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Apparent Molar Volume and Isentropic Compressibility of Trisodium Citrate in Water and in Aqueous Solutions of Polyvinylpyrrolidone at T = (283.15 to 308.15) K

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Precise density and sound velocity measurements have been carried out on trisodium citrate in aqueous solutions of 0.000, 0.002, and 0.004*m* polyvinylpyrrolidone (PVP) at T = (283.15 to 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 from which the apparent molar volume and apparent molar isentropic compressibility of the solutions at infinite dilution have also been calculated at each temperature. The results show a positive transfer volume of trisodium citrate from an aqueous PVP solution to a more concentrated PVP solution. This indicates that the size of trisodium citrate is larger in a solution with higher PVP concentration. The apparent molar isentropic compressibility of trisodium citrate in aqueous PVP solutions is negative, which implies that the water molecules around the trisodium citrate are less compressible than the water molecules in the bulk solutions.

Introduction

Ternary aqueous solutions of trisodium citrate and polyvinylpyrrolidone (PVP) separate into a trisodium citrate-rich and a PVP-rich phase over part of the composition space. Aqueous two-phase systems of this nature are useful for the separation and purification of biomaterials where the employment of a nonpolar solvent/aqueous phase system would lead to degradation of biological activity.[1,2] Citrate is biodegradable and nontoxic and could be discharged into biological wastewater treatment plants, and therefore, the citrates can be considered as a substitute for inorganic salts because the citrate forms an aqueous two-phase system with PVP which is suitable for protein extraction. Thermodynamic properties of aqueous polymer−salt systems are necessary for a fundamental understanding of the phase-forming ability and also for the development of theoretical models for the prediction of the partitioning behavior of the two-phase system. In addition to aqueous two-phase systems, aqueous solutions of sodium citrate are of a considerable significance in many other biochemical and chemical processes, and this salt is produced in large quantities and used in food, cosmetic, pharmaceutical, and chemical industries.[3−6] In our previous works,[7,8] liquid−liquid and vapor−liquid equilibria of aqueous PVP + trisodium citrate systems have been studied at different temperatures. The present work is a continuation of these studies and presents experimental data on the density and sound velocity of trisodium citrate in aqueous solutions of 0.000, 0.002, and 0.004*m* polyvinylpyrrolidone at T = (283.15 to 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 density of aqueous trisodium citrate solutions,[9−11] there are however no experimental data on the ultrasonic velocity of aqueous solutions of trisodium citrate in the literature. Furthermore, data on volumetric and isentropic compressibility behavior of trisodium citrate in aqueous PVP solutions, which is a very important system with respect to its use in biotechnology, are scarce. Recently, Murugesan and Perumalsamy[12] measured the densities and viscosities for ternary aqueous solutions of polyethylene glycol and sodium citrate at different temperatures.

Experimental Section

Materials. PVP (average molar mass = 10 000) was obtained from Merck. The manufacturer has characterized this polymer as polyvidon 25 with lot number k34372143 516. Sodium citrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) was obtained from Merck (GR, min 99.5 %). The polymer and salt were used without further purification, and double-distilled, deionized water was used.

Apparatus and Procedures. The aqueous solutions were prepared by mass, using an analytical balance (Sartorius CP124S) with a precision of ± 0.1 mg. 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 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. The reproducibility of density and ultrasonic velocity measurements was better than $\pm 3.0 \cdot 10^{-6}$ g·cm^{-3} and ± 0.1 m·s^{-1}, respectively.

Results and Discussion

Experimental data of density (d) and sound velocity (u) for various trisodium citrate solutions determined at T = (283.15, 288.15, 293.15, 298.15, 303.15, and 308.15) K are given in Table 1. The dependence of density and ultrasonic velocity on temperature and concentration has been calculated by means of the following equation:

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

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Table 1. Experimental Density d/(g·cm^{-3}) and Ultrasonic Velocity u/(m·s^{-1}) of Na_3Cit in Aqueous PVP 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
$m_p = 0.000$ mol·kg^{-1}												
0.0253	1.004627	1454.17	1.003962	1472.3	1.00301	1488.39	1.001804	1502.5	1.000366	1514.76	0.998718	1525.33
0.0347	1.00641	1456.41	1.005723	1474.46	1.004752	1490.48	1.00353	1504.5	1.002081	1516.71	1.000422	1527.23
0.0507	1.009393	1459.93	1.008669	1477.88	1.00767	1493.82	1.006422	1507.75	1.004953	1519.89	1.003273	1530.31
0.076	1.014051	1465.53	1.013274	1483.29	1.012227	1499.05	1.01094	1512.79	1.009435	1524.79	1.007728	1535.08
0.1014	1.018671	1470.95	1.017842	1488.58	1.01675	1504.16	1.015425	1517.78	1.013888	1529.63	1.012153	1539.78
0.1327	1.024275	1477.58	1.023383	1495.01	1.022239	1510.37	1.020869	1523.83	1.019292	1535.49	1.017524	1545.47
0.1799	1.032629	1487.27	1.031649	1504.39	1.030429	1519.49	1.028996	1532.7	1.027365	1544.11	1.025548	1553.86
0.216	1.03891	1494.72	1.037865	1511.57	1.036591	1526.45	1.035109	1539.43	1.033438	1550.64	1.031587	1560.23
0.2191	1.039473	1495.39	1.038425	1512.23	1.037148	1527.08	1.035663	1540.01	1.033987	1551.22	1.032135	1560.81
0.2524	1.045153	1502.08	1.044051	1518.71	1.042723	1533.37	1.041197	1546.11	1.039486	1557.15	1.037603	1566.56
0.2523	1.045189	1502.06	1.044084	1518.72	1.042758	1533.4	1.041231	1546.15	1.03952	1557.2	1.037636	1566.6
0.2812	1.050011	1507.78	1.048862	1524.27	1.047495	1538.74	1.045933	1551.33	1.044193	1562.23	1.042284	1571.49
0.3639	1.063676	1524.31	1.062401	1540.19	1.060929	1554.15	1.059274	1566.28	1.057454	1576.7	1.055473	1585.55
0.3716	1.064917	1525.76	1.063635	1541.59	1.06215	1555.52	1.060489	1567.6	1.058659	1577.98	1.056673	1586.8
0.4483	1.07725	1540.89	1.07586	1556.22	1.074287	1569.65	1.072545	1581.25	1.070647	1591.24	1.068602	1599.68
0.4985	1.085108	1550.62	1.083655	1565.61	1.082027	1578.72	1.080236	1590.06	1.078298	1599.78	1.076212	1607.96
0.656	1.10896	1581.01	1.107325	1594.89	1.10554	1606.98	1.103608	1617.35	1.101547	1626.22	1.09936	1633.61
0.8285	1.13383	1613.99	1.132025	1626.62	1.130088	1637.56	1.128028	1646.89	1.125848	1654.78	1.123559	1661.28
1.0294	1.161051	1651.38	1.159082	1662.53	1.156995	1672.15	1.154801	1680.28	1.152508	1687.06	1.150118	1692.54
1.3173	1.197375	1703.56	1.19521	1712.59	1.192948	1720.28	1.190603	1726.67	1.188172	1731.9	1.185659	1735.92
$m_p = 0.002$ mol·kg^{-1}												
0.0104	1.006086	1460.74	1.005404	1478.37	1.004436	1494.01	1.003212	1507.67	1.001757	1519.56	1.000092	1529.74
0.0256	1.008921	1464.34	1.008203	1481.84	1.007205	1497.39	1.005957	1510.95	1.004482	1522.73	1.002798	1532.83
0.0349	1.010653	1466.48	1.009912	1483.94	1.008896	1499.4	1.007633	1512.89	1.006144	1524.64	1.004451	1534.67
0.0578	1.014842	1471.74	1.014053	1488.9	1.012995	1504.21	1.011694	1517.57	1.010177	1529.16	1.008457	1539.08
0.0742	1.01779	1475.18	1.016967	1492.38	1.015879	1507.57	1.014556	1520.83	1.013016	1532.35	1.011278	1542.17
0.1143	1.024916	1483.77	1.024011	1500.69	1.022855	1515.62	1.021474	1528.64	1.019883	1539.92	1.018104	1549.52
0.1471	1.030664	1490.65	1.029699	1507.33	1.028488	1522.07	1.027059	1534.89	1.025435	1545.96	1.023622	1555.41
0.1881	1.037724	1499.19	1.036688	1515.45	1.035417	1529.95	1.033936	1542.52	1.032262	1553.4	1.030408	1562.66
0.2632	1.050352	1514.16	1.049191	1530.1	1.047814	1544.09	1.04624	1556.25	1.044488	1566.7	1.042567	1575.55
0.3804	1.069338	1537.23	1.068007	1552.37	1.066483	1565.65	1.06478	1577.09	1.062916	1586.92	1.060898	1595.22
0.5105	1.08954	1563.26	1.088043	1577.4	1.086374	1589.88	1.084547	1600.59	1.082573	1609.73	1.080461	1617.37
$m_p = 0.004$ mol·kg^{-1}												
0.0117	1.010457	1470.76	1.009717	1487.84	1.0087	1502.94	1.007432	1516.07	1.005937	1527.49	1.004233	1537.21
0.0249	1.012854	1473.87	1.012085	1490.86	1.011041	1505.86	1.009752	1518.92	1.008242	1530.24	1.006523	1539.88
0.0375	1.01516	1476.96	1.014363	1493.87	1.013296	1508.77	1.011987	1521.77	1.010457	1533.03	1.008726	1542.48
0.0551	1.01829	1480.72	1.017456	1497.48	1.016358	1512.25	1.015023	1525.14	1.01347	1536.27	1.011719	1545.72
0.073	1.021474	1484.68	1.020605	1501.31	1.019475	1515.98	1.018111	1528.78	1.016537	1539.77	1.014765	1549.14
0.1051	1.027065	1491.59	1.026133	1507.84	1.024951	1522.32	1.023544	1534.88	1.021928	1545.71	1.020124	1554.92
0.1665	1.037572	1504.22	1.036529	1520.21	1.035249	1534.27	1.033758	1546.44	1.032076	1556.94	1.030211	1565.83
0.2218	1.046814	1515.62	1.045678	1531.08	1.04432	1544.78	1.04276	1556.65	1.041017	1566.85	1.039101	1575.44
0.2857	1.057267	1528.28	1.056032	1543.42	1.054589	1556.73	1.052956	1568.21	1.051149	1578.03	1.049181	1586.30
0.3999	1.075196	1550.36	1.073802	1564.67	1.072224	1577.24	1.070474	1588.04	1.068564	1597.30	1.066506	1605.01
0.4747	1.086687	1564.78	1.085202	1578.53	1.083539	1590.66	1.081718	1601.08	1.079748	1609.87	1.077633	1617.19

where m_s and m_p are the molality of the salt and polymer, 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 P_1, P_2, P_3, P_4, P_5, and P_6 along with the corresponding absolute relative deviation (ARD) for density and sound velocity of investigated systems are given in Table 2. On the basis of the obtained ARD values, we conclude that eq 1 can be successfully used for the correlation of the investigated physical properties at different temperatures and concentrations. In fact, for each property, one set of parameters has been successfully used to correlate all experimental data measured at six temperatures and three polymer molalities.

The apparent molar volumes of the trisodium citrate V_ϕ in aqueous PVP solutions were computed from the density of the solution by using the following equation:[13]

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

where M_s and M_p are the molar mass of the salt and polymer, respectively, and d and d_0 are the densities of the solution and solvent, respectively. For ternary systems, PVP + water is considered as the solvent. In Figure 1, comparison of the apparent molar volume of trisodium citrate measured in this work with those taken from refs 9 and 11 has been made at $T = 298.15$ K. Figure 1 shows that there is good agreement between our data and those taken from ref 9. Conversely, measured data in this work do not agree well with those taken from ref 11.

A Redlich−Mayer-type equation[14,15] of the form

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

was used to obtain V_ϕ^0, the limiting apparent molar volume of trisodium citrate at different temperatures and PVP 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 expressed in polynomial form with $(T - 283.15)$ K as a variable, as follows:

$$V_\phi^0 = A^0 + A^1(T - 283.15) + A^2(T - 283.15)^2 \tag{4}$$

$$S_v = S_v^0 + S_v^1(T - 283.15) + S_v^2(T - 283.15)^2 \tag{5}$$

$$B_v = B_v^0 + B_v^1(T - 283.15) + B_v^2(T - 283.15)^2 \tag{6}$$

The coefficients of these equations and the corresponding absolute relative deviation for V_ϕ at each temperature and PVP concentration are given in Tables 3 and 4, respectively. The

Table 2. Fitting Parameters of Equation 1 along with the Corresponding Absolute Relative Deviation, ARD, for Density and Sound Velocity

	parameters					
property	P_1	P_2	P_3	P_4	P_5	P_6
density	0.7590	299.2009	216.7164	−60.0277	−797.9956	1.6721
sound velocity	1869.4835	−27.4717	17.1748	−3.3507	174.6625	4036.96

$ARD^a \cdot 10^5$ (for Density)

	temperature					
system	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
Na_3Cit + PVP(0.000*m*) + H_2O	58.70	39.46	36.3	33.12	30.18	44.8
Na_3Cit + PVP(0.002*m*) + H_2O	40.33	8.75	28.2	28.03	17.65	38.00
Na_3Cit + PVP(0.004*m*) + H_2O	40.89	46.55	56.37	57.69	54.59	60.46

$ARD^a \cdot 10^2$ (for Sound Velocity)

	temperature					
system	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
Na_3Cit + PVP(0.000*m*) + H_2O	0.17	0.03	0.06	0.08	0.05	0.03
Na_3Cit + PVP(0.002*m*) + H_2O	0.05	0.05	0.10	0.08	0.02	0.10
Na_3Cit + PVP(0.004*m*) + H_2O	0.03	0.08	0.09	0.04	0.06	0.21

[a] $\mathrm{ARD} = \frac{1}{\mathrm{NP}} \sum \left[\frac{d_{\mathrm{exptl}} - d_{\mathrm{calcd}}}{d_{\mathrm{exptl}}} \right].$

Table 3. Fitting Parameters of Equations 4, 5, and 6 for V_ϕ and of Equations 12, 13, and 14 for $10^4 \cdot K_\phi$

V_ϕ

	temperature								
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
Na_3Cit + PVP(0.000*m*) + H_2O	58.20032	0.55047	−0.00677	36.4112	−0.30067	0.00224	−7.65008	−0.00075	0.00185
Na_3Cit + PVP(0.002*m*) + H_2O	60.28026	0.53039	−0.00728	34.15292	−0.28695	0.00534	−8.08119	−0.00533	−0.00092
Na_3Cit + PVP(0.004*m*) + H_2O	62.52543	0.54054	−0.00733	26.67073	−0.31935	0.00492	−1.21965	−0.00086	0.00033

$10^4 \cdot K_\phi$

	temperature								
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
Na_3Cit + PVP(0.000*m*) + H_2O	−2.53815	0.05086	−0.00091	1.71724	−0.06924	0.00160	−0.48140	0.03441	−0.00088
Na_3Cit + PVP(0.002*m*) + H_2O	−1.85945	0.04248	−0.00058	−0.66575	−0.06476	0.00103	1.64660	0.04691	−0.00079
Na_3Cit + PVP(0.004*m*) + H_2O	−2.30909	0.03183	−0.00037	1.25257	−0.02516	0.00025	−0.19540	0.01012	−0.00008

values of V_ϕ^0 at different temperatures and PVP concentrations calculated from eq 4 and the coefficients presented in Table 3 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 with other ions. It follows, therefore, that V_ϕ^0 is unaffected by ion + ion interaction and is a measure only of the ion + solvent interaction.[16,17] In Figures 2 to 4, the temperature and concentration dependence of V_ϕ have been given. From Figures 2 to 4, it can be seen that the apparent molar volumes of trisodium citrate in water and in aqueous PVP solutions increase with an increase in the salt molality. For the low concentrations of trisodium citrate, the small volume of trisodium citrate 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 versus concentration plots.[16] This is attributed to the phenomenon described in terms of destructive overlap of cospheres,[18,19] resulting in a net decrease of solvation, thereby increasing the solute volume. The effect of temperature on the V_ϕ^0 of trisodium citrate in aqueous PVP solutions has been shown in Figure 5. As can be seen from Figure 5, the infinite dilution apparent molar volume of trisodium citrate in aqueous PVP solutions increases with increasing temperature. 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

$$V_\phi^0\,(\mathrm{Na_3Cit}) = 3V_\phi^0\,(\mathrm{Na^+}) + V_\phi^0\,(\mathrm{Cit^{3-}}) \qquad (7)$$

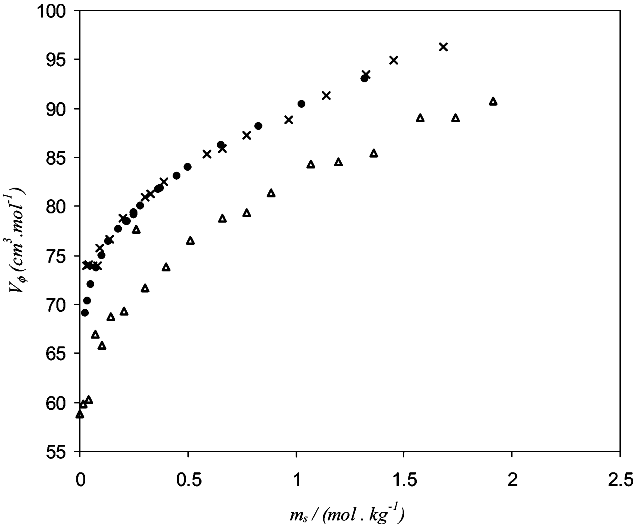

Figure 1. Plot of apparent molar volume of Na_3Cit, V_ϕ, in water against molality of the salt, m_s, at 298.15 K: ●, this work; ×, ref 9; △, ref 11.

Table 4. Absolute Relative Deviation, ARD, of V_ϕ and K_ϕ for the Investigated Systems at Different Temperatures

	ARD·10^2					
	temperature					
system	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
			V_ϕ			
$Na_3Cit + PVP(0.000m) + H_2O$	0.36	0.35	0.34	0.34	0.32	0.31
$Na_3Cit + PVP(0.002m) + H_2O$	0.08	0.11	0.11	0.09	0.09	0.10
$Na_3Cit + PVP(0.004m) + H_2O$	0.27	0.24	0.24	0.22	0.22	0.20
			K_ϕ			
$Na_3Cit + PVP(0.000m) + H_2O$	−0.77	−0.49	−0.26	−0.18	−0.18	−0.27
$Na_3Cit + PVP(0.002m) + H_2O$	−2.43	−2.83	−3.31	−3.64	−3.96	−4.33
$Na_3Cit + PVP(0.004m) + H_2O$	−0.32	−0.44	−0.46	−0.51	−0.46	−0.54

Table 5. Values of $V_\phi^0/(cm^3 \cdot mol^{-1})$, $E_\phi^0/(cm^3 \cdot mol^{-1} \cdot K^{-1})$, and $K_\phi^0/(cm^3 \cdot mol^{-1} \cdot kPa^{-1})$ of Trisodium Citrate at Different Temperatures and PVP Concentrations

	temperature					
system	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
			V_ϕ^0			
$Na_3Cit + PVP(0.000m) + H_2O$	58.200	60.783	63.028	64.934	66.502	67.731
$Na_3Cit + PVP(0.002m) + H_2O$	60.280	62.750	64.856	66.598	67.976	68.990
$Na_3Cit + PVP(0.004m) + H_2O$	62.525	65.045	67.198	68.984	70.404	71.458
			E_ϕ^0			
$Na_3Cit + PVP(0.000m) + H_2O$	0.5505	0.4828	0.4151	0.3474	0.2797	0.2120
$Na_3Cit + PVP(0.002m) + H_2O$	0.5304	0.4576	0.3848	0.3120	0.2392	0.1664
$Na_3Cit + PVP(0.004m) + H_2O$	0.5405	0.4672	0.3939	0.3206	0.2473	0.1740
			$K_\phi^0 \cdot 10^4$			
$Na_3Cit + PVP(0.000m) + H_2O$	−2.538	−2.307	−2.121	−1.980	−1.885	−1.835
$Na_3Cit + PVP(0.002m) + H_2O$	−1.859	−1.662	−1.493	−1.353	−1.242	−1.160
$Na_3Cit + PVP(0.004m) + H_2O$	−2.309	−2.159	−2.028	−1.915	−1.820	−1.745

The infinite dilution apparent molar volume of ions can be expressed as the sum of two contributions:[20]

$$V_\phi^0(\text{ion}) = V_\phi^0(\text{int}) + V_\phi^0(\text{elect}) \qquad (8)$$

where $V_\phi^0(\text{int})$ is the intrinsic (related to the size of the ions and to packing effects) apparent molar volume and $V_\phi^0(\text{elect})$ is the electrostriction apparent molar volume related to ion−solvent interactions (i.e., the decrease in volume due to hydration). The term $\partial V_\phi^0(\text{int})/\partial T$ contributes negligibly to the overall temperature dependence of $V_\phi^0(\text{ion})$, and therefore an increase in the V_ϕ^0 by increasing temperature occurs with loss of hydration. Also, as can be seen from Figures 2 to 4, the initial slopes of V_ϕ against molality of sodium citrate are positive, the magnitude of which increases with decreasing temperature. This is because at higher temperatures ion−solvent interactions are weakened. The infinite dilution apparent molar expansibility can be obtained by differentiating eq 4 with respect to temperature

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

The E_ϕ^0 values of sodium citrate at different temperatures and PVP concentrations are also given in Table 5. As mentioned

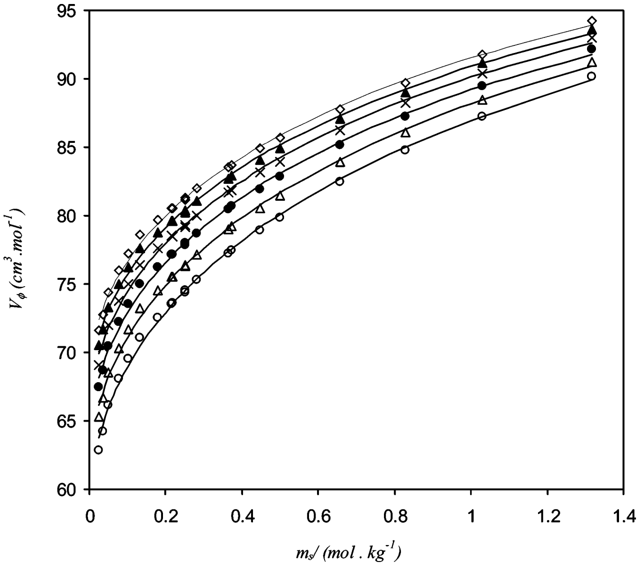

Figure 2. Plot of apparent molar volume of Na_3Cit, V_ϕ, in water against molality of the salt, m_s, at different temperatures: ○, T = 283.15 K; △, T = 288.15 K; ●, T = 293.15 K; ×, T = 298.15 K; ▲, T = 303.15 K; ◇, T = 308.15 K; —, calculated by eqs 3−6.

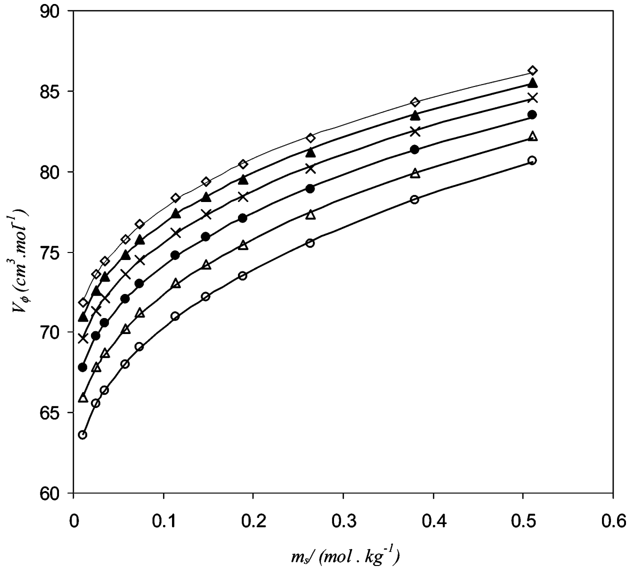

Figure 3. Plot of apparent molar volume of Na_3Cit, V_ϕ, in aqueous solution of 0.002m PVP against molality of the salt, m_s, at different temperatures: ○, T = 283.15 K; △, T = 288.15 K; ●, T = 293.15 K; ×, T = 298.15 K; ▲, T = 303.15 K; ◇, T = 308.15 K; —, calculated by eqs 3−6.

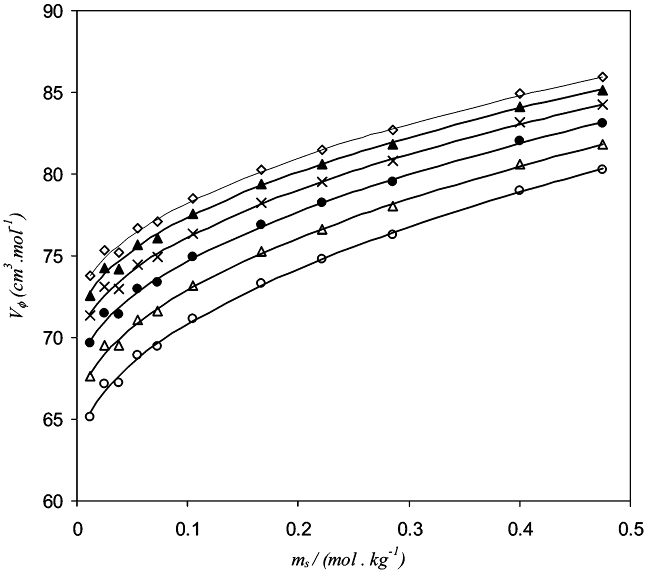

Figure 4. Plot of apparent molar volume of Na_3Cit, V_ϕ, in aqueous solution of 0.004*m* PVP against molality of the salt, m_s, at different temperatures: ○, $T = 283.15$ K; △, $T = 288.15$ K; ●, $T = 293.15$ K; ×, $T = 298.15$ K; ▲, $T = 303.15$ K; ◇, $T = 308.15$ K; —, calculated by eqs 3−6.

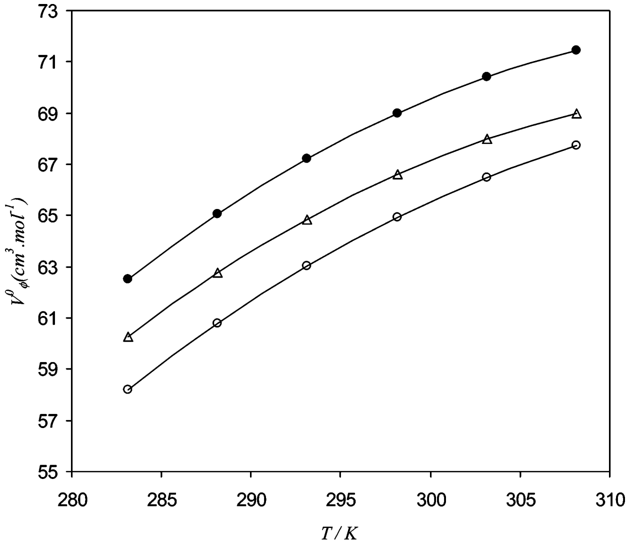

Figure 5. Plot of infinite dilution apparent molar volume of Na_3Cit, V^0_ϕ, against temperature: ○, in water; △, in aqueous solution of 0.002*m* PVP; ●, in aqueous solution of 0.004*m* PVP.

above, $E^0_\phi = (\partial V^0_\phi(\text{elect})/\partial T)_P$. From Table 5, we note that at each temperature E^0_ϕ values have a positive value and decrease with 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 PVP solutions). In fact, the infinite dilution isobaric expansivity of solution ($Na_3Cit + PVP + H_2O$) is greater than the isobaric expansivity of solvent ($PVP + H_2O$).

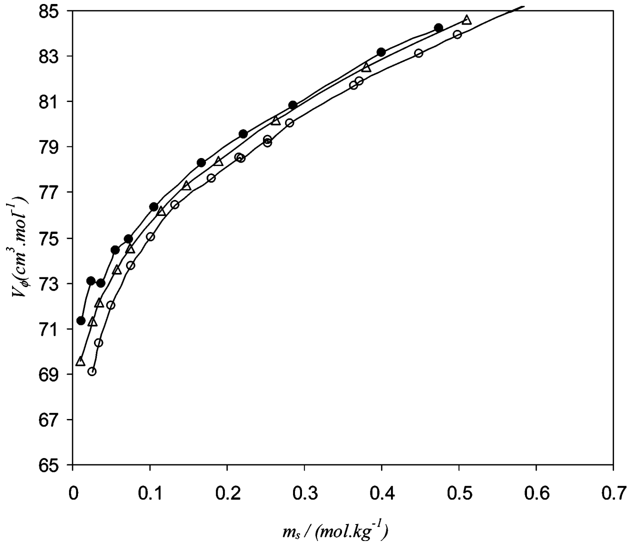

Figure 6. Plot of apparent molar volume of Na_3Cit, V_ϕ, against molality of the salt, m_s, at $T = 298.15$ K: ○, in water; △, in aqueous solution of 0.002*m* PVP; ●, in aqueous solution of 0.004*m* PVP.

Figure 6 shows a positive transfer volume of Na_3Cit from an aqueous solution to an aqueous PVP solution. This indicates that the sodium citrate ions in aqueous PVP solutions are larger than those in aqueous solutions and that the value of V_ϕ increases as the concentration of PVP increases. The apparent molar volumes of transfer, $\Delta_t V^0_\phi$, at infinite dilution for trisodium citrate from water to aqueous PVP solutions are listed in Table 6 at each temperature. As mentioned above, a ternary aqueous solution of PVP and trisodium citrate separates into a PVP-rich phase and a salt-rich phase over part of the composition space.[8] The formation of aqueous two-phase systems clearly indicates the mutual exclusion of the ions and the polymer and their high affinity for the solvent. It is possible that even in homogeneous systems (below the phase boundary) the ions are excluded from the near surface region of the polymer in solution. With an increase in the concentration of the polymer or the salt, the extent of exclusion will increase. Ultimately, the system could reach a state where, for entropic reasons, phase formation would become favorable. Exclusion of ions from the polymer molecule−water interface itself can occur for a number of reasons. Both the polymer and the ion are strongly hydrated in solution. Because of the hydration sheath, the near-surface region of the polymer may not be accessible to structure-making ions. Exclusion can occur also by repulsive interaction between the anions and the anionic-like imide group on the pyrrolidone ring especially in the presence of nonbonding cations such as K^+, NH_4^+, and Na^+. Ananthapadmanabhan and Goddard,[21] using the turbidimetric titration technique, have shown that for a series of sodium salts two-phase formation occurs with anions such as sulfate which have a marked salting-out effect on nonelectrolytes but that for large, singly charged ions such as iodide only one phase exists. The same authors also found that for a series of sulfates the salting-out effects of the anions are offset by di- and trivalent cations which are believed to coordinate to the ether oxygens to produce a salting-in effect. There are two factors which have an effect on the apparent molar volume of trisodium citrate in aqueous PVP solutions. (1) The strong attractive interactions due to the hydrogen-bond formations between the imide nitrogen of the PVP chain and water molecules induce the dehydration of ions and therefore increase the V_ϕ. (2) Repulsive interactions between the anion and the anionic-like imide group on the pyrrolidone ring increase the apparent molar volume of trisodium citrate.

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 Laplace−Newton's 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

Table 6. Values of $\Delta_t V_\phi^0$/(cm^3·mol^{-1}) for Trisodium Citrate from Water to Aqueous PVP Solutions at Different Temperatures

	temperature					
system	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
			$\Delta_t V_\phi^0$			
$Na_3Cit + PVP(0.000m) + H_2O$	0.000	0.000	0.000	0.000	0.000	0.000
$Na_3Cit + PVP(0.002m) + H_2O$	2.080	1.967	1.828	1.664	1.474	1.259
$Na_3Cit + PVP(0.004m) + H_2O$	4.325	4.262	4.17	4.050	3.902	3.727

an example, in Figure 7, the isentropic compressibilities are plotted versus the molality of trisodium citrate for a binary aqueous solution of Na_3Cit. From Figure 7, we note that at each working temperature, as the concentration of trisodium citrate 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 extent by the charge on the ions,[20] 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 molecules are electrostricted, the amount of bulk water decreases causing the compressibility to decrease. Also, Figure 7 shows 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[20] for electrolytes with large hydration numbers, such as $MgSO_4$ and Na_2SO_4, the concentration dependence of κ_s is more negative than that for 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[22] the compressibility of water also decreases with temperature to a minimum κ_s value near 319.15 K. It has been postulated[22] 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, whereas it is positive for the less-structured form. At temperatures below 319.15 K, the structured form is the predominant species, whereas at high temperatures, the nonstructured form predominates. As can be seen from Figure 7, the value of $\partial\kappa_s/\partial T$ is much less negative in dilute electrolyte solution than in water, and as the concentration increases, $\partial\kappa_s/\partial T$ becomes less negative. The isentropic compressibility isotherms of aqueous Na_3Cit + PVP solutions have a form similar to those of aqueous Na_3Cit solutions.

In Figure 8, the values of κ_s are plotted as a function of salt concentration at various PVP concentrations at 298.15 K. Figure 8 shows that at each temperature at a constant salt concentration the value of κ_s decreases as the concentration of PVP increases. This effect can be attributed to the strong attractive interactions due to the hydration of polymer segments therefore decreasing the amount of bulk water and also incorporation of ionic species into the PVP chain. In fact, as can be seen from Figure 8, at each working temperature as the concentration of PVP is increased, κ_s of the water + PVP solution is decreased due to the combined effect of hydration of polymer segments and breaking of the three-dimensional network structure of water.

The apparent molar isentropic compressibility K_ϕ is defined as

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

Similar to the apparent molar volume, the apparent molar isentropic compressibility of the Na_3Cit, K_ϕ, in water and in aqueous PVP solutions was computed from the density and sound velocity experimental data according to the following equation:

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

where κ_s and κ_{s0} are the isentropic compressibility of the solution and solvent, respectively. For systems containing both trisodium

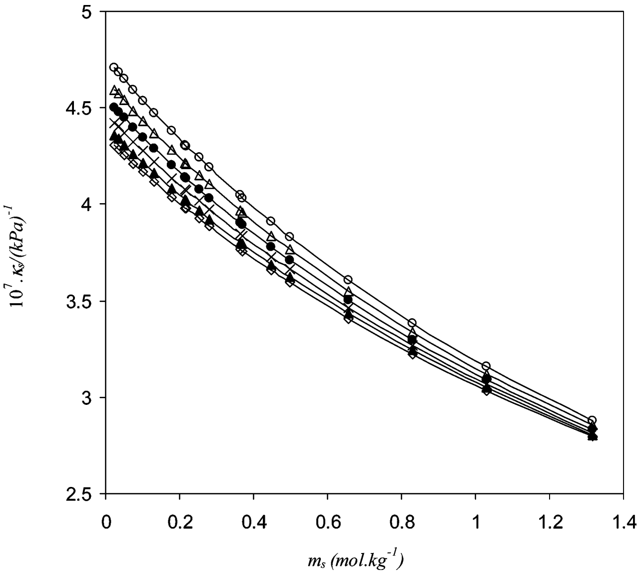

Figure 7. Plot of isentropic compressibility κ_s of Na_3Cit + water solutions against molality of the salt, m_s, at different temperatures: ○, $T = 283.15$ K; △, $T = 288.15$ K; ●, $T = 293.15$ K; ×, $T = 298.15$ K; ▲, $T = 303.15$ K; ◇, $T = 308.15$ K.

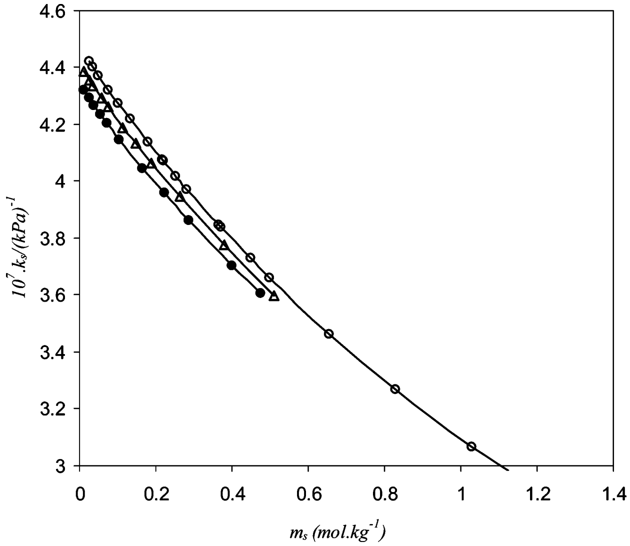

Figure 8. Plot of isentropic compressibility against molality of the salt, m_s, at $T = 298.15$ K: ○, in water; △, in aqueous solution of 0.002*m* PVP; ●, in aqueous solution of 0.004*m* PVP.

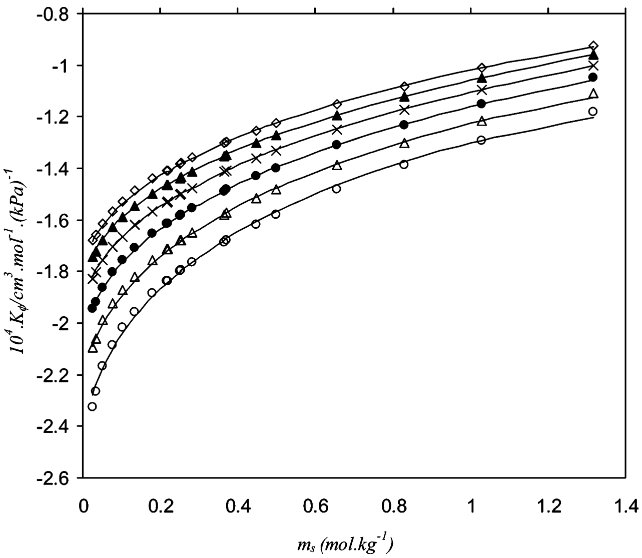

Figure 9. Plot of apparent molar isentropic compressibility of Na_3Cit, K_ϕ, in water against molality of the salt, m_s, at different temperatures: ○, T = 283.15 K; △, T = 288.15 K; ●, T = 293.15 K; ×, T = 298.15 K; ▲, T = 303.15 K; ◇, T = 308.15 K; —, calculated by eqs 13−16.

citrate and PVP, PVP + water is considered as the solvent. An equation of the form[23]

$$K_\phi = K_\phi^0 + S_k m_s^{0.5} + B_k m_s \tag{13}$$

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:

$$K_\phi^0 = A^0 + A^1(T - 283.15) + A^2(T - 283.15)^2 \tag{14}$$

$$S_k = S_k^0 + S_k^1(T - 283.15) + S_k^2(T - 283.15)^2 \tag{15}$$

$$B_k = B_k^0 + B_k^1(T - 283.15) + B_k^2(T - 283.15)^2 \tag{16}$$

The coefficients of these equations and the corresponding absolute relative deviation for $10^4 K_\phi$ at each temperature and PVP concentration are also given in Tables 3 and 4, respectively. The values of K_ϕ^0 at different temperatures and PVP concentrations calculated from eq 14 and the coefficients presented in Table 3 are also given in Table 5. In Figure 9, the temperature and concentration dependence of K_ϕ have been given for Na_3Cit + water solutions. From Figure 9, it can be seen that the value of apparent molar isentropic compressibility of trisodium citrate in water (and also in PVP solutions) is negative and it increases with increasing concentration of trisodium citrate and temperature. As can be seen from Table 5, K_ϕ^0 values are negative and they increase with increasing temperature. Also, it is seen that the values of K_ϕ^0 at each temperature follow the order Na_3Cit + PVP(0.002m) + H_2O > Na_3Cit + PVP(0.004m) + H_2O > Na_3Cit + PVP(0.000m) + H_2O. The negative values of K_ϕ and K_ϕ^0 of trisodium citrate in aqueous PVP solutions indicate that the water molecules around the trisodium citrate ions are less compressible than the water molecules in the bulk solution. By differentiating eq 8 with respect to pressure, we obtain

$$K_\phi^0(\text{ion}) = K_\phi^0(\text{int}) + K_\phi^0(\text{elect}) \tag{17}$$

where $K_\phi^0(\text{int}) = -(\partial V_\phi^0(\text{int})/\partial P)_T$ is the intrinsic apparent molar compressibility and $K_\phi^0(\text{elect}) = -(\partial V_\phi^0(\text{elect})/\partial P)_T$ is the electrostriction apparent molar compressibility. Because the effect of pressure on the volume of crystals is small, one would expect K_ϕ^0(int) to be positive and close to zero.[24] Thus, K_ϕ^0(ion) is due mainly to K_ϕ^0(elect). In fact, the negative values of K_ϕ and K_ϕ^0 of trisodium citrate in aqueous PVP solutions 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 temperatures the water molecules around the sodium citrate become more compressible than the water molecules in the bulk solution.

Conclusions

Experimental data at T = (283.15 to 308.15) K of density and sound velocity of trisodium citrate in water and in water + PVP 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 trisodium citrate from an aqueous solution to an aqueous PVP solution. Also, the results show that the apparent molar volumes of trisodium citrate increase as the concentration of sodium citrate increases. The apparent molar isentropic compressibility of trisodium citrate in both binary and ternary solutions has negative values at each temperature. The negative values of apparent molar isentropic compressibility of trisodium citrate imply that the water molecules around the trisodium citrate ions are less compressible than the water molecules in the bulk solutions.

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