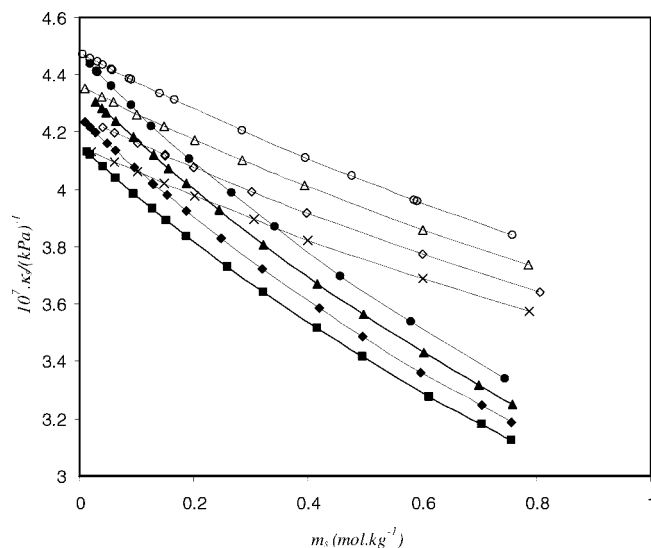
Figure 6. Plot of isentropic compressibility κ_s of K_3Cit in aqueous solution of 0.72 m alanine against molality of the salt, m_s, at different temperatures: ○, T = 283.15 K; Δ, T = 288.15 K; •, T = 293.15 K; ×, T = 298.15 K; ▲, T = 303.15 K; •, T = 308.15 K.

Figure 7. Plot of isentropic compressibility, κ_s, against molality of the salt, m_s, at $T = 298.15$ K: $\bigcirc$, KH_2Cit in water; $\triangle$, KH_2Cit in aqueous solution of 0.23 m alanine; $\diamond$, KH_2Cit in aqueous solution of 0.47 m alanine; $\times$, KH_2Cit in aqueous solution of 0.72 m alanine; $\bullet$, K_3Cit in water (data taken from ref 28); $\blacktriangle$, K_3Cit in aqueous solution of 0.23 m alanine; $\blacklozenge$, K_3Cit in aqueous solution of 0.47 m alanine; $\blacksquare$, K_3Cit in aqueous solution of 0.72 m alanine.

Figure 8. Plot of apparent molar isentropic compressibility of KH_2Cit, K_φ, in an aqueous solution of 0.47 m alanine against molality of the salt, m_s, at different temperatures: $\bigcirc$, $T = 283.15$ K; $\triangle$, $T = 288.15$ K; $\bullet$, $T = 293.15$ K; $\times$, $T = 298.15$ K; $\blacktriangle$, $T = 303.15$ K; $\diamond$, $T = 308.15$ K; —, calculated by eqs 13 to 16.

interactions due to the hydration of alanine, therefore decreasing the amount of bulk water. Close examination of Figure 7 indicates that by increasing the concentration of alanine the decrease in κ_s of the aqueous solutions of KH_2Cit is larger than for the aqueous solutions of K_3Cit. In fact, as can be seen from Figure 7, at each working temperature, as the concentration of alanine is increased, κ_s of the water + alanine solution is decreased due to the combined effect of hydration of alanine molecules and breaking of the three-dimensional network structure of water.

The apparent molar isentropic compressibility K_φ is defined as

$$K_\varphi = -\left(\frac{\partial V_\varphi}{\partial P}\right)_T \qquad (11)$$

The apparent molar isentropic compressibility of the studied electrolytes, K_φ, in water and in aqueous alanine solutions was computed from the density and sound velocity experimental data according to the following equation[30]

$$K_\varphi = \frac{1000}{m_s d d_0}(\kappa_s d_0 - \kappa_{s0}d) + \frac{M_s \kappa_s}{d} \qquad (12)$$

where κ_s and κ_{s0} are the isentropic compressibility of the solution and solvent, respectively. For systems containing salt and alanine, alanine + water is considered as the solvent. An equation of the form[39]

$$K_\varphi = K_\varphi^0 + S_k m_s^{0.5} + B_k m_s \qquad (13)$$

was used for correlating the experimental apparent molar isentropic compressibility data. Similar to the apparent molar volume, the temperature dependence of K_φ^0, S_k, and B_k was expressed in polynomial form with $(T - 283.15)$ K as a variable, as follows

$$K_\varphi^0 = A^0 + A^1(T - 283.15) + A^2(T - 283.15)^2 \qquad (14)$$

$$S_k = S_k^0 + S_k^1(T - 283.15) + S_k^2(T - 283.15)^2 \qquad (15)$$

$$B_k = B_k^0 + B_k^1(T - 283.15) + B_k^2(T - 283.15)^2 \qquad (16)$$

The coefficients of these equations for $10^4 K_\varphi$ are also given in Table 4.

The errors in V_φ and K_φ values were obtained using the equations

$$\delta V_\varphi = \left(\frac{M_s}{d} - V_\varphi\right)\frac{\delta m_s}{m_s} + \left(V_\varphi + \frac{1000}{m_s d_0}\right)\frac{\delta d}{d} \qquad (17)$$

$$\delta K_\varphi = \left(\frac{M_s \kappa_s}{d} - K_\varphi\right)\frac{\delta m_s}{m_s} + \left(K_\varphi + \frac{1000\kappa_{s0}}{m_s d_0}\right)\frac{\delta d}{d} + \left(K_\varphi + \frac{1000\kappa_{s0}}{m_s d_0}\right)\frac{\delta\kappa_s}{\kappa_s} \qquad (18)$$

$$\delta\kappa_s = \kappa_s\left(\frac{2\delta u}{u} + \frac{\delta d}{d}\right) \qquad (19)$$

The estimated uncertainties at the lowest concentration are (1.1, 1.3, 0.4, and 0.8) $cm^3 \cdot mol^{-1}$ in V_φ and $(1.2 \cdot 10^{-5}, 8.2 \cdot 10^{-6}, 2.0 \cdot 10^{-6}$, and $4.2 \cdot 10^{-6})$ $cm^3 \cdot mol^{-1} \cdot kPa^{-1}$ in K_φ, respectively, for KH_2Cit in aqueous solutions of (0.00, 0.23, 0.47, and 0.72) $mol \cdot kg^{-1}$ of alanine. For K_3Cit solutions, the uncertainties at the lowest concentration are (0.7, 1.9, and 1.4) $cm^3 \cdot mol^{-1}$ in V_φ and $(3.1 \cdot 10^{-6}, 8.9 \cdot 10^{-6}$, and $6.5 \cdot 10^{-6})$ $cm^3 \cdot mol^{-1} \cdot kPa^{-1}$ in K_φ, respectively, for $m_a = (0.23, 0.47$, and 0.72) $mol \cdot kg^{-1}$.

In Figures 8 and 9, the temperature and concentration dependencies of K_φ have been given, respectively, for KH_2Cit and K_3Cit in aqueous solutions of 0.47 $mol \cdot kg^{-1}$ of alanine. From Figures 8 and 9, it can be seen that the values of apparent molar isentropic compressibility are negative, and they increase with increasing concentration of electrolytes and temperature. The negative values of K_φ of the investigated electrolytes in aqueous alanine solutions indicate that the water molecules around the ions are less compressible than the water molecules in the bulk solution. In fact, the negative values of K_φ are attributed to the strong attractive interactions due to the hydration of ions at low temperatures. By increasing temperature, ion–solvent interactions are weakened, and therefore, at high
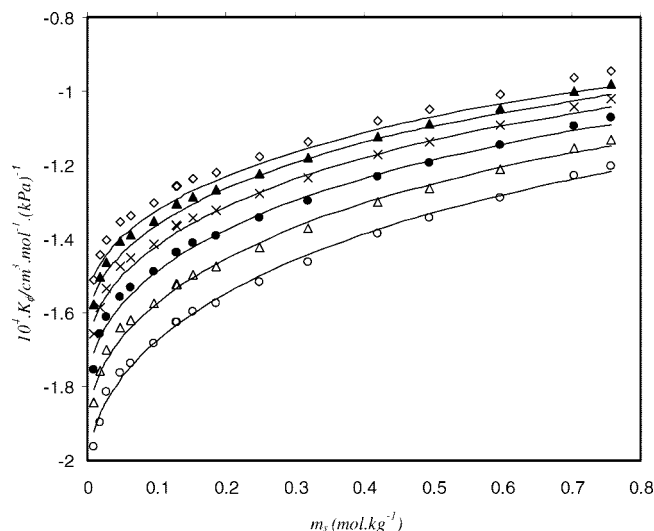
Figure 9. Plot of apparent molar isentropic compressibility of K_3Cit, K_φ, in aqueous solutions of 0.47 m alanine against molality of the salt, m_s, at different temperatures: $\bigcirc$, $T = 283.15$ K; $\triangle$, $T = 288.15$ K; $\bullet$, $T = 293.15$ K; $\times$, $T = 298.15$ K; $\blacktriangle$, $T = 303.15$ K; $\diamond$, $T = 308.15$ K; —, calculated by eqs 13 to 16.
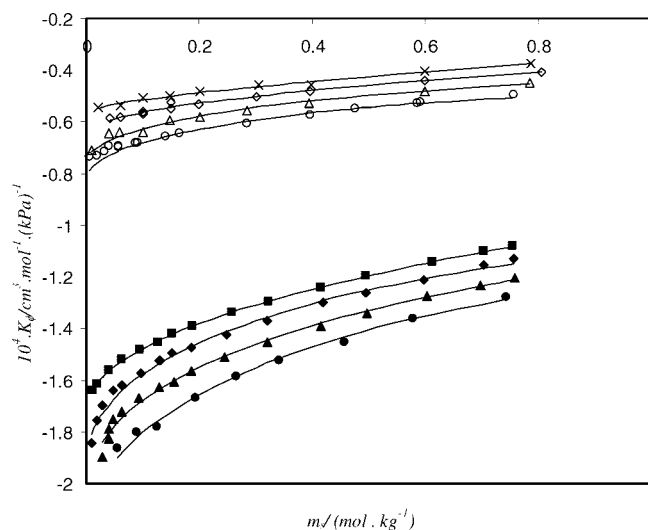

Figure 10. Plot of apparent molar isentropic compressibility of the investigated electrolytes, K_φ, against molality of the salt, m_s, at $T = 288.15$ K: $\bigcirc$, KH_2Cit in water; $\triangle$, KH_2Cit in aqueous solution of 0.23 m alanine; $\diamond$, KH_2Cit in aqueous solution of 0.47 m alanine; $\times$, KH_2Cit in aqueous solution of 0.72 m alanine; $\bullet$, K_3Cit in water (data taken from ref 28); $\blacktriangle$, K_3Cit in aqueous solution of 0.23 m alanine; $\blacklozenge$, K_3Cit in aqueous solution of 0.47 m alanine; $\blacksquare$, K_3Cit in aqueous solution of 0.72 m alanine; —, calculated by eqs 13 to 16.

temperatures the water molecules around the ions become more compressible than those at lower temperatures.

In Figure 10, the values of K_φ are plotted as a function of salt concentration at various alanine concentrations at 288.15 K, for KH_2Cit and K_3Cit. Figure 10 shows that at each temperature at a constant salt concentration the values of K_φ of investigated electrolytes increase as the concentration of alanine increases. The attractive interactions between alanine and water molecules induce the dehydration of ions, and therefore at high alanine concentrations, the water molecules around the ions become more compressible than those at lower alanine concentrations. Figure 10 shows that at each temperature the apparent molar isentropic compressibilities of K_3Cit are more negative than those of KH_2Cit, which implies that the water molecules around the K_3Cit ions are less compressible than

the water molecules around the KH_2Cit ions. This is because the interactions between Cit^{3-} and water are stronger than the interactions between H_2Cit^{1-} and water. Figure 10 also shows that the effect of concentration of alanine on the isentropic compressibilities of K_3Cit is more that those of KH_2Cit. As mentioned above, the neutral dipolar form of alanine ($^+NH_3-$ $(CH_3CH)-COO^-$) which is a predominant species in an aqueous solution of K_3Cit has a better ability to dehydrate ions than the cationic form of alanine ($^+NH_3-(CH_3CH)-COOH$) which is a predominant species in an aqueous solution of KH_2Cit. In fact, by increasing the concentration of alanine, the K_3Cit ion–water interactions are more weakened than the KH_2Cit ion–water interactions, and therefore at each temperature and at a constant salt concentration, by increasing the concentration of alanine, the increase in compressibility of water molecules around the ions of K_3Cit is larger than that for the water molecules around the ions of KH_2Cit.

Conclusions

Experimental data at $T = (283.15$ to $308.15)$ K of density and sound velocity of potassium dihydrogen citrate and trispotassium citrate in water and in water + alanine have been reported. The values of apparent molar volumes and isentropic compressibilities of solutions were calculated from the measured data. The results show a positive transfer volume of salts from an aqueous solution to an aqueous alanine solution. The apparent molar isentropic compressibility of investigated salts in both binary and ternary solutions has negative values at each temperature. The negative values of apparent molar isentropic compressibility imply that the water molecules around the ions are less compressible than the water molecules in the bulk solutions.

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