Vapor−Liquid Equilibria, Density, and Speed of Sound of Aqueous Solutions of Sodium Dihydrogen Citrate or Disodium Hydrogen Citrate

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Vapor−liquid equilibrium data (water activity, vapor pressure, osmotic coefficient, and activity coefficient) of binary aqueous sodium dihydrogen citrate or disodium hydrogen citrate solutions were obtained through the isopiestic method at $T = 298.15$ K. Density and speed of sound measurements were carried out on the aqueous solutions of the mentioned electrolytes at $T = (288.15$ to $308.15)$ K at atmospheric pressure. From the experimental density and speed of sound data, the apparent molar volume and isentropic compressibility values were evaluated and fitted to the Pitzer equation from which the apparent molar volume and apparent molar isentropic compressibility of the solutions at infinite dilution were calculated at each temperature within the above-mentioned range.

Introduction

Aqueous solutions of citric ions are of considerable importance in many biochemical and chemical reactions[1−3] (e.g., formation of metal complexes[4]). Citric acid and their neutral and acidic salts are produced in large quantities and used in food, cosmetic, pharmaceutical, and chemical industries.[1−3] Citrate is biodegradable and nontoxic and could be discharged into biological wastewater treatment plants; therefore, the citrates can be considered as a substitute for inorganic salts, because the citrate forms an aqueous two-phase system with poly(ethylene glycol) and poly(vinyl pyrrolidone) which are suitable for biomolecular extraction.[5−7] Because of the potential use of these organic salts, accurate experimental values of thermodynamic properties are needed. The published thermodynamic properties for these systems are limited, and new measurements are needed to supplement these studies. Regarding the aqueous solutions of sodium citrate salts, some experimental properties have been investigated in the literature.[8−12] Apelblat[8] measured the enthalpies of solution of these salts in water in a Parr calorimeter. Apelblat and Manzurola[9] determined the apparent molar volume of disodium hydrogen citrate (Na_2HCit) in aqueous solutions at 298.15 K from the experimental density data. Patterson and Woolley[10] determined the apparent molar volumes and apparent molar heat capacities for both sodium dihydrogen citrate (NaH_2Cit) and Na_2HCit in aqueous solutions at the pressure $p = 0.35$ MPa and at temperatures $278.15 \leq T/\mathrm{K} \leq 393.15$. Apelblat and Manzurola[11,12] also measured the freezing temperature lowering of aqueous solutions of NaH_2Cit and Na_2HCit and vapor pressures of saturated aqueous solutions of Na_2HCit in the temperature range (277 to 317) K using an electronic hygrometer. As far as we know, there is no information about the density of aqueous solutions of NaH_2Cit and Na_2HCit at atmospheric pressure and at different temperatures. Furthermore, to the best of our knowledge, the sound velocity and vapor−liquid equilibria properties for the nonsaturated aqueous NaH_2Cit and Na_2HCit solutions have not been reported.

The present work presents experimental data on the vapor−liquid equilibria of binary $NaH_2Cit + H_2O$ and $Na_2HCit + H_2O$ solutions at 298.15 K. This work also presents the experimental data for density and speed of sound of NaH_2Cit and $Na_2HCit + H_2O$ solutions at $T = (288.15, 293.15, 298.15, 303.15,$ and $308.15)$ K at atmospheric pressure, and the values of apparent molar volume, V_ϕ, and apparent molar isentropic compressibility, κ_ϕ, are then calculated from the measured data.

Experimental Section

Materials. NaH_2Cit (> 99.0 %), Na_2HCit (> 99.0 %), and NaCl (> 99.5 %) were obtained from Fluka, Riedel-de Haen, and Merck, respectively. The salts were used without further purification. Double-distilled and deionized water was used.

Apparatus and Procedures. The aqueous solutions were prepared by mass, using an analytical balance (Sartorius CP124S) with a precision of $\pm 1 \cdot 10^{-4}$ g. In this study, the isopiestic method was used to obtain the water activity of the investigated aqueous solutions. The isopiestic apparatus used in this work was similar to the one used by Ochs et al.[13] It is based on a phenomenon that different solutions, when connected through the vapor space, approach equilibrium by transferring solvent mass by distillation. Equilibrium is established once the temperature and pressure are uniform throughout the system, provided that no concentration gradients exist in the liquid phase. At equilibrium, the chemical potentials of the solvent in each of the solutions in the closed system are identical. The equality of the solvent chemical potential implies the equality of the solvent activity. Since the solvent activity is known for one or more standard solutions, it will be known for each solution within the isopiestic system. The apparatus used for determination of water activity in the binary water + NaH_2Cit or Na_2HCit solutions consisted of a five-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions, two flasks contained the pure NaH_2Cit or Na_2HCit solutions, and the central flask was used as a water reservoir. The apparatus was held in a constant-temperature bath at least 7 days for Na_2HCit and 12 days for NaH_2Cit (depending on the salt concentration) for equilibrium. During the equilibration process the manifold was removed at least once a day, and

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the samples were agitated. After the third day the samples were not agitated but left in the bath to approach their final equilibrium conditions. The temperature was controlled to within ± 0.05 K. After equilibrium had been reached, the manifold assembly was removed from the bath, and each flask was weighed with an analytical balance with a precision of $\pm 1 \cdot 10^{-4}$ g. From the mass of each flask after equilibrium and the initial mass of salt and polymer, the mass fraction of each solution was calculated. The water activity for the standard aqueous NaCl solutions at different concentrations and temperatures has been calculated from the correlation of Colin et al.[14] It was assumed that the equilibrium condition was reached when the differences between the mass fractions of each duplicate were less than 0.1 %. In all cases, averages of the duplicate are reported as the total isopiestic mass fraction. The accuracy of the method depends upon the standard solutions, sample mixing during the equilibrium period, temperature stability, and the time allowed for the equilibrium process. The uncertainty in the measurement of solvent activity was estimated to be less than $\pm 6 \cdot 10^{-4}$.

The density and speed of sound 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 the working temperature with a precision of 0.001 K. The apparatus was calibrated with double-distilled, deionized, and degassed water and dry air at atmospheric pressure. Densities and speed of sounds can be measured to $\pm 10^{-6}$ $g \cdot cm^{-3}$ and $\pm 10^{-2}$ $m \cdot s^{-1}$, respectively, under the most favorable conditions. The uncertainties of density and ultrasonic velocity measurements were $\pm 3 \cdot 10^{-6}$ $g \cdot cm^{-3}$ and $\pm 10^{-1}$ $m \cdot s^{-1}$, respectively.

Table 1. Isopiestic Equilibrium Molalities, Osmotic Coefficients, Water Activities, and Vapor Pressures of Aqueous Solutions of Na_2HCit and NaH_2Cit at $T = 298.15$ K

m_1 / $mol \cdot kg^{-1}$	m^* / $mol \cdot kg^{-1}$	Φ	a_2	p / kPa	γ_2	$\gamma_\pm$
			Na_2HCit (1) + Water (2)			
0.2817	0.3688	0.806	0.9878	3.130	1.0028	0.3754
0.2939	0.3778	0.792	0.9875	3.129	1.0032	0.3709
0.3096	0.3885	0.770	0.9872	3.128	1.0037	0.3653
0.3227	0.4046	0.773	0.9866	3.126	1.0038	0.3609
0.3856	0.4766	0.759	0.9843	3.119	1.0048	0.3419
0.4011	0.4893	0.753	0.9838	3.117	1.0051	0.3377
0.4258	0.5165	0.750	0.9829	3.114	1.0055	0.3314
0.4592	0.5383	0.724	0.9822	3.112	1.0066	0.3234
0.4761	0.5584	0.726	0.9815	3.110	1.0068	0.3196
0.4822	0.5675	0.728	0.9812	3.109	1.0068	0.3183
0.5501	0.6353	0.714	0.9790	3.102	1.0081	0.3045
0.6381	0.7316	0.710	0.9758	3.092	1.0094	0.2894
0.6827	0.7763	0.706	0.9743	3.087	1.0103	0.2826
0.6915	0.7838	0.705	0.9740	3.086	1.0104	0.2813
0.6951	0.7894	0.707	0.9738	3.086	1.0104	0.2808
0.6997	0.7951	0.708	0.9736	3.085	1.0104	0.2801
1.0183	1.1136	0.689	0.9628	3.051	1.0158	0.2451
1.0900	1.1837	0.688	0.9603	3.043	1.0169	0.2392
1.1069	1.1935	0.682	0.9600	3.042	1.0174	0.238
1.2465	1.3455	0.688	0.9547	3.025	1.0190	0.2285
1.3292	1.4155	0.682	0.9522	3.017	1.0206	0.2236
1.5788	1.6882	0.694	0.9425	2.986	1.0229	0.2120
1.6352	1.7421	0.694	0.9405	2.98	1.0236	0.2098
1.6586	1.7566	0.690	0.9400	2.978	1.0243	0.209
1.7309	1.8255	0.690	0.9375	2.97	1.0252	0.2066
1.7880	1.9055	0.701	0.9345	2.961	1.0248	0.2048
1.9336	2.0246	0.693	0.9301	2.947	1.0273	0.2010
1.9280	2.0396	0.702	0.9295	2.945	1.0264	0.2011
1.9996	2.1149	0.704	0.9267	2.936	1.0268	0.1995
2.3273	2.4356	0.711	0.9145	2.897	1.0295	0.1942
2.3928	2.5005	0.712	0.9120	2.889	1.0299	0.1936
2.4387	2.5388	0.711	0.9105	2.885	1.0305	0.1931
			NaH_2Cit (1) + Water (2)			
0.3252	0.2995	0.849	0.9901	3.137	1.0017	0.6096
0.4619	0.4154	0.829	0.9863	3.125	1.0027	0.5638
0.5944	0.5274	0.820	0.9826	3.113	1.0036	0.5312
0.7158	0.6206	0.803	0.9795	3.104	1.0048	0.5087
0.7377	0.6427	0.810	0.9787	3.101	1.0047	0.5052
0.7458	0.6482	0.805	0.9786	3.101	1.0049	0.5040
0.7565	0.6519	0.801	0.9784	3.100	1.0051	0.5024
0.7666	0.6593	0.798	0.9782	3.099	1.0052	0.5009
0.7800	0.6796	0.810	0.9775	3.097	1.0050	0.4991
0.9089	0.7801	0.801	0.9741	3.086	1.0060	0.4840
1.0963	0.9500	0.813	0.9684	3.068	1.0067	0.4707

Results and Discussion

Isopiestic Results. In the present work, the isopiestic measurements at $T = 298.15$ K were carried out for NaH_2Cit (1) + H_2O (2) and Na_2HCit (1) + H_2O (2) solutions to study the vapor−liquid equilibria behavior of these systems. For an understanding of the interactions in liquids, the activity or osmotic coefficients of the different components are of great interest. They are the most relevant thermodynamic reference data, and they are often the starting point of any modeling.[15−17] At isopiestic equilibrium, the activity of the solvent in the reference and sample solutions must be the same. By definition, the osmotic coefficient Φ is related to the solvent activity a_2 as[18]

$$\Phi = -\frac{\ln a_2}{\nu m M_2} \tag{1}$$

where ν is the stoichiometric number of the solute, m is the molality of solution, and M_2 is the molecular weight of the solvent. The isopiestic equilibrium molalities with reference standard solutions of NaCl in water as reported in Table 1 enabled the calculation of the osmotic coefficients, Φ, of the solutions of NaH_2Cit or Na_2HCit in water from[18]

$$\Phi = \frac{\nu^* \Phi^* m^*}{\nu m} \tag{2}$$

where ν^* and ν are the sums of the stoichiometric numbers of anions and cations in the reference solution and the solution of NaH_2Cit or Na_2HCit, respectively, m is the molality of the NaH_2Cit or Na_2HCit solution, m^* is the molality of the reference standard in isopiestic equilibrium with this solution, and Φ^* is the osmotic coefficient of the isopiestic reference standard, calculated at m^*. The necessary Φ^* values at any m^* were obtained from the correlation of Colin et al.[14] From the calculated osmotic coefficient data, the activity of water in the salt solution and the vapor pressure of this solution were determined at isopiestic equilibrium molalities, with the help of the eq 1 and the following relation:[19]

$$\ln a_2 = \ln\left(\frac{p}{p_2^o}\right) + \frac{(B_2^o - V_2^o)(p - p_2^o)}{RT} \tag{3}$$

where B_2^o is the second virial coefficient of water vapor, V_2^o is the molar volume of liquid water, and p_2^o is the vapor pressure of pure water. The second virial coefficients of water vapor were calculated using the equation provided by Rard and Platford.[19] Molar volumes of liquid water were calculated using the density of water at different temperatures.[20] The vapor pressures of pure water were calculated using the equation of state of Saul and Wagner.[21]

In Figures 1, 2, and 3, respectively, a comparison of the experimental osmotic coefficient, water activity, and vapor pressure depression data for the NaH_2Cit + H_2O system with those for the Na_2HCit + H_2O system has been made at $T =$

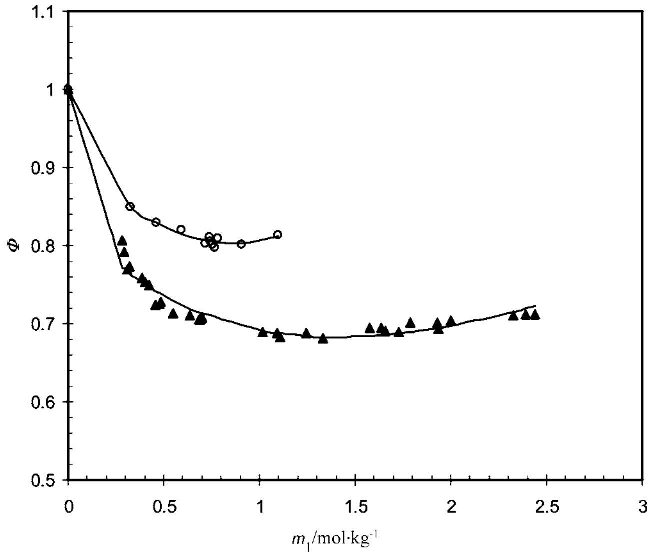

Figure 1. Plot of osmotic coefficient Φ of NaH_2Cit (1) + H_2O (2) and Na_2HCit (1) + H_2O (2) systems against the molality of the salt, m_1, at $T = 298.15$ K: ○, $NaH_2Cit + H_2O$; ▲, $Na_2HCit + H_2O$; —, calculated by the Pitzer model.[23,24]

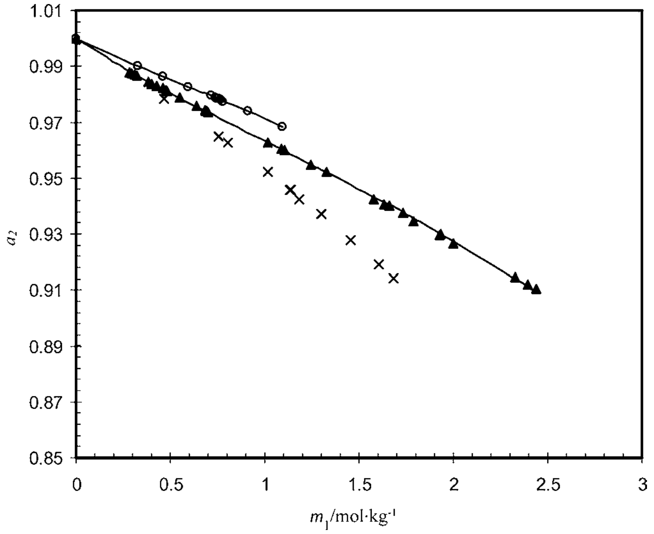

Figure 2. Plot of water activity a_2 of sodium citrate salt solutions against the molality of the salt, m_1, at $T = 298.15$ K: ○, NaH_2Cit (1) + H_2O (2); ▲, Na_2HCit (1) + H_2O (2); ×, Na_3Cit (1) + H_2O (2);[22] —, calculated by the Pitzer model.[23,24]

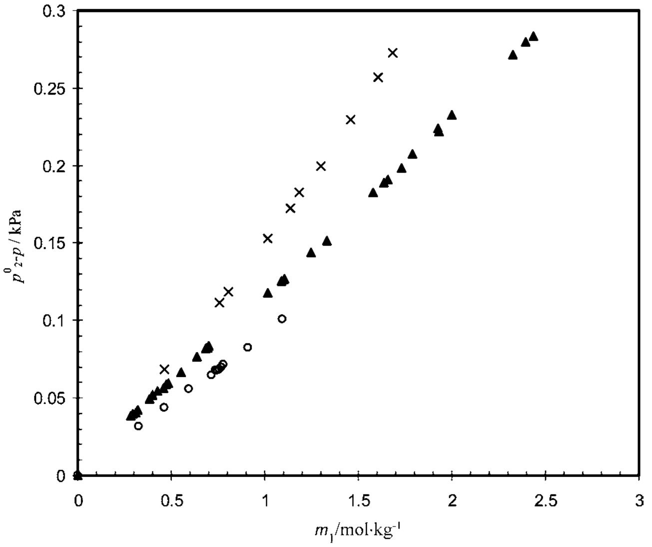

Figure 3. Plot of vapor pressure depression $p_2^0 - p$ of sodium citrate salt solutions against the molality of the salt, m_1, at $T = 298.15$ K: ○, NaH_2Cit (1) + H_2O (2); ▲, Na_2HCit (1) + H_2O (2); ×, Na_3Cit (1) + H_2O (2).[22]

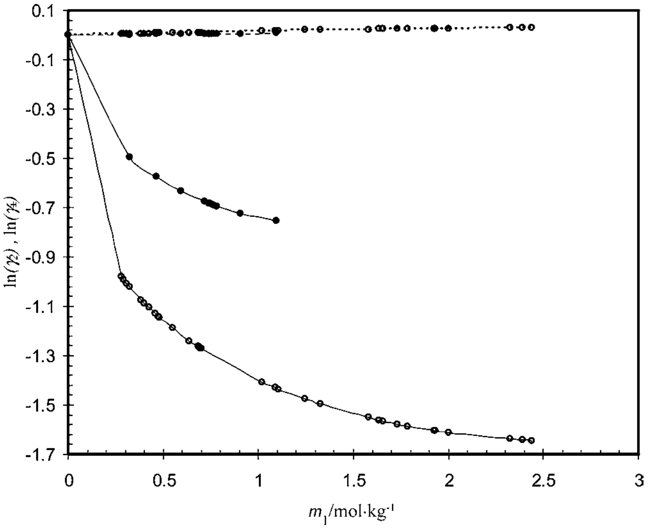

Figure 4. Plot of water activity coefficient, $\ln(\gamma_2)$ (dotted lines), and mean molal activity coefficients, $\ln(\gamma_\pm)$ (solid lines), of NaH_2Cit (1) + H_2O (2) and Na_2HCit (1) + H_2O (2) systems against the molality of the salt, m_1, at $T = 298.15$ K: ●, $NaH_2Cit + H_2O$; ○, $Na_2HCit + H_2O$.

298.15 K. In Figure 2, the water activity data of $Na_3Cit + H_2O$ system (taken from ref 22) have also been shown. Similarly, in Figure 3 the vapor pressure depression data of $Na_3Cit + H_2O$ system (taken from ref 22) have also been given. As can be seen, in the same solute molality, water activity and vapor pressure depression of the investigated binary aqueous solutions respectively have the order of $NaH_2Cit > Na_2HCit > Na_3Cit$[22] and $Na_3Cit > Na_2HCit > NaH_2Cit$. These salts share a common cation (Na^+) but contain anions with different valence. The anion Cit^{3-} (with a higher valence), because of the larger valence/size ratio, hydrates more water molecules than the anions $HCit^{2-}$ and H_2Cit^{1-} (with a lower valence), and therefore we may expect that the vapor pressure depression for Na_3Cit solutions will be greater than those for Na_2HCit solutions which, in turn, will be larger than those for NaH_2Cit solutions. Aqueous solutions of Na_3Cit because of the stronger ion−water interactions have smaller water activities than those of Na_2HCit and NaH_2Cit. As can be seen from Figures 2 and 3, the salt molality dependence of the water activity or vapor pressure depression follows the order $Na_3Cit > Na_2HCit > NaH_2Cit$, implying that the anion−water interactions for anions with higher valence are stronger than the anion−water interactions for anions with a lower valence. Apelblat[8] obtained the molar enthalpies of solutions of sodium citrate salts as: $\Delta_{sol}H_m(298.14\text{ K}, m = 0.02817\text{ mol}\cdot\text{kg}^{-1}) = (6.78 \pm 0.16)\text{ kJ}\cdot\text{mol}^{-1}$ for $Na_3Cit\cdot 2H_2O$; $\Delta_{sol}H_m(298.41\text{ K}, m = 0.01759\text{ mol}\cdot\text{kg}^{-1}) = (23.28 \pm 0.63)\text{ kJ}\cdot\text{mol}^{-1}$ for Na_2HCit; and $\Delta_{sol}H_m(298.37\text{ K}, m = 0.01175\text{ mol}\cdot\text{kg}^{-1}) = (27.79 \pm 0.23)\text{ kJ}\cdot\text{mol}^{-1}$ for NaH_2Cit. These results show that the solution of NaH_2Cit in water is more endothermic than Na_2HCit, which, in turn, is more endothermic than Na_3Cit, which supports the above explanations about vapor−liquid equilibria behavior of the investigated systems.

The water activity was used to obtain the solvent activity coefficient, γ_2. Calculated water activity coefficients, γ_2, of the investigated aqueous solutions are also given in Table 1. From the experimental osmotic coefficient data and the Pitzer's model,[23,24] the mean molal activity coefficients, $\gamma_\pm$, were calculated, and the calculated values are also given in Table 1. The variations of γ_2 and $\gamma_\pm$ with the solute concentration are

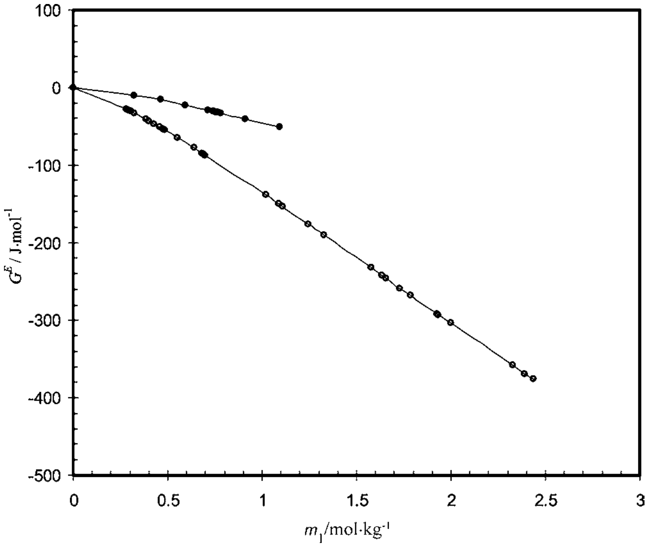

Figure 5. Plot of the molar excess Gibbs energy, G^E, of NaH_2Cit (1) + H_2O (2) and Na_2HCit (1) + H_2O (2) systems against the molality of the salt, m_1, at T = 298.15 K: ●, NaH_2Cit (1) + H_2O (2); ○, Na_2HCit (1) + H_2O (2).

shown in Figure 4. For both systems, $\gamma_\pm < 1$ (negative deviations from ideal-solution behavior) and decreased along with an increase in the solute concentration. Furthermore, the observed trend for the calculated $\gamma_\pm$ of investigated solutions is similar to those obtained for Φ. The calculated water activity coefficients are very slightly larger than unity (positive deviations from ideal-solution behavior) and increase as solute concentration increases. The following relation was used to obtain the mole fraction mean ionic activity coefficient, $\gamma_\pm^{(x)}$, from the molal mean ionic activity coefficient $\gamma_\pm$:[18]

$$\ln \gamma_\pm^{(x)} = \ln \gamma_\pm + \ln(1 + M_2 \upsilon m) \qquad (4)$$

The activity coefficient data, which had been converted to mole fraction scale, were used to calculate the molar excess Gibbs energy (G^E) of solutions, and the values are shown in Figure 5. The values of molar excess Gibbs energy are negative and decrease with the increase in concentration of the solutes. Furthermore, the values of G^E for the Na_2HCit + water system are more negative than those for the NaH_2Cit + water system.

Volumetric and Isentropic Compressibility Results. Experimental data of density (d) and sound velocity (u) for various NaH_2Cit and Na_2HCit solutions determined at T = (288.15, 293.15, 298.15, 303.15, and 308.15) K are given in Table 2. The apparent molar volumes of NaH_2Cit (1) and Na_2HCit (1), $V_{\phi,1}$, in aqueous solutions were calculated from the density of the solution by using the following equation:[25]

$$V_{\phi,1} = \frac{(d_0 - d)}{m_1 d d_0} + \frac{M_1}{d} \qquad (5)$$

where M_1 and m_1 are the molar mass and molality of the salt, respectively, and d and d_0 are the densities of the solution and solvent, respectively. In Figure 6, the concentration dependence of $V_{\phi,1}$ of NaH_2Cit and Na_2HCit in pure water has been given at T = (288.15, 298.15, and 308.15) K. In Figure 6 the apparent molar volume of Na_2HCit in water taken from ref 9 at T = 298.15 K has also been given. As can be seen, there is a good agreement between our data and those taken from ref 9. We have tested the reliability of the Pitzer equation in the correlation of the experimental apparent molar volume data for the investigated aqueous solutions at different temperatures. The Pitzer equation for apparent molar volume has the form:[24]

$$V_{\phi,1} = V^0_{\phi,1} + \nu|z_c z_a|\left(\frac{A_V}{2b}\right)\ln(1 + bI^{1/2}) + RT[B_V \nu(\nu_c \nu_a/\nu)m_1 + (\nu_c \nu_a)^{1.5} C_V m_1^2] \qquad (6)$$

where ν_c and ν_a are the number of cations and anions and $\nu = \nu_c + \nu_a$; the subscripts c and a are used for the cation and anion, respectively; z_c and z_a are the number of charges on cations and anions, respectively; $V^0_{\phi,1}$ is the infinite dilution apparent molar volume of the salt; I is the total ionic strength; R is the gas constant; T is the thermodynamic temperature; and A_V is the Pitzer−Debye−Hückel limiting slope (A_V values at different temperatures were taken from the literature[24]). B_V is defined by the following equation:[24]

$$B_V = 2\beta^0_V + 2\beta^1_V\left(\frac{1}{\alpha^2 I}\right)\left[1 - \left(1 + \alpha I^{1/2} - \frac{\alpha^2 I}{2}\right) \times \exp(-\alpha I^{1/2})\right] \qquad (7)$$

where β^0_V, β^1_V, and C_V are pressure derivative parameters of Pitzer's ion interaction parameters for the osmotic coefficient expression. The parameter b is given the value 1.2 kg$^{1/2}$·mol$^{-1/2}$ for all electrolytes, and α is 2.0 for all 1:1 and 2:1 electrolytes;[24,26] b and α are taken as temperature-independent.

The coefficients of these equations, standard errors in the fitting parameters along with the corresponding absolute relative deviation for $V_{\phi,1}$ at each temperature, are given in Table 3. The values of the infinite dilution apparent molar volume, $V^0_{\phi,1}$, of NaH_2Cit and Na_2HCit in aqueous solutions have also been given in Table 3. Apelblat and Manzurola[9] obtained the value of 86.12 cm^3·mol^{-1} for the infinite dilution apparent molar volume of Na_2HCit in pure water at T = 298.15 K, which agrees very well with the value (86.157 cm^3·mol^{-1}) obtained in this work. At infinite dilution, each ion is surrounded only by the solvent molecules and is infinitely distant from other ions. It follows, therefore, that the infinite dilution apparent molar volume is unaffected by ion + ion interaction, and it is a measure only of the ion + solvent interaction.[27] In Figure 6 the apparent molar volume of Na_3Cit in water taken from ref 28 have also been given. From Figure 6, it can be seen that the apparent molar volumes of Na_2HCit and Na_3Cit[28] in water increase with an increase in the salt molality. Figure 6 also shows that the slope of $V_{\phi,1}$ against salt concentration for Na_3Cit is larger than those for Na_2HCit. However, a close examination of $V_{\phi,1}$ data for NaH_2Cit indicates that the plot of $V_{\phi,1}$ of NaH_2Cit against salt molality shows a minimum about 0.05·10^{-3} mol·g^{-1}. In the electrolyte solutions, the solute−solute interactions are characterized by positive slopes of $V_{\phi,1}$ versus concentration plots. This is attributed to the phenomenon, described in terms of destructive overlap of cospheres,[29,30] resulting in a net decrease of solvation, thereby increasing the solute volume. As can be expected, the positive slope of $V_{\phi,1}$ versus concentration of Na_3Cit is larger than those of NaH_2Cit and Na_2HCit. The infinite dilution apparent molar volume of ions can be expressed as the sum of two contributions:[31]

$$V^0_{\phi,1}(\text{ion}) = V^0_{\phi,1}(\text{int}) + V^0_{\phi,1}(\text{elect}) \qquad (8)$$

Table 2. Experimental Density *d* and Speed of Sound *u* of Aqueous Solutions of Na_2HCit and NaH_2Cit at Different Temperatures

	$T = 288.15$ K		$T = 293.15$ K		$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K	
m_1 / $mol \cdot kg^{-1}$	d / $g \cdot cm^{-3}$	u / $m \cdot s^{-1}$	d / $g \cdot cm^{-3}$	u / $m \cdot s^{-1}$	d / $g \cdot cm^{-3}$	u / $m \cdot s^{-1}$	d / $g \cdot cm^{-3}$	u / $m \cdot s^{-1}$	d / $g \cdot cm^{-3}$	u / $m \cdot s^{-1}$
Na_2HCit (1) + Water (2)										
0.0000	0.999099	1466.25	0.998203	1482.66	0.997043	1497.00	0.995645	1509.44	0.994029	1520.12
0.0095	1.000549	1468.24	0.999632	1484.28	0.998455	1498.47	0.997044	1510.77	0.995414	1521.44
0.0114	1.000839	1468.58	0.999920	1484.59	0.998740	1498.78	0.997324	1511.07	0.995691	1521.69
0.0133	1.001129	1468.97	1.000206	1484.95	0.999021	1499.12	0.997605	1511.38	0.995970	1521.98
0.0150	1.001384	1469.21	1.000457	1485.20	0.999268	1499.34	0.997849	1511.62	0.996213	1522.22
0.0172	1.001709	1469.62	1.000780	1485.58	0.999588	1499.72	0.998164	1511.95	0.996524	1522.54
0.0187	1.001928	1469.90	1.000992	1485.83	0.999800	1499.94	0.998374	1512.18	0.996735	1522.76
0.0210	1.002285	1470.31	1.001347	1486.22	1.000150	1500.33	0.998719	1512.55	0.997077	1523.10
0.0229	1.002564	1470.57	1.001623	1486.49	1.000422	1500.59	0.998990	1512.80	0.997344	1523.35
0.0267	1.003125	1471.14	1.002177	1487.08	1.000970	1501.14	0.999532	1513.35	0.997881	1523.88
0.0307	1.003729	1471.86	1.002772	1487.76	1.001560	1501.79	1.000116	1513.96	0.998461	1524.47
0.0344	1.004280	1472.45	1.003318	1488.35	1.002099	1502.35	1.000650	1514.51	0.998990	1525.00
0.0374	1.004732	1473.03	1.003764	1488.87	1.002539	1502.86	1.001087	1514.97	0.999421	1525.44
0.0570	1.007641	1476.32	1.006634	1491.99	1.005379	1505.81	1.003899	1517.84	1.002212	1528.19
0.0771	1.010578	1479.59	1.009538	1495.12	1.008253	1508.80	1.006746	1520.70	1.005035	1530.94
0.0953	1.013222	1482.49	1.012153	1497.89	1.010839	1511.45	1.009308	1523.27	1.007575	1533.38
0.1157	1.016162	1485.72	1.015055	1500.98	1.013714	1514.42	1.012157	1526.09	1.010401	1536.09
0.1332	1.018672	1488.43	1.017537	1503.58	1.016168	1516.89	1.014588	1528.48	1.012815	1538.39
0.1542	1.021643	1491.62	1.020481	1506.55	1.019085	1519.76	1.017479	1531.25	1.015682	1541.05
0.1773	1.024897	1495.12	1.023696	1509.96	1.022265	1523.04	1.020631	1534.36	1.018810	1544.02
0.1964	1.027565	1497.99	1.026334	1512.75	1.024877	1525.70	1.023222	1536.92	1.021378	1546.48
0.2144	1.030073	1500.72	1.028813	1515.35	1.027334	1528.22	1.025657	1539.32	1.023798	1548.79
0.2229	1.031249	1502.02	1.029972	1516.61	1.028484	1529.41	1.026798	1540.47	1.024927	1549.89
0.2509	1.035092	1506.17	1.033780	1520.61	1.032256	1533.24	1.030539	1544.12	1.028639	1553.40
0.2830	1.039466	1510.93	1.038111	1525.17	1.036548	1537.59	1.034797	1548.29	1.032867	1557.41
0.2965	1.041296	1512.87	1.039924	1527.03	1.038343	1539.39	1.036577	1550.02	1.034635	1559.07
0.3375	1.046821	1518.89	1.045394	1532.8	1.043766	1544.92	1.041957	1555.32	1.039976	1564.17
NaH_2Cit (1) + Water (2)										
0.0093	1.000172	1467.66	0.999260	1483.68	0.998086	1497.87	0.996675	1510.20	0.995048	1520.82
0.0117	1.000436	1467.93	0.999519	1483.91	0.998341	1498.11	0.996930	1510.41	0.995300	1521.03
0.0125	1.000534	1467.95	0.999616	1483.98	0.998436	1498.15	0.997022	1510.51	0.995390	1521.11
0.0138	1.000676	1468.14	0.999756	1484.14	0.998576	1498.33	0.997161	1510.61	0.995527	1521.21
0.0155	1.000872	1468.32	0.999956	1484.32	0.998772	1498.48	0.997353	1510.76	0.995720	1521.36
0.0163	1.000965	1468.43	1.000042	1484.41	0.998856	1498.55	0.997436	1510.83	0.995802	1521.43
0.0187	1.001239	1468.69	1.000313	1484.69	0.999125	1498.80	0.997702	1511.05	0.996063	1521.64
0.0202	1.001416	1468.90	1.000486	1484.80	0.999296	1498.91	0.997872	1511.18	0.996232	1521.76
0.0209	1.001487	1468.91	1.000557	1484.88	0.999364	1499.01	0.997940	1511.26	0.996299	1521.83
0.0240	1.001853	1469.26	1.000915	1485.22	0.999720	1499.31	0.998290	1511.55	0.996648	1522.10
0.0279	1.002290	1469.76	1.001347	1485.64	1.000146	1499.70	0.998715	1511.89	0.997067	1522.43
0.0327	1.002844	1470.18	1.001894	1486.05	1.000685	1500.09	0.999246	1512.30	0.997594	1522.79
0.0376	1.003395	1470.76	1.002438	1486.59	1.001222	1500.61	0.999776	1512.74	0.998119	1523.22
0.0409	1.003780	1471.11	1.002817	1486.94	1.001597	1500.93	1.000147	1513.10	0.998486	1523.54
0.0470	1.004468	1471.80	1.003494	1487.56	1.002266	1501.51	1.000810	1513.61	0.999141	1524.05
0.0681	1.006848	1473.99	1.005843	1489.69	1.004587	1503.50	1.003105	1515.48	1.001413	1525.80
0.0937	1.009709	1476.78	1.008667	1492.28	1.007375	1505.92	1.005862	1517.76	1.004146	1527.94
0.1194	1.012549	1479.51	1.011469	1494.84	1.010145	1508.31	1.008602	1520.00	1.006858	1530.06
0.1440	1.015246	1482.03	1.014129	1497.24	1.012774	1510.55	1.011204	1522.12	1.009436	1532.05
0.1678	1.017828	1484.56	1.016679	1499.56	1.015295	1512.73	1.013699	1524.18	1.011906	1533.98
0.1911	1.020349	1486.98	1.019169	1501.81	1.017758	1514.86	1.016135	1526.16	1.014317	1535.84
0.2165	1.023066	1489.46	1.021859	1504.12	1.020417	1517.01	1.018768	1528.24	1.016928	1537.8
0.2412	1.025702	1492.00	1.024455	1506.50	1.022983	1519.27	1.021310	1530.34	1.019446	1539.77
0.2934	1.031202	1497.28	1.029891	1511.48	1.028359	1523.96	1.026632	1534.74	1.024719	1543.90
0.3205	1.034039	1499.95	1.032692	1513.99	1.031131	1526.34	1.029376	1536.99	1.027441	1546.00
0.3395	1.036010	1501.78	1.034641	1515.75	1.033060	1528.00	1.031284	1538.53	1.029332	1547.47
0.3728	1.039434	1505.07	1.038027	1518.84	1.036409	1530.90	1.034603	1541.23	1.032621	1550.03
0.3936	1.041567	1507.06	1.040136	1520.74	1.038498	1532.68	1.036672	1542.92	1.034673	1551.61

where $V^0_{\phi,1}$(int) is the intrinsic apparent molar volume and $V^0_{\phi,1}$(elect) is the electrostriction apparent molar volume due to the hydration of the solute (i.e., the decrease in volume due to hydration). The $V^0_{\phi,1}$(int) is made up of two terms, the van der Waals volume and the volume due to packing effects. The term $(\partial V^0_{\phi,1}(\text{int}))/(\partial T)$ contributes negligibly to the overall temperature dependence of $V^0_{\phi,1}$, and therefore an increase in the $V^0_{\phi,1}$ by increasing temperature occurs with a loss of hydration. The temperature dependence of $V^0_{\phi,1}$ was expressed by the following equation:[32]

$$V^0_{\phi,1} = a + bT^{0.5} + c\ln(T) \tag{9}$$

and from which the infinite dilution apparent molar expansibilities, $E^0_{\phi,1}$, were obtained as:[32]

$$E^0_{\phi,1} = \left(\frac{\partial V^0_{\phi,1}}{\partial T}\right)_P = \frac{b}{2T^{0.5}} + \frac{c}{T} \tag{10}$$

The values of the obtained parameters *a*, *b*, and *c* along with the corresponding standard errors are given in Table 4. From Figure 7, it can be seen that the values of $E^0_{\phi,1}$ are positive and decrease by increasing temperature. For the investigated temperature range, the values of $E^0_{\phi,1}$ for the investigated salts in water follow the order $NaH_2Cit < Na_2HCit < Na_3Cit$. Since $(\partial C^0_p/$

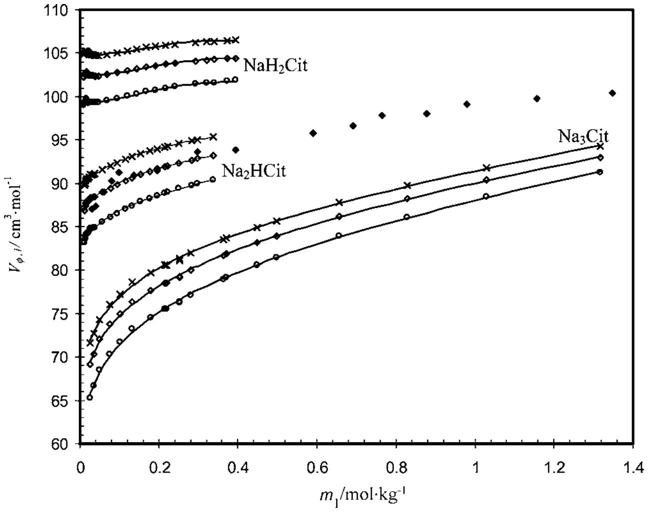

Figure 6. Plot of the apparent molar volume of NaH_2Cit, Na_2HCit, and Na_3Cit (taken from ref 28), $V_{\phi,1}$, in water against the molality of the salt, m_1, at different temperatures: ○, $T = 288.15$ K; ◇, $T = 298.15$ K; ◆, $T = 298.15$ K (ref 9); ×, $T = 308.15$ K; —, calculated by eq 6.

$\partial P)_T = -T(\partial^2 V^0_{\phi,1}/\partial T^2)_P$, a negative value of $(\partial^2 V^0_{\phi,1}/\partial T^2)_P$ seems to associate with a structure-breaking solute, and a positive one is associated with a structure-making solute.[33] All solutes investigated in this work are structure-breakers based on the negative values of $(\partial^2 V^0_{\phi,1}/\partial T^2)_P$. It was found that the values of $(\partial^2 V^0_{\phi,1}/\partial T^2)_P$ for solutes investigated in this work become less negative by increasing temperature and at each temperature the magnitude of $(\partial^2 V^0_{\phi,1}/\partial T^2)_P$, and therefore structure-breaker property of the investigated solutes follows the order $Na_3Cit > Na_2HCit \gg NaH_2Cit$.

On the basis of the speed of sound and density values, the isentropic compressibility, β, values were calculated for the investigated mixtures from Laplace−Newton's equation:

$$\beta = d^{-1}u^{-2} \tag{11}$$

where u is the speed of sound. In Figure 8, the salt concentration dependence of the isentropic compressibilities is shown for sodium citrate salts in pure water at $T = (288.15, 298.15$, and $308.15)$ K. From Figure 8, it can be seen that the values of β decrease by increasing salt concentration and temperature, and at the same condition, the values of β for the investigated solutions follow the order $NaH_2Cit > Na_2HCit > Na_3Cit$. In fact for low electrolyte concentrations, the compressibility of an aqueous electrolyte 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 molecules are electrostricted, the amount of bulk water decreases, causing the compressibility to decrease. Also in the temperature range investigated in this work, the compressibility of water decreases with temperature, and therefore, the values of β of the investigated electrolyte solutions also decrease with temperature. It has been shown that[31] the concentration dependence of β becomes greater as the number of water molecules affected by the ions increases. Figure 8 shows that the concentration dependence of β 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. Figure 8 also shows that, at each temperature, the salt concentration dependence of β follows the order $Na_3Cit > Na_2HCit > NaH_2Cit$, which can

Table 3. Pitzer's Model Parameters and the Corresponding Absolute Relative Deviation, dev, for Apparent Molar Volume and Isentropic Compressibility of Na_2HCit and NaH_2Cit in Water at Different Temperatures

T	$V^0_{\phi,1}$					$\kappa^0_{\phi,1}\cdot 10^4$				
K	cm³·mol⁻¹	$\beta^0_V\cdot 10^4$	$\beta^1_V\cdot 10^3$	$C_V\cdot 10^4$	dev[a]·10²	cm³·mol⁻¹·kPa⁻¹	$\beta^0_\kappa\cdot 10^8$	$\beta^1_\kappa\cdot 10^8$	$C_\kappa\cdot 10^8$	dev·10²
					Na_2HCit (1) + Water (2)					
288.15	82.2720 ± 0.1282	−2.3257 ± 8.2460	6.1736 ± 2.0339	16.001 ± 18.919	0.124	−1.7158 ± 0.0170	5.0679 ± 1.0957	−19.4018 ± 2.7024	−10.5756 ± 2.5141	−1.082
293.15	84.3467 ± 0.1281	1.3783 ± 8.1013	4.3103 ± 1.9980	6.8209 ± 18.588	0.109	−1.3803 ± 0.0042	−0.3068 ± 0.2672	−2.1697 ± 0.6590	0.0990 ± 0.6131	−0.254
298.15	86.1574 ± 0.1330	3.9975 ± 8.2669	2.7728 ± 2.0389	0.5083 ± 18.968	0.110	−1.2380 ± 0.0050	−1.2384 ± 0.3138	1.3018 ± 0.7739	1.9654 ± 0.7200	−0.313
303.15	87.5071 ± 0.1359	0.4774 ± 8.3061	3.1620 ± 2.0486	6.6172 ± 19.058	0.127	−1.1093 ± 0.0058	−2.4444 ± 0.3521	5.4073 ± 0.8683	4.3525 ± 0.8078	−0.428
308.15	88.8800 ± 0.1066	5.8612 ± 6.4116	1.1331 ± 1.5813	−5.1989 ± 14.7109	0.093	−1.0603 ± 0.0033	−1.9827 ± 0.1984	4.2928 ± 0.4894	3.4861 ± 0.4553	−0.306
	$V^0_{\phi,1}$					$\kappa^0_{\phi,1}\cdot 10^4$				
	cm³·mol⁻¹	β^0_V	β^1_V	C_V	dev·10²	cm³·mol⁻¹·kPa⁻¹	$\beta^0_\kappa\cdot 10^8$	$\beta^1_\kappa\cdot 10^8$	$C_\kappa\cdot 10^8$	dev·10²
					NaH_2Cit (1) + Water (2)					
288.15	99.3665 ± 0.0981	0.0108 ± 0.0023	−0.0164 ± 0.0039	−0.0200 ± 0.0048	0.103	−1.0264 ± 0.0160	19.9754 ± 3.7247	−40.0177 ± 6.3004	−36.4588 ± 7.7943	−1.989
293.15	101.0490 ± 0.0741	0.0107 ± 0.0017	−0.0166 ± 0.0029	−0.0196 ± 0.0036	0.086	−0.7286 ± 0.0035	0.3378 ± 0.7981	−2.2245 ± 1.3500	−0.8366 ± 1.6700	−0.403
298.15	102.6137 ± 0.0837	0.0111 ± 0.0019	−0.0180 ± 0.0032	−0.0203 ± 0.0039	0.083	−0.6069 ± 0.0040	−3.7933 ± 0.9047	5.9615 ± 1.5304	6.6673 ± 1.8932	−0.674
303.15	103.9105 ± 0.0882	0.0111 ± 0.0020	−0.0183 ± 0.0033	−0.0204 ± 0.0041	0.093	−0.5142 ± 0.0039	−6.2747 ± 0.8664	11.0027 ± 1.4654	11.0463 ± 1.8129	−0.817
308.15	105.1565 ± 0.0943	0.0123 ± 0.0021	−0.0208 ± 0.0035	−0.0227 ± 0.0043	0.102	−0.4634 ± 0.0043	−6.4726 ± 0.9455	11.4448 ± 1.5994	11.4894 ± 1.9786	−0.970

[a] dev $= (1/NP)\Sigma[|\phi_{exp} - \phi_{cal}|/\phi_{exp}]$.

Table 4. Fitting Parameters *a*, *b*, and *c* of Equation 9

parameter system	*a*	*b*	*c*
NaH_2Cit + water	−4037.1483 ± 467.7274	−114.3481 ± 14.6574	1073.1159 ± 126.5147
Na_2HCit + water	−6763.7890 ± 1161.3524	−197.2110 ± 36.3938	1799.9055 ± 314.1319
Na_3Cit + water[28]	−8653.6906 ± 87.6314	−254.7100 ± 2.7461	2302.1474 ± 23.7033

be held for the number of water molecules affected by the ions produced from the dissociation of these electrolytes.

Similar to the apparent molar volume, the apparent molar isentropic compressibility of the solutes, $\kappa_{\phi,1}$, in water was calculated from the density and sound velocity experimental data according to the following equation:[31]

$$\kappa_{\phi,1} = \frac{(\beta d_0 - \beta_0 d)}{m_1 d d_0} + \frac{M_1 \beta}{d} \qquad (12)$$

where β and β_0 are the isentropic compressibility of the solution and solvent, respectively. In Figure 9, the salt concentration dependence of the $\kappa_{\phi,1}$ is shown for sodium citrate salts in aqueous solutions at T = (288.15, 298.15, and 308.15) K. The apparent molar isentropic compressibility can also be expressed by the following Pitzer equation:[24]

$$\kappa_{\phi,1} = \kappa^0_{\phi,1} - \nu|z_c z_a|\left(\frac{A_\kappa}{2b}\right)\ln(1 + bI^{1/2}) - RT[B_\kappa \nu(\nu_c \nu_a/\nu)m_1 + (\nu_c \nu_a)^{1.5} C_\kappa m_1^{\,2}] \qquad (13)$$

where B_κ is a binary interaction parameter which is defined as:

$$B_\kappa = 2\beta^0_\kappa + 2\beta^1_\kappa\left(\frac{1}{\alpha^2 I}\right)\left[1 - \left(1 + \alpha I^{1/2} - \frac{\alpha^2 I}{2}\right)\exp(-\alpha I^{1/2})\right] \qquad (14)$$

The values of b and α in eqs 13 and 14 are same as those in eqs 6 and 7. The results of fitting $\kappa_{\phi,1}$ values to eq 13 are also given in Table 3. The values of the infinite dilution apparent molar isentropic compressibility, $\kappa^0_{\phi,1}$, at different temperatures are also given in Table 3. The values of the apparent molar isentropic compressibility of NaH_2Cit, Na_2HCit, and Na_3Cit are negative and increase by increasing temperature, increasing concentration of electrolyte, and decreasing charge on the anion of electrolyte. The negative values of the apparent molar isentropic compressibility (loss of compressibility of the medium) imply that the water molecules around the solute are less compressible than the water molecules in the bulk solutions. In fact, the negative values of $\kappa_{\phi,1}$ of the investigated solutions are attributed to the strong attractive interactions because of the hydration of ions at low temperatures. By increasing the temperature, ion−water interactions are weakened, and therefore some water molecules are released into the bulk, thereby making the medium more compressible. By increasing the salt concentration, the ion−ion interaction increases, resulting in a net

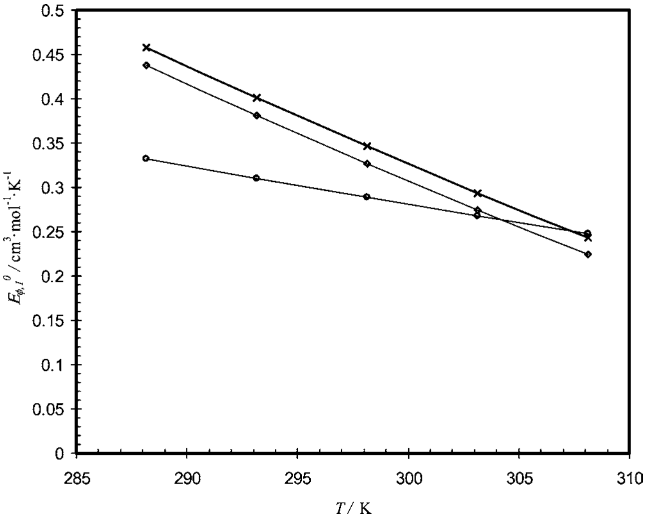

Figure 7. Plot of the infinite dilution apparent molar expansibilities, $E^0_{\phi,1}$, of sodium citrate salts in water against temperatures, T: ○, NaH_2Cit; ◇, Na_2HCit; ×, Na_3Cit.[28]

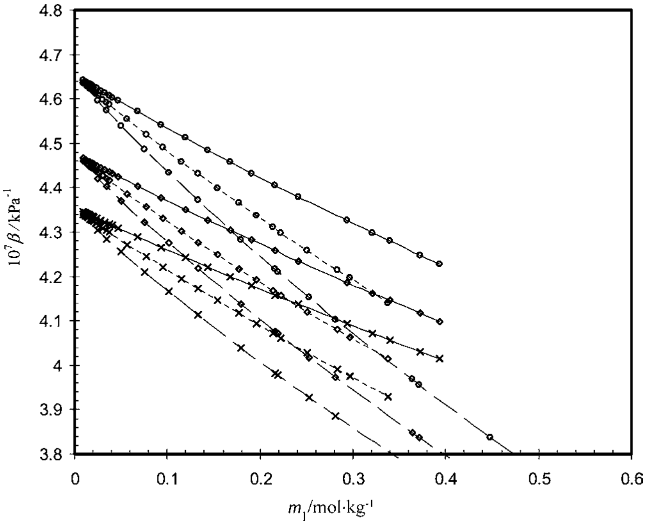

Figure 8. Plot of isentropic compressibility, β, of solutions of NaH_2Cit (solid lines), Na_2HCit (dotted lines), and Na_3Cit[28] (dashed lines) in water against the molality of the salt, m_1, at different temperatures: ○, T = 288.15 K; ◇, T = 298.15 K; ×, T = 308.15 K.

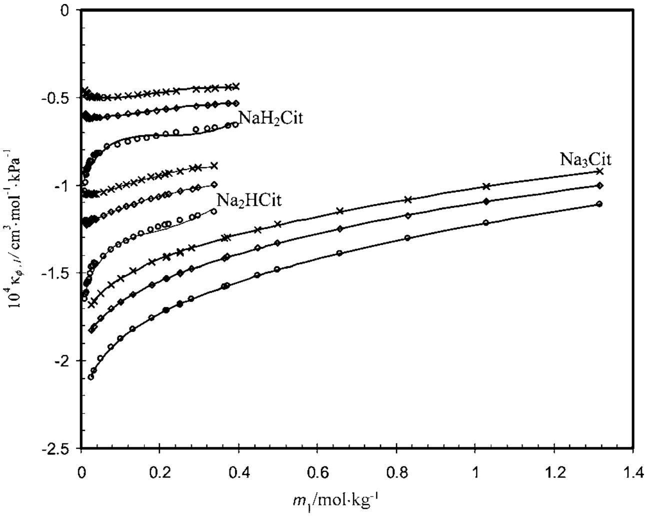

Figure 9. Plot of the apparent molar isentropic compressibility of NaH_2Cit, Na_2HCit, and Na_3Cit,[28] $\kappa_{\phi,1}$, in water against the molality of the salt, m_1, at different temperatures: ○, T = 288.15 K; ◇, T = 298.15 K; ×, T = 308.15 K; —, calculated by eq 13.

decrease of solvation, thereby increasing the amount of bulk water and making the medium more compressible. In fact, on ion association, some water molecules associated with the ions are released into the bulk, thereby making the medium more compressible.

Figure 9 and Table 3 show that, at the same conditions, the $\kappa_{\phi,1}$ and $\kappa^0_{\phi,1}$ values of Na_3Cit are more negative than those of Na_2HCit which, in turn, are more negative than those of NaH_2Cit, indicating that the loss of compressibility of the medium in the presence of the investigated salts follows the order $Na_3Cit > Na_2HCit > NaH_2Cit$. This is because the anion−water interactions for anions with a higher valence are stronger than the anion−water interactions for anions with a lower valence. Figure 9 also shows that the slope of $\kappa_{\phi,1}$ against salt concentration follows the order $Na_3Cit > Na_2HCit > NaH_2Cit$. In the case of the ion with higher valence, more water molecule was associated with the ion compared to the ion with a lower valence; hence on ion association (cation−anion interactions), a greater number of water molecules are released into the bulk, thereby making the medium more compressible. Furthermore, because of stronger cation−anion interactions, ion association in the Na_3Cit system is larger than those in the Na_2HCit system which, in turn, is larger than the ion association in the NaH_2Cit system.

Conclusions

In the first part of this work, the accurate vapor−liquid equilibrium data (water activity, vapor pressure, osmotic coefficient, and activity coefficient) for NaH_2Cit + water and Na_2HCit + water systems were determined through the isopiestic method at $T = 298.15$ K. The results obtained in this work and those of ref 22 for Na_3Cit + water system show that the salt concentration dependence of the water activity and vapor pressure depression follow the order $Na_3Cit > Na_2HCit > NaH_2Cit$, implying that the ions with a higher valence hydrate more water molecules than the ions with a lower valence. Mean activity coefficients and molar excess Gibbs energy of studied systems were calculated from the Pitzer model. The values of molar excess Gibbs energy are negative and decrease with the increase in concentration of the solutes and for Na_2HCit + water system are more negative than those for NaH_2Cit + water system.

In the second part of this work, the apparent molar volumes and apparent molar isentropic compressibilities of NaH_2Cit and Na_2HCit in aqueous solution were calculated from the precise measured density and speed of sound data at $T = (288.15, 293.15, 298.15, 303.15, \text{and } 308.15)$ K, and these data were also fitted to the corresponding Pitzer equation from which the values of the standard partial molar volumes, $V^0_{\phi,1}$, and isentropic compressibilities, $\kappa^0_{\phi,1}$, for both salts were determined. All solutes investigated in this work are structure-breakers based on the negative values of $(\partial^2 V^0_{\phi,1}/\partial T^2)_P$, and the values of $(\partial^2 V^0_{\phi,1}/\partial T^2)_P$ become less negative by increasing temperature. At each temperature the magnitude of $(\partial^2 V^0_{\phi,1}/\partial T^2)_P$ and therefore the structure-breaker property of the investigated solutes follow the order $Na_3Cit > Na_2HCit \gg NaH_2Cit$. The values of the apparent molar isentropic compressibility of NaH_2Cit, Na_2HCit, and Na_3Cit are negative and become less negative by increasing temperature, increasing the concentration of the electrolyte and decreasing the charge on the anion of the electrolyte.

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