

# Thermodynamic Properties of Tripotassium Citrate in Water and in Aqueous Solutions of Polypropylene Oxide 400 over a Range of Temperatures

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Precise density and sound velocity measurements have been carried out on tripotassium citrate in aqueous solutions of polypropylene oxide (PPO) 400 over a range of temperatures at atmospheric pressure. The data obtained are used to calculate the apparent molar volume and isentropic compressibility as a function of temperature and concentration. Apparent molar volume and isentropic compressibility values have been 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 tripotassium citrate from pure water to an aqueous PPO solution. The apparent molar isentropic compressibility of tripotassium citrate in aqueous PPO solutions is negative which implies that the water molecules around the tripotassium citrate are less compressible than the water molecules in the bulk solutions.

## Introduction

Ternary aqueous solutions of tripotassium citrate and polypropylene oxide (PPO) separate into a tripotassium citrate-rich and a PPO-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.<sup>1,2</sup> 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 PPO which is suitable for protein extraction. In addition to aqueous two-phase systems, aqueous solutions of potassium citrate are of 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.<sup>3–6</sup>

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. The volumetric properties of polymer or electrolyte solutions have proven to be a very useful tool in elucidating the structural interactions (i.e., solute–solvent, solute–solute, and solvent–solvent) occurring in solution, because they may give us an indirect insight into the conformational feature of the components in solution. This work presents the results of a comprehensive study of the apparent molar volume,  $V_\phi$ , and apparent molar isentropic compressibility,  $K_\phi$ , of tripotassium citrate in aqueous solutions of (0.00, 0.051, and 0.104) *m* PPO at  $T = (288.15 \text{ to } 313.15) \text{ K}$ . Although there is one report on the density of aqueous tripotassium citrate solutions at 298.15 K,<sup>7</sup> there are however no experimental data on the ultrasonic velocity of aqueous solutions of tripotassium

citrate in the literature. Furthermore, volumetric and isentropic compressibility behavior of tripotassium citrate in aqueous PPO solutions, which is a very important system in respect to its use in biotechnology, is scarce.

## Experimental Procedures

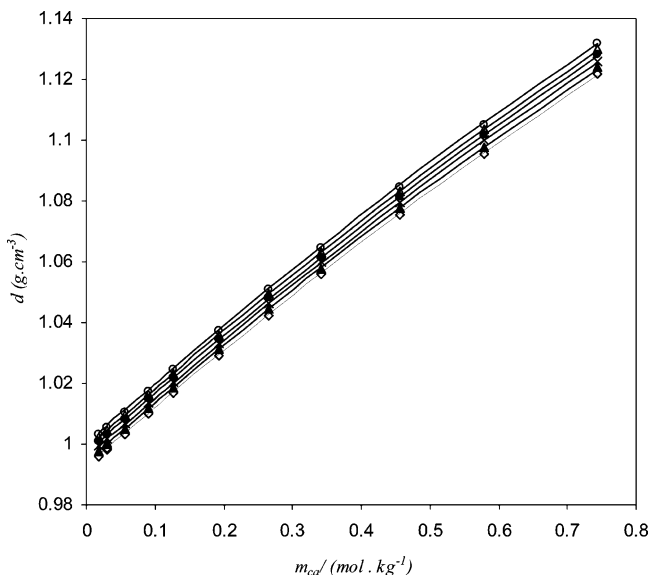
**Materials.** PPO with a quoted molar mass of 400 was obtained from Fluka. The manufacturer has characterized this polymer as P400 with lot and filling code 1252304 and 20206282, respectively. Potassium citrate ( $\text{C}_6\text{H}_5\text{K}_3\text{O}_7\cdot\text{H}_2\text{O}$ ) was obtained from Fluka. The polymer and salt were used without further purification, and double distilled, deionized water was used.

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

## Results and Discussion

In the present work, to describe thermodynamic properties of both binary aqueous solutions of  $\text{K}_3\text{Cit}$  and ternary aqueous PPO solutions of  $\text{K}_3\text{Cit}$ , densities and ultrasound measurements for tripotassium citrate in aqueous solutions of (0.00, 0.051, and 0.104) *m* PPO at different salt concentrations were made at  $T = (288.15, 293.15, 298.15, 303.15, 308.15, \text{ and } 313.15) \text{ K}$  to study the variation in apparent molar volumes, compressibilities, and expansibilities with salt concentration, PPO concentration, and temperature. Experimental data of density ( $d$ ) and sound velocity ( $u$ ) for various tripotassium citrate solutions determined at  $T = (288.15, 293.15, 298.15, 303.15, 308.15, \text{ and } 313.15) \text{ K}$  are given in Table 1. The experimental

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**Figure 1.** Plot of density,  $d$ , of  $K_3Cit$  in water against molality of the salt,  $m_{ca}$ , at different temperatures:  $\circ$ ,  $T = 288.15$  K;  $\triangle$ ,  $T = 293.15$  K;  $\bullet$ ,  $T = 298.15$  K;  $\times$ ,  $T = 303.15$  K;  $\blacktriangle$ ,  $T = 308.15$  K;  $\diamond$ ,  $T = 313.15$  K; —, calculated by eq 1.

density and ultrasonic velocity data have been fitted to the following equation

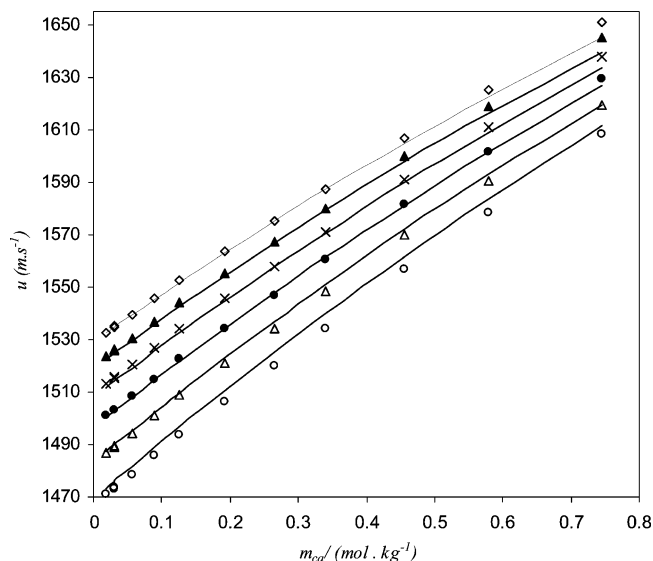
$$F = P_1 \exp\left(\frac{P_2 + P_3 w_{ca} + P_4 w_{ca}^{1.5}}{T - P_5}\right) + P_6 w_p \quad (1)$$

where  $w_{ca}$  and  $w_p$  are the weight fraction 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  $P_6$  for density are  $0.6343 \pm 0.0002$ ,  $695.1 \pm 0.6$ ,  $1023.0 \pm 14.8$ ,  $-8.41 \pm 0.69$ ,  $-1239.28 \pm 0.04$ , and  $0.0806 \pm 0.0012$ , respectively, and for sound velocity are  $1781.0023 \pm 0.0002$ ,  $-18.3915 \pm 0.0571$ ,  $47.4824 \pm 3.5048$ ,  $-0.1098 \pm 0.0247$ ,  $192.5621 \pm 0.0011$ , and  $569.9166 \pm 0.0013$ , respectively. Also, the obtained overall absolute relative deviations ( $ARD = 1/NP \sum [|F_{\text{exptl}} - F_{\text{calcd}}|/F_{\text{exptl}}]$ ) for density and sound velocity have been obtained as  $2.364 \cdot 10^{-4}$  and  $0.10 \cdot 10^{-2}$ , respectively. On the basis of the obtained ARD values, we conclude that eq 1 can be 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 concentrations. For example, the temperature and concentration dependence of  $d$  and  $u$  for binary aqueous solution of  $K_3Cit$ , respectively, have been shown in Figures 1 and 2.

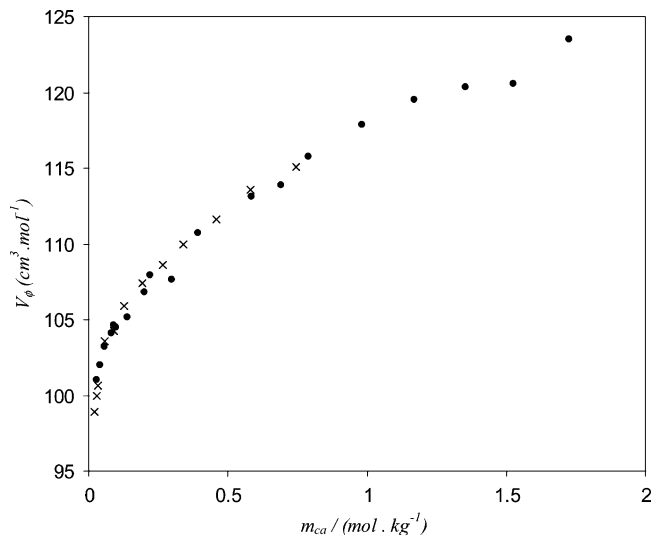
The apparent molar volumes of the tripotassium citrate  $V_\phi$  in aqueous PPO solutions were computed from the density of the solution by using the following equation

$$V_\phi = \frac{1000 + m_p M_p}{m_{ca} d d_0} (d_0 - d) + \frac{M_{ca}}{d} \quad (2)$$

where  $M_{ca}$  and  $M_p$  are the molar mass of the salt and polymer, respectively;  $m_{ca}$  and  $m_p$  are the molality of the salt and polymer, respectively; and  $d$  and  $d_0$  are the densities of the solution and solvent, respectively. For ternary systems, the PPO + water is considered as the solvent. In Figure 3, comparison of the apparent molar volume of tripotassium citrate measured in this work with those taken from ref 7 has been made at  $T = 298.15$



**Figure 2.** Plot of sound velocity,  $u$ , of  $K_3Cit$  in water against molality of the salt,  $m_{ca}$ , at different temperatures:  $\circ$ ,  $T = 288.15$  K;  $\triangle$ ,  $T = 293.15$  K;  $\bullet$ ,  $T = 298.15$  K;  $\times$ ,  $T = 303.15$  K;  $\blacktriangle$ ,  $T = 308.15$  K;  $\diamond$ ,  $T = 313.15$  K; —, calculated by eq 1.



**Figure 3.** Plot of apparent molar volume of  $K_3Cit$ ,  $V_\phi$ , in water against molality of the salt,  $m_{ca}$ , at  $T = 298.15$  K:  $\times$ , this work;  $\bullet$ , ref 7.

K. Figure 3 shows that there is a good agreement between our data and those taken from ref 7.

A Redlich–Mayer-type equation<sup>8,9</sup> of the form

$$V_\phi = V_\phi^0 + S_v m_{ca}^{0.5} + B_v m_{ca} \quad (3)$$

was used to obtain  $V_\phi^0$ , the limiting apparent molar volume of tripotassium citrate at different temperatures and PPO 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  $V_\phi^0$ ,  $S_v$ , and  $B_v$  was expressed in polynomial form with  $(T - 288.15)$  K as a variable, as follows

$$V_\phi^0 = A^0 + A^1(T - 288.15) + A^2(T - 288.15)^2 \quad (4)$$

$$S_v = S_v^0 + S_v^1(T - 288.15) + S_v^2(T - 288.15)^2 \quad (5)$$

$$B_v = B_v^0 + B_v^1(T - 288.15) + B_v^2(T - 288.15)^2 \quad (6)$$

The coefficients of these equations at each PPO concentration obtained from the correlation of experimental data by the

**Table 1. Experimental Density,  $d/(g \cdot cm^{-3})$ , and Ultrasonic Velocity,  $u/(m \cdot s^{-1})$ , of  $K_3Cit$  in Aqueous PPO Solutions at Different Temperatures**

$m_{ca}$ mol·kg <sup>-1</sup>	T = 288.15 K		T = 293.15 K		T = 298.15 K		T = 303.15 K		T = 308.15 K		T = 313.15 K	
	$d$	$u$	$d$	$u$	$d$	$u$	$d$	$u$	$d$	$u$	$d$	$u$
	$m_p = 0.000 \text{ mol} \cdot \text{kg}^{-1}$											
0.0185	1.002985	1470.84	1.002055	1486.65	1.000869	1500.77	0.999449	1513.03	0.997814	1523.63	0.995982	1532.66
0.0304	1.005444	1473.36	1.004498	1489.14	1.003294	1503.17	1.001859	1515.37	1.000214	1525.92	0.998370	1534.88
0.0310	1.005554	1473.50	1.004607	1489.30	1.003402	1503.32	1.001966	1515.53	1.000320	1526.06	0.998478	1535.02
0.0558	1.010504	1478.63	1.009514	1494.30	1.008273	1508.14	1.006810	1520.21	1.005139	1530.62	1.003277	1539.47
0.0899	1.017350	1485.66	1.016305	1501.09	1.015017	1514.73	1.013517	1526.58	1.011812	1536.80	1.009924	1545.48
0.1258	1.024328	1493.78	1.023229	1508.97	1.021896	1522.43	1.020354	1534.12	1.018619	1544.21	1.016703	1552.75
0.1931	1.037252	1506.52	1.036058	1521.24	1.034645	1534.27	1.033034	1545.57	1.031241	1555.32	1.029275	1563.61
0.2653	1.050765	1519.92	1.049481	1534.20	1.047986	1546.75	1.046308	1557.71	1.044457	1567.09	1.042445	1575.01
0.3412	1.064508	1534.32	1.063129	1548.08	1.061560	1560.22	1.059818	1570.73	1.057912	1579.70	1.055859	1587.34
0.4565	1.084708	1556.72	1.083212	1569.72	1.081538	1581.18	1.079706	1591.14	1.077724	1599.68	1.075604	1606.89
0.5796	1.105191	1578.42	1.103584	1590.56	1.101814	1601.35	1.099898	1610.62	1.097847	1618.50	1.095668	1625.09
0.7446	1.131731	1608.14	1.129910	1619.39	1.128108	1629.25	1.126099	1637.71	1.123967	1644.87	1.121716	1650.80
	$m_p = 0.051 \text{ mol} \cdot \text{kg}^{-1}$											
0.0308	1.007224	1488.02	1.006212	1502.65	1.004947	1515.57	1.003456	1526.79	1.001755	1536.34	0.999862	1544.38
0.0681	1.014578	1495.63	1.013504	1510.03	1.012189	1522.75	1.010655	1533.71	1.008919	1543.05	1.006994	1550.90
0.0957	1.019901	1501.12	1.018787	1515.34	1.017437	1527.88	1.015876	1538.70	1.014113	1547.88	1.012168	1555.60
0.1295	1.026381	1507.56	1.025222	1521.59	1.023831	1533.92	1.022232	1544.56	1.020443	1553.61	1.018473	1561.21
0.1981	1.039219	1520.79	1.037965	1534.34	1.036495	1546.33	1.034829	1556.49	1.032982	1565.21	1.030969	1572.47
0.2651	1.051418	1533.36	1.050080	1546.48	1.048539	1557.99	1.046815	1567.88	1.044917	1576.26	1.042860	1583.23
0.3467	1.065830	1548.39	1.064401	1561.00	1.062782	1572.04	1.060993	1581.49	1.059040	1589.49	1.056933	1596.12
0.4719	1.087299	1570.99	1.085749	1582.80	1.084022	1593.14	1.082139	1602.02	1.080107	1609.47	1.077928	1615.53
0.5408	1.098683	1583.06	1.097067	1594.45	1.095290	1604.40	1.093361	1612.88	1.091288	1619.99	1.089002	1624.82
	$m_p = 0.104 \text{ mol} \cdot \text{kg}^{-1}$											
0.0261	1.007855	1500.10	1.006785	1513.79	1.005467	1525.73	1.003923	1535.98	1.002169	1544.61	1.000225	1551.75
0.0681	1.015973	1508.60	1.014838	1522.02	1.013466	1533.69	1.011875	1543.66	1.010085	1552.07	1.008107	1559.02
0.0991	1.021883	1514.73	1.020705	1527.86	1.019292	1539.30	1.017669	1549.08	1.015852	1557.33	1.013851	1564.14
0.1330	1.028203	1521.38	1.026979	1534.17	1.025527	1545.40	1.023872	1555.04	1.022025	1563.13	1.020001	1569.79
0.1968	1.039913	1532.90	1.038602	1545.46	1.037080	1556.65	1.035363	1565.65	1.033467	1573.41	1.031401	1579.76
0.2814	1.054941	1548.36	1.053532	1560.42	1.051924	1570.80	1.050135	1579.65	1.048176	1587.00	1.046056	1592.98
0.3545	1.067674	1561.46	1.066185	1572.88	1.064508	1582.88	1.062662	1591.32	1.060653	1598.31	1.058481	1603.88
0.4733	1.087454	1581.90	1.085852	1592.69	1.084080	1602.00	1.082149	1609.82	1.079997	1615.48	1.077487	1617.08
0.5805	1.104639	1600.24	1.102950	1610.34	1.101094	1619.05	1.098979	1624.91	1.096541	1627.18	1.094088	1629.45

**Table 2. Fitting Parameters of Equations 4, 5, and 6 for  $V_\phi$  and Equations 14, 15, and 16 for  $10^4 K_\phi$** 

system	$V_\phi$								
	parameters								
	$A^0$	$A^1$	$A^2$	$S_v^0$	$S_v^1$	$S_v^2$	$B_v^0$	$B_v^1$	$B_v^2$
$K_3cit + PPO(0.000 \text{ m}) + H_2O$	92.10834	0.372587	-0.005896	33.782335	-0.172118	0.005744	-11.204287	-0.000801	-0.003007
$K_3cit + PPO(0.051 \text{ m}) + H_2O$	94.617127	0.388741	-0.006103	27.931307	-0.208312	0.004987	-7.323984	-0.005335	-0.000801
$K_3cit + PPO(0.104 \text{ m}) + H_2O$	93.752477	0.53989	-0.008548	28.869024	-0.46834	0.00005	-6.24647	0.000468	0.015458
system	$10^4 K_\phi$								
	parameters								
	$A^0$	$A^1$	$A^2$	$S_k^0$	$S_k^1$	$S_k^2$	$B_k^0$	$B_k^1$	$B_k^2$
$K_3cit + PPO(0.000 \text{ m}) + H_2O$	-2.227749	0.054496	-0.001212	1.494385	-0.109082	0.003081	-0.470396	0.076797	-0.00231
$K_3cit + PPO(0.051 \text{ m}) + H_2O$	-2.039419	0.028059	-0.000455	1.14566	-0.027965	0.000689	-0.259086	0.013888	-0.000432
$K_3cit + PPO(0.104 \text{ m}) + H_2O$	-1.916951	0.025687	-0.000321	0.852259	-0.022444	0.000023	0.000488	0.006846	0.000494

simplex method are given in Table 2. The overall absolute relative percentage deviations of  $V_\phi$  for all temperatures are 0.39, 0.09, and 0.14, respectively, for  $K_3cit + PPO(0.000 \text{ m}) + H_2O$ ,  $K_3cit + PPO(0.051 \text{ m}) + H_2O$  and  $K_3cit + PPO(0.104 \text{ m}) + H_2O$  systems. The values of  $V_\phi^0$  at different temperatures and PPO concentrations calculated from eq 4 and the coefficients presented in Table 2 are given in Table 3. 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 being infinitely distant with other ions. It follows, therefore, that  $V_\phi^0$  is unaffected by ion + ion interaction and is a measure only of the ion + solvent interaction.<sup>10,11</sup> In Figure 4, the temperature and concentration dependence of  $V_\phi$  for  $K_3Cit$  in water has been given. The similar behavior has been obtained for  $V_\phi$  of  $K_3Cit$  in aqueous PPO solutions. From Figure 4, it can be seen that the apparent molar volumes of tripotassium citrate in water and in aqueous PPO

solutions increase with an increase in the salt molality. For the low concentrations of tripotassium citrate, the small volume of tripotassium 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  $V_\phi$  against salt concentration is attributed to these interactions. In the electrolyte solutions, the solute-solute interactions are characterized by positive slopes of  $V_\phi$  vs concentration plots.<sup>10</sup> This is attributed to the phenomenon, described in terms of destructive overlap of cospheres,<sup>12,13</sup> resulting in a net decrease of solvation, thereby increasing the solute volume. The effect of temperature on the  $V_\phi^0$  of tripotassium citrate in aqueous PPO solutions has been shown in Figure 5. As can be seen from Figure 5, the infinite dilution apparent molar volume of tripotassium citrate in aqueous PPO solutions increases with increasing temperature. In fact, the infinite dilution apparent molar volume is equal to the infinite

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

system	temperature					
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
			$V_{\phi}^0$			
K <sub>3</sub> cit + PPO(0.000 <i>m</i> ) + H <sub>2</sub> O	92.108	93.824	95.245	96.371	97.202	97.738
K <sub>3</sub> cit + PPO(0.051 <i>m</i> ) + H <sub>2</sub> O	94.617	96.408	97.894	99.075	99.951	100.521
K <sub>3</sub> cit + PPO(0.104 <i>m</i> ) + H <sub>2</sub> O	93.752	96.238	98.297	99.928	101.131	101.907
			$E_{\phi}^0$			
K <sub>3</sub> cit + PPO(0.000 <i>m</i> ) + H <sub>2</sub> O	0.373	0.314	0.255	0.196	0.137	0.078
K <sub>3</sub> cit + PPO(0.051 <i>m</i> ) + H <sub>2</sub> O	0.389	0.328	0.267	0.206	0.145	0.084
K <sub>3</sub> cit + PPO(0.104 <i>m</i> ) + H <sub>2</sub> O	0.540	0.454	0.369	0.283	0.198	0.112
			$K_{\phi}^0 10^4$			
K <sub>3</sub> cit + PPO(0.000 <i>m</i> ) + H <sub>2</sub> O	-2.2277	-1.9856	-1.8040	-1.6830	-1.6226	-1.6228
K <sub>3</sub> cit + PPO(0.051 <i>m</i> ) + H <sub>2</sub> O	-2.0394	-1.9105	-1.8043	-1.7209	-1.6602	-1.6223
K <sub>3</sub> cit + PPO(0.104 <i>m</i> ) + H <sub>2</sub> O	-1.9170	-1.7965	-1.6922	-1.6039	-1.5316	-1.4754

dilution partial molar volume; therefore, due to the additivity principle at infinite dilution, we have

$$V_{\phi}^0(\text{K}_3\text{Cit}) = 3V_{\phi}^0(\text{K}^+) + V_{\phi}^0(\text{Cit}^{3-}) \quad (7)$$

The infinite dilution apparent molar volume of ions can be expressed as the sum of two contributions<sup>14</sup>

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

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  $V_{\phi}^0$  by increasing temperature occurs with a loss of hydration. Also, as can be seen from Figure 4, the initial slopes of  $V_{\phi}^0$  against molality of tripotassium 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

$$E_{\phi}^0 = \left( \frac{\partial V_{\phi}^0}{\partial T} \right)_P = A^1 + 2A^2(T - 288.15) \quad (9)$$

The  $E_{\phi}^0$  values of tripotassium citrate at different temperatures and PPO concentrations are also given in Table 3. As mentioned above,  $E_{\phi}^0 = (\partial V_{\phi}^0(\text{elect})/\partial T)_P$ . From Table 3, we note that at each temperature  $E_{\phi}^0$  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 PPO solutions). In fact, the infinite dilution isobaric expansivity of solution (K<sub>3</sub>Cit + PPO + H<sub>2</sub>O) is greater than the isobaric expansivity of solvent (PPO + H<sub>2</sub>O).

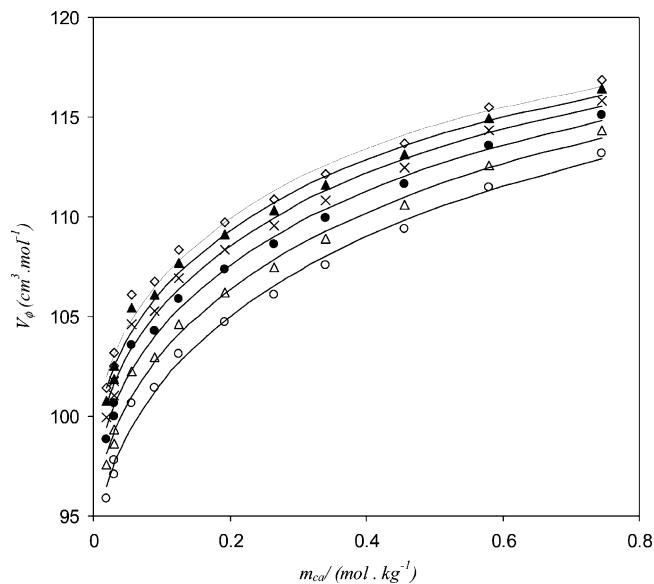
Figure 6 shows a positive transfer volume of K<sub>3</sub>Cit from an aqueous solution to an aqueous PPO solution. This indicates that the potassium citrate ions in aqueous PPO solutions are larger than those in aqueous solutions. As mentioned above, the ternary aqueous solution of PPO and tripotassium citrate separates into a PPO-rich phase and a salt-rich phase over part of the composition space. 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.<sup>15,16</sup> 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 polyether group of PPO especially in the presence of nonbonding cations like K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and Na<sup>+</sup>. Ananthapadmanabhan and Goddard,<sup>17</sup> 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 tripotassium citrate in aqueous PPO solutions. (1) The strong attractive interactions due to the hydrogen-bond formations between ether oxygen of the PPO chain and the water molecule induce the dehydration of ions and therefore increase the  $V_{\phi}$ . (2) Repulsive interactions between the anion and the anionic-like polyether group of PPO increase the apparent molar volume of tripotassium citrate.

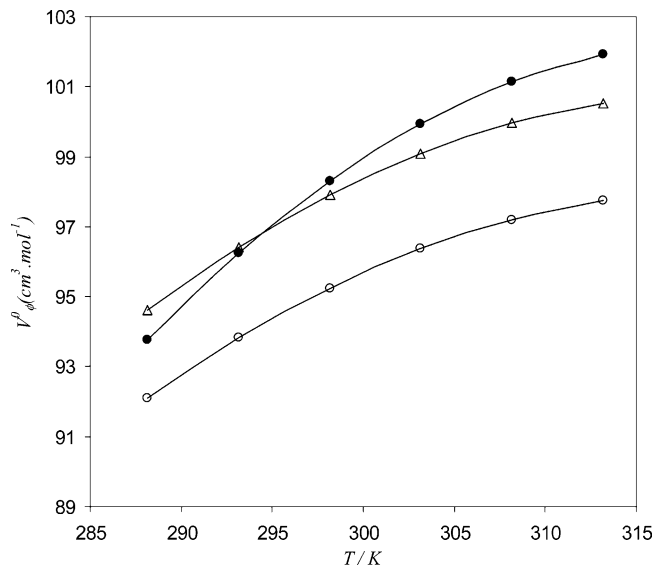
On the basis of the sound velocity and density values, the isentropic compressibility,  $\kappa_s$  (kPa<sup>-1</sup>), values were calculated for the investigated mixtures from Laplace-Newton's equation

$$\kappa_s = d^{-1}u^{-2} \quad (10)$$

where  $u$  (m·s<sup>-1</sup>) is sound velocity. The isentropic compressibility of all the solutions decreases with increasing concentration. As an example, in Figure 7, the isentropic compressibilities are plotted vs the molality of tripotassium citrate for binary aqueous solution of K<sub>3</sub>Cit. From Figure 7, we note that at each working temperature as the concentration of tripotassium citrate is increased  $\kappa_s$  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,<sup>14</sup> we can assume that the compressibility of a solution is mainly due to the effect of pressure on the bulk (unhydrated) water

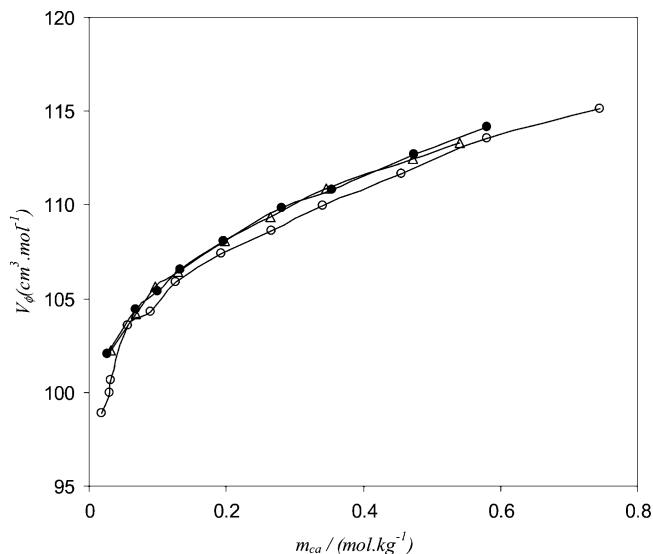


**Figure 4.** Plot of apparent molar volume of  $K_3Cit$ ,  $V_\phi$ , in water against molality of the salt,  $m_{ca}$ , at different temperatures:  $\circ$ ,  $T = 288.15$  K;  $\triangle$ ,  $T = 293.15$  K;  $\bullet$ ,  $T = 298.15$  K;  $\times$ ,  $T = 303.15$  K;  $\blacktriangle$ ,  $T = 308.15$  K;  $\diamond$ ,  $T = 313.15$  K; —, calculated by eqs 3 to 6.

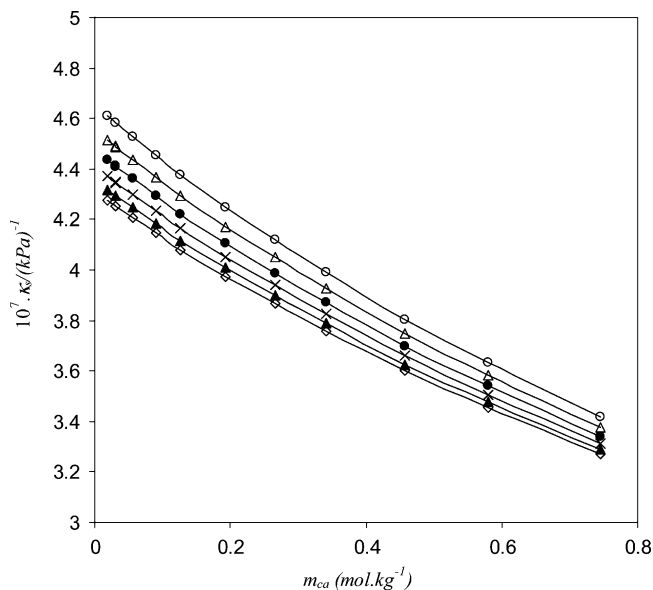


**Figure 5.** Plot of infinite dilution apparent molar volume of  $K_3Cit$ ,  $V_\phi^0$ , against temperature:  $\circ$ , in water;  $\triangle$ , in aqueous solution of  $0.051$  m PPO;  $\bullet$ , in aqueous solution of  $0.104$  m PPO.

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  $\kappa_s$  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<sup>14</sup> that for electrolytes with large hydration numbers, such as  $MgSO_4$  and  $Na_2SO_4$ , the concentration dependence of  $\kappa_s$  is more negative than that for electrolytes such as  $NaCl$  with small hydration numbers. The temperature dependence of  $\kappa_s$ ,  $\partial\kappa_s/\partial T$ , is also negative for all the solutions studied in this work. It has been shown<sup>18</sup> that the compressibility of water also decreases with temperature to a minimum  $\kappa_s$  value near  $319.15$  K. It has been postulated<sup>18</sup> 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



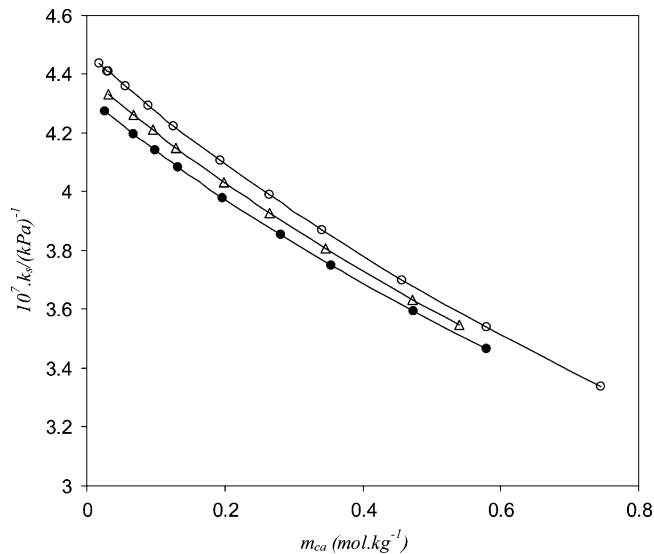
**Figure 6.** Plot of apparent molar volume of  $K_3Cit$ ,  $V_\phi$ , against molality of the salt,  $m_{ca}$ , at  $T = 298.15$  K:  $\circ$ , in water;  $\triangle$ , in aqueous solution of  $0.051$  m PPO;  $\bullet$ , in aqueous solution of  $0.104$  m PPO.



**Figure 7.** Plot of isentropic compressibility  $\kappa_s$ , of  $K_3Cit$  + water solutions against molality of the salt,  $m_{ca}$ , at different temperatures:  $\circ$ ,  $T = 288.15$  K;  $\triangle$ ,  $T = 293.15$  K;  $\bullet$ ,  $T = 298.15$  K;  $\times$ ,  $T = 303.15$  K;  $\blacktriangle$ ,  $T = 308.15$  K;  $\diamond$ ,  $T = 313.15$  K.

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  $K_3Cit$  + PPO solutions have a form similar to those of aqueous  $K_3Cit$  solutions.

In Figure 8, the values of  $\kappa_s$  are plotted as a function of salt concentration at various PPO concentrations at  $298.15$  K. Figure 8 shows that at each temperature at a constant salt concentration the values of  $\kappa_s$  decrease as the concentration of PPO increases. This effect can be attributed to the strong attractive interactions due to the hydration of polymer segments which decreases the amount of bulk water and also incorporation of ionic species into the PPO chain. In fact, as can be seen from Figure 8, at



**Figure 8.** Plot of isentropic compressibility against molality of the salt,  $m_{ca}$ , at  $T = 298.15$  K: ○, in water; Δ, in aqueous solution of  $0.051$  m PPO; ●, in aqueous solution of  $0.104$  m PPO.

each working temperature, as the concentration of PPO is increased,  $\kappa_s$  of the water + PPO 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  $K_\phi$  is defined as

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

The apparent molar isentropic compressibility of  $K_3Cit$ ,  $K_\phi$ , in water and in aqueous PPO solutions was computed from the density and sound velocity experimental data according to the following equation

$$K_\phi = \frac{1000 + m_p M_p (\kappa_s d_0 - \kappa_{s0} d)}{m_{ca} d d_0} + \frac{M_{ca} \kappa_s}{d} \quad (12)$$

where  $\kappa_s$  and  $\kappa_{s0}$  are the isentropic compressibility of the solution and solvent, respectively. For systems containing both tripotassium citrate and PPO, the PPO + water is considered as the solvent. An equation of the form<sup>19</sup>

$$K_\phi = K_\phi^0 + S_k m_{ca}^{0.5} + B_k m_{ca} \quad (13)$$

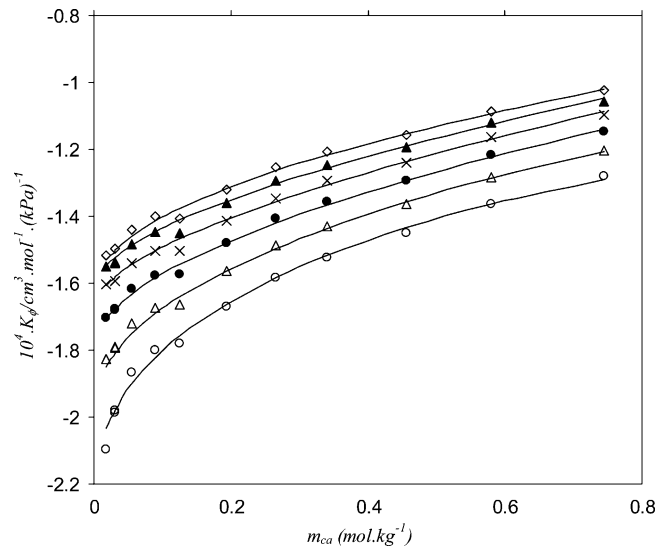
was used for correlating the experimental apparent molar isentropic compressibility data. Similar to the apparent molar volume, the temperature dependence of  $K_\phi^0$ ,  $S_k$ , and  $B_k$  was expressed in polynomial form with  $(T - 288.15)$  K as a variable, as follows

$$K_\phi^0 = A^0 + A^1(T - 288.15) + A^2(T - 288.15)^2 \quad (14)$$

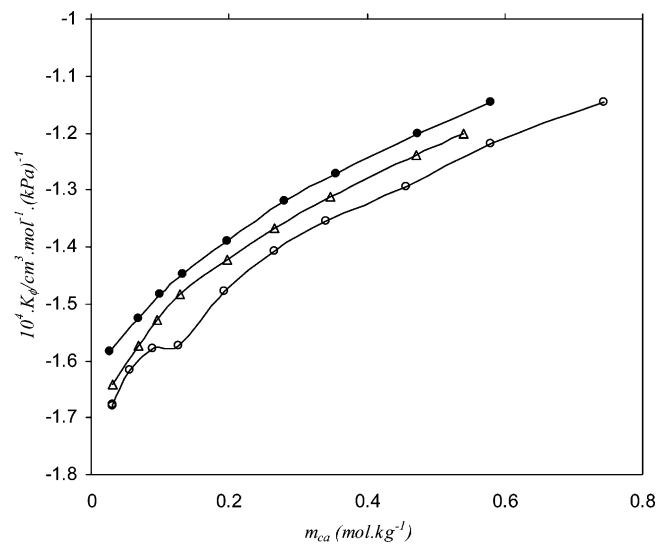
$$S_k = S_k^0 + S_k^1(T - 288.15) + S_k^2(T - 288.15)^2 \quad (15)$$

$$B_k = B_k^0 + B_k^1(T - 288.15) + B_k^2(T - 288.15)^2 \quad (16)$$

The coefficients of these equations for  $10^4 K_\phi$  at each temperature and PPO concentrations are also given in Table 2. The values of the  $K_\phi^0$  at different temperatures and PPO concentrations calculated from eq 14 and the coefficients presented in Table 2 are also given in Table 3. In Figure 9, the temperature and concentration dependence of  $K_\phi$  have been



**Figure 9.** Plot of apparent molar isentropic compressibility of  $K_3Cit$ ,  $K_\phi$ , in water against molality of the salt,  $m_{ca}$ , at different temperatures: ○,  $T = 288.15$  K; Δ,  $T = 293.15$  K; ●,  $T = 298.15$  K; ×,  $T = 303.15$  K; ▲,  $T = 308.15$  K; ◇,  $T = 313.15$  K; —, calculated by eqs 13 to 16.



**Figure 10.** Plot of apparent molar isentropic compressibility of  $K_3Cit$ ,  $K_\phi$ , against molality of the salt,  $m_{ca}$ , at  $T = 298.15$  K: ○, in water; Δ, in aqueous solution of  $0.051$  m PPO; ●, in aqueous solution of  $0.104$  m PPO.

given for  $K_3Cit$  + water solutions. From Figure 9, it can be seen that the value of apparent molar isentropic compressibility of tripotassium citrate in water (and also in PPO solutions) is negative, and it increases with increasing concentration of tripotassium citrate and temperature. As can be seen from Table 3,  $K_\phi^0$  values are negative, and they increase with increasing temperature and PPO concentration. The negative values of  $K_\phi$  and  $K_\phi^0$  of tripotassium citrate in aqueous PPO solutions indicate that the water molecules around the tripotassium citrate ions are less compressible than the water molecules in the bulk solution. By differentiating eq 8 with respect to pressure, we obtain

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

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  $K_{\phi}^0(\text{int})$  to be positive and close to zero.<sup>20</sup> Thus  $K_{\phi}^0(\text{ion})$  is due mainly to  $K_{\phi}^0(\text{elect})$ . In fact, the negative values of  $K_{\phi}$  and  $K_{\phi}^0$  of tripotassium citrate in aqueous PPO solutions is 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 potassium citrate become more compressible than those at lower temperatures.

In Figure 10, the values of  $K_{\phi}$  are plotted as a function of salt concentration at various PPO concentrations at 298.15 K. Figure 10 shows that at each temperature at a constant salt concentration the value of  $K_{\phi}$  of tripotassium citrate increases as the concentration of PPO increases. The strong hydrogen-bond interactions between ether oxygen of the PPO chain and water molecule induce the dehydration of ions, and therefore at high PPO concentrations, the water molecules around the potassium citrate become more compressible than those at lower PPO concentrations.

### Conclusions

Experimental data at  $T = (288.15 \text{ to } 313.15) \text{ K}$  of density and sound velocity of tripotassium citrate in water and in water + PPO 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 tripotassium citrate from an aqueous solution to an aqueous PPO solution. Also, the results show that the apparent molar volumes of tripotassium citrate increase as the concentration of potassium citrate increases. The apparent molar isentropic compressibility of tripotassium citrate in both binary and ternary solutions has negative values at each temperature. The negative values of apparent molar isentropic compressibility of tripotassium citrate imply that the water molecules around the tripotassium citrate ions are less compressible than the water molecules in the bulk solutions.

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