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Effect of sodium phosphate salts on the thermodynamic properties of aqueous solutions of poly(ethylene oxide) 6000 at different temperatures

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ABSTRACT

Precise density, sound velocity, water activity, and phase diagram measurements have been carried out on polyethylene oxide (PEO) in aqueous solutions of sodium di-hydrogen phosphate, di-sodium hydrogen phosphate, and tri-sodium phosphate over a range of temperatures at atmospheric pressure. The experimental density and sound velocity data are used to calculate the apparent specific volume and isentropic compressibility as a function of temperature and concentration. It was found that both of the apparent specific volume and isentropic compressibility of PEO in aqueous solutions increase by increasing temperature and charge on the anion of electrolytes. The results show that the slope of constant water activity lines increased with increasing the temperature and charge on the anion of electrolytes and the vapour pressure depression for an aqueous (PEO + sodium phosphate) system is more than the sum of those for the corresponding binary solutions. Furthermore, the effect of temperature and type of anion of salt on the salting-out effect of polyethylene oxide by sodium phosphate salts has been studied.

1. Introduction

It has long been recognized that the mixture of aqueous solutions of two mutually incompatible water-soluble polymers (for instance, polyethylene oxide (PEO) and dextran) or one polymer and one inorganic salt (for instance, PEO and sodium phosphate) forms a stable two-phase liquid system, where the only solvent is water. This phenomenon was first reported by Beijerinck a century ago, but these systems have only started to receive greater attention after Albertson's proposition for their use in bioseparation processes [1] in the late 1950s. Since then, considerable effort has been devoted to the compilation of phase equilibrium data on these aqueous two-phase systems and on their application to purification of a variety of biomolecules. Most of these results have been thoroughly reviewed elsewhere [2,3]. Ternary aqueous solutions of sodium phosphate salts and polyethylene oxide (PEO) separate into a sodium phosphate-rich and a PEO-rich phase over part of the composition space [4]. Aqueous two-phase systems of this nature can also be useful for the separation and purification of biomaterials where the employment of a non-polar solvent/aqueous phase system would lead to degradation of biological activity. Tanuja *et al.* have applied aqueous (PEO + sodium phosphate) two-phase system for real protein separation processes [5].

This work presents the results of a comprehensive study of the apparent specific volume, ϕ_V, and apparent specific isentropic compressibility, ϕ_K, of PEO in aqueous solutions of (0.000 and 0.144) mol · kg^{-1} sodium di-hydrogen phosphate (NaH_2PO_4), di-sodium hydrogen phosphate (Na_2HPO_4), and tri-sodium phosphate (Na_3PO_4) at T = (293.15, 298.15, and 303.15) K; this work also presents (vapour + liquid) equilibrium behaviour of ternary (PEO + NaH_2PO_4 + H_2O, PEO + Na_2HPO_4 + H_2O, and PEO + Na_3PO_4 + H_2O) solutions at T = (298.15 and 308.15) K and (liquid + liquid) equilibria of these ternary systems at T = (298.15, 303.15, 308.15, 313.15, and 318.15) K. Although the effect of anion charge of electrolytes on the salting-out effect of polyethylene oxide by electrolytes has been studied [4,6,7], however, as far as we know there are no reports about the effect of charge on the anion on the volumetric and (vapour + liquid) equilibrium behaviour of PEO in aqueous solutions in the literature.

2. Experimental

2.1. Materials

Sodium di-hydrogen phosphate, di-sodium hydrogen phosphate, tri-sodium phosphate, sodium chloride, and polyethylene oxide were obtained from Merck. PEO had a nominal molecular mass of 6000. The manufacturer has characterized this polymer with charge/lot number S35317 203. The polymer and salts were

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TABLE 1
Experimental density $d/(g \cdot cm^{-3})$ and ultrasonic velocity $u/(m \cdot s^{-1})$ of PEO in aqueous solutions of sodium phosphate at different temperatures

m_{wp}	T = 293.15 K		T = 298.15 K		T = 303.15 K	
	$d/(g \cdot cm^{-3})$	$u/(m \cdot s^{-1})$	$d/(g \cdot cm^{-3})$	$u/(m \cdot s^{-1})$	$d/(g \cdot cm^{-3})$	$u/(m \cdot s^{-1})$
			In water			
0.0040	0.998872	1485.03	0.997696	1499.07	0.996283	1511.30
0.0082	0.999558	1487.46	0.998369	1501.30	0.996943	1513.33
0.0123	1.000229	1489.82	0.999024	1503.46	0.997587	1515.34
0.0204	1.001547	1494.42	1.000318	1507.71	0.998854	1519.28
0.0253	1.002333	1497.22	1.001084	1510.36	0.999608	1521.66
0.0310	1.003262	1500.44	1.001995	1513.25	1.000497	1524.39
0.0363	1.004092	1503.43	1.002802	1516.13	1.001290	1527.03
0.0417	1.004959	1506.39	1.003650	1518.77	1.002119	1529.49
0.0472	1.005795	1509.38	1.004472	1521.62	1.002926	1532.04
0.0527	1.006657	1512.42	1.005317	1524.35	1.003752	1534.62
0.0636	1.008330	1518.48	1.006951	1529.99	1.005354	1539.71
0.0752	1.010067	1524.58	1.008654	1535.52	1.007022	1544.88
0.0869	1.011810	1530.95	1.010353	1541.44	1.008689	1550.24
0.1109	1.015271	1543.47	1.013737	1552.89	1.011997	1560.84
0.1361	1.018795	1556.50	1.017178	1564.90	1.015366	1571.77
0.1761	1.024134	1576.08	1.022393	1582.77	1.020460	1588.16
0.2195	1.029612	1596.30	1.027734	1601.28	1.025680	1604.99
0.2480	1.033010	1608.88	1.031048	1612.70	1.028913	1615.44
			In aqueous solutions of 0.144 m NaH_2PO_4			
0.0100	1.013419	1504.60	1.012100	1517.83	1.010575	1529.22
0.0122	1.013752	1505.77	1.012431	1518.84	1.010892	1530.23
0.0150	1.014189	1507.47	1.012857	1520.48	1.011312	1531.63
0.0204	1.014998	1510.43	1.013650	1523.16	1.012086	1534.20
0.0257	1.015805	1513.52	1.014437	1526.07	1.012858	1536.79
0.0307	1.016564	1516.34	1.015181	1528.60	1.013586	1539.21
0.0362	1.017362	1519.27	1.015961	1531.37	1.014356	1541.60
0.0415	1.018152	1522.25	1.016733	1534.02	1.015106	1544.18
0.0472	1.018967	1525.40	1.017529	1537.00	1.015888	1546.84
0.0525	1.019754	1528.38	1.018302	1539.69	1.016643	1549.38
0.0637	1.021354	1534.51	1.019864	1545.37	1.018172	1554.54
0.0752	1.022982	1540.64	1.021458	1550.96	1.019730	1559.75
0.0873	1.024661	1547.13	1.023096	1556.98	1.021335	1565.18
0.1109	1.027840	1559.36	1.026202	1568.12	1.024369	1575.44
0.1363	1.031149	1572.15	1.029427	1579.87	1.027523	1586.17
0.1760	1.036109	1591.25	1.034272	1597.30	1.032252	1602.11
0.2193	1.041212	1610.86	1.039239	1615.24	1.037108	1618.40
0.2499	1.044674	1624.05	1.042610	1627.24	1.040393	1629.35
			In aqueous solutions of 0.144 m Na_2HPO_4			
0.0079	1.019158	1513.29	1.017776	1526.37	1.016185	1537.72
0.0306	1.022490	1526.27	1.021033	1538.28	1.019376	1548.64
0.0359	1.023243	1529.29	1.021770	1541.12	1.020098	1551.18
0.0462	1.024724	1535.15	1.023218	1546.51	1.021517	1556.15
0.0528	1.025634	1538.53	1.024110	1549.56	1.022387	1559.02
0.0642	1.027225	1545.25	1.025662	1555.85	1.023911	1564.73
0.0747	1.028641	1550.39	1.027048	1560.45	1.025263	1568.98
0.0862	1.030168	1556.46	1.028538	1566.07	1.026722	1574.02
0.1106	1.033343	1568.91	1.031639	1577.43	1.029753	1584.49
0.1361	1.036549	1581.66	1.034769	1589.10	1.032815	1595.07
0.1720	1.040866	1598.70	1.038980	1604.60	1.036922	1609.26
0.2168	1.045967	1618.73	1.043949	1622.90	1.041772	1625.85
0.2506	1.049612	1632.87	1.047500	1635.70	1.045232	1637.50
			In aqueous solutions of 0.144 m Na_3PO_4			
0.0081	1.027814	1524.03	1.026342	1536.86	1.024672	1547.98
0.0100	1.028101	1525.25	1.026616	1538.05	1.024933	1549.00
0.0151	1.028816	1528.13	1.027315	1540.69	1.025620	1551.40
0.0201	1.029514	1530.95	1.028003	1543.21	1.026297	1553.81
0.0315	1.031092	1537.29	1.029546	1549.03	1.027807	1559.16
0.0362	1.031749	1540.06	1.030184	1551.67	1.028431	1561.53
0.0419	1.032506	1543.13	1.030927	1554.40	1.029163	1564.23
0.0478	1.033308	1546.45	1.031711	1557.52	1.029921	1566.86
0.0525	1.033938	1549.01	1.032328	1559.80	1.030530	1569.02
0.0638	1.035420	1555.14	1.033774	1565.49	1.031943	1574.13
0.0739	1.036696	1560.41	1.035023	1570.21	1.033168	1578.50
0.0865	1.038326	1567.13	1.036611	1576.41	1.034718	1584.13
0.1105	1.041295	1579.27	1.039518	1587.45	1.037561	1594.23
0.1331	1.043989	1590.39	1.042138	1597.65	1.040119	1603.46
0.1752	1.048798	1610.03	1.046833	1615.45	1.044702	1619.68
0.2194	1.053533	1629.14	1.051437	1632.88	1.049186	1635.43
0.2491	1.056582	1641.30	1.054411	1643.86	1.052086	1645.38