Original Article

Thermodynamics of Mixed Electrolyte solutions: An EMF study of Activity and Osmotic coefficients of NaCl in NaCl-$Ca(NO_3)_2$-H_2O system at 25, 35 and 450C

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Abstract

Electromotive force measurements have been carried out on the system NaCl-Ca(NO3)2-H2O at I = 0.5,1.0, 2.0 and 3.0 mol kg-1 and at 25, 35 and 45oC using a cell consisting of sodium ion-selective electrode and an Ag/AgCl electrode. The data are analysed using the Pitzer and Harned equations. The osmotic coefficients, activity coefficients of Ca (NO3)2 and excess free energies of the aqueous mixtures have been estimated at 25oC.Pitzer formulism made use to describe the properties of concentrated electrolyte mixtures.

Keywords: Activity coefficient, osmotic coefficients, Pitzer parameters, emf.

INTRODUCTION

Aqueous electrolyte solutions and their thermodynamic properties play an important role in understanding the behavior of water from different sources which are useful in several fields1. However, the ternary mixtures of aqueous alkali metal halides with alkaline earth metal nitrates have not received much attention. Xu et al.2 Estimated the activity coefficients of NaCl in the systems NaCl-Mg(NO3)2-H2O, NaCl-Ca(NO3)2-H2O, NaCl-Sr(NO3)2-H2O at 25o. However, we could not find much work in the literature on the activity and osmotic coefficient data of the system NaCl-Ca(NO3)2-H2O at 35 and 450C. Hence, in the present study the mean ionic activity coefficients of aqueous NaCl solutions in the systems NaCl-Ca(NO3)2-H2O were estimated at 25, 35 and 45o and at total ionic strengths of 0.5, 1.0, 2.0 and 3.0 mol kg-1 using emf studies3-5

Experimental

The cell consisted of Na-ion selective electrode (Elico, ENA) and an Ag/AgCl electrode 12 immersed in a mixture of aqueous NaCl and Ca(NO3)2 solution placed in a double-walled glass vessel whose temperature was maintained within ±0.01oC. The cell arrangement was

Na	NaCl (m_A)	Ag/AgCl
Ion-selective	+SSS	
Electrode	$Ca(NO_3)_2$ (m_B)	electrode

Deionised, double-distilled water was used for preparation of all stock solutions. Analytical grade sodium chloride (Merck) and Ca(NO3)2 calcium nitrate (s.d.chem.) were used without further purification and drying. The stock solutions of NaCl were standardized volumetrically. AgNO3 and Ca(NO3)2 solutions were standardized volumetrically using EDTA. All solutions were prepared by weight. Also all titrations and dilutions were made using weight burettes. The electrodes were connected to a high-impedence (≈1012Ω) unit gain amplifier. The output of this amplifier was measured by a Keithley DMM 191 electrometer/multimeter. The accuracy of the emf measurements was up to 0.01 mV.

The electrodes were first standardized at each of the ionic strengths studied. At every ionic strength a set of four experiments was carried out. In the first set, NaCl solution was taken in a double-walled glass cell and conductance water was added in successive aliquots. The potential difference was noted after each addition and equilibration. This set of results was used to calibrate the electrodes. In the second set, NaCl solution was taken in the cell and Ca(NO3)2 solution was added in successive aliquots. The third set was made by starting with Ca(NO3)2 solution and adding NaCl solution in aliquots. The overlapping portion between the second and third sets was used to test the reproducibility and accuracy of the measurements. In the fourth set, Ca(NO3)2 solution was taken in the cell and the emfs were noted after adding conductance water in aliquots. This set of results was used to calculated the selectivity coefficient of Na-Ion-selective electrode toward Ca2+ ion in Ca(NO3)2 solution. The solubility of Ca(NO3)2 in water is low (0.391 M at 250). Therefore, the experiments could be carried out up to a maximum ionic strength of 3.0 mol kg-1 only

Results and Discussion

The emfs of sodium ion-selective electrode vs Ag/AgCl electrode in NaCl-Ca(NO3)2-H2O system are given by the equation

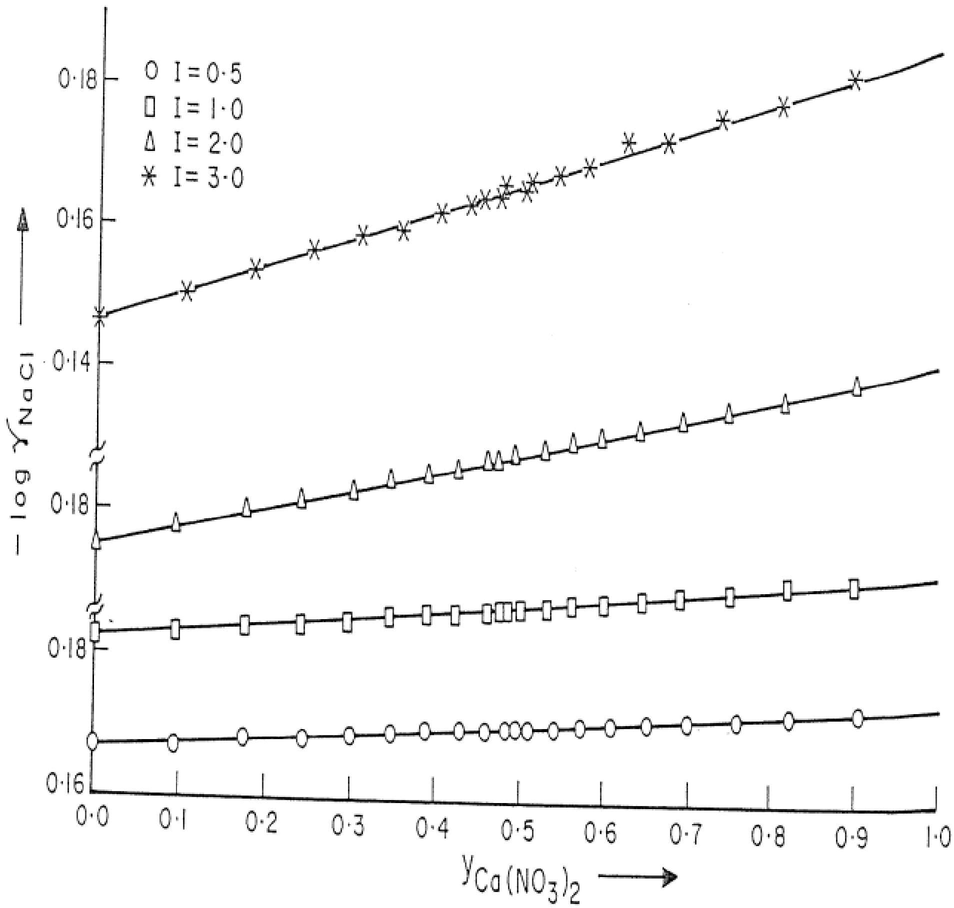
$$E = E_o + k \log (a_{Na} a_{Cl} + K a^{1/2}_{Ca}\, a_{Cl}) \quad (1)$$

Where, k = (RT/F)ln10 which is the Nernst slope and Eo is the emf due to the sodium chloride solution at unit activity. The selectivity coefficient (K) values were in the range 10-5 to 10-4 at the ionic strengths studied, and hence Ka1/2Ca, aCl term in eqn. (1) could be neglected. As aNa = (mA+2mB)γ+ and aCl= mAγ-, eqn. (1) could be rearranged as

$$\gamma^2_{\pm} = [1/(m_{Na} m_{Cl})]\ 10^{(E-Eo)/k} \quad (2)$$

Hence the mean activity coefficients (γ±) of NaCl could be determined by substituting the emfs of the cell with NaCl + Ca(NO3)2 mixture, i.e. E in eqn. (2). The experimental mean ionic activity coefficients of NaCl in aqueous NaCl + Ca(NO3)2 system were determined at I = 0.5, 1.0, 2.0, and 3.0mol kg-1 and at 25, 35 and 45oC and are listed in Table 1, at different values of the ionic strength fractions (yB) of Ca(NO3)2, where yB = 3mB/(mA + 3mB). The plots of log γNaCl VS yCa(NO3)2 at all the ionic strengths studied are shown in Fig.1.

Figure-1



Activity Coefficients of NaCl in NaCl-Ca$(NO_3)_2$-H_2O System at 25°C

Table 1-Mean Activity coefficient of NaCl in the NaCl-Ca$(NO_3)_2$-H_2O system

I = 0.5		I = 1.0		I = 2.0		I = 3.0	
$y_{Ca(NO3)2}$	$-\log\Upsilon_{NaCl}$	$y_{Ca(NO3)2}$	$-\log\Upsilon_{NaCl}$	$y_{Ca(NO3)2}$	$-\log\Upsilon_{NaCl}$	$y_{Ca(NO3)2}$	$-\log\Upsilon_{NaCl}$
Temp. = 25° C							
0.0965	0.1673	0.0953	0.1828	0.0958	0.1778	0.9996	0.1505
0.1760	0.1679	0.1741	0.1836	0.1749	0.1799	0.1811	0.1538
0.2427	0.1684	0.2402	0.1840	0.2412	0.1815	0.2491	0.1565
0.2994	0.1690	0.2965	0.1847	0.2977	0.1830	0.3067	0.1587
0.3482	0.1693	0.3451	0.1852	0.3463	0.1843	0.3560	0.1606
0.3906	0.1698	0.3874	0.1859	0.3887	0.1855	0.3989	0.1624
0.4278	0.1698	0.4245	0.1860	0.4259	0.1865	0.4363	0.1638
0.4608	0.1700	0.4574	0.1863	0.4588	0.1874	0.4486	0.1643
0.4837	0.1700	0.4732	0.1864	0.4697	0.1875	0.4694	0.1650

0.4902	0.1703	0.4868	0.1868	0.4882	0.1880	0.4747	0.1663
0.5101	0.1700	0.4995	0.1867	0.4960	0.1882	0.4988	0.1662
0.5394	0.1702	0.5289	0.1870	0.5254	0.1890	0.5042	0.1668
0.5724	0.1705	0.5620	0.1874	0.5585	0.1900	0.5375	0.1678
0.6096	0.1708	0.5995	0.1878	0.5961	0.1909	0.5755	0.1692
0.6521	0.1709	0.6424	0.1882	0.6392	0.1919	0.6193	0.1710
0.7008	0.1713	0.6919	0.1888	0.6889	0.1934	0.6704	0.1730
0.7575	0.1717	0.7496	0.1894	0.7470	0.1948	0.7306	0.1757
0.8241	0.1724	0.8180	0.1905	0.8158	0.1966	0.8027	0.1784
0.9036	0.1730	0.8998	0.1908	0.8985	0.1991	0.8905	0.1819

Temp. = 35° C

0.5000	0.1678	0.0944	0.1818	0.0967	0.1722	0.0986	0.1450
0.1715	0.1682	0.1726	0.1824	0.1764	0.1730	0.1796	0.1483
0.2370	0.1690	0.2383	0.1829	0.2431	0.1738	0.2471	0.1509
0.2928	0.1695	0.2944	0.1832	0.2998	0.1745	0.3045	0.1535
0.3411	0.1698	0.3427	0.1835	0.3487	0.1750	0.3536	0.1555
0.3831	0.1703	0.3849	0.1839	0.3911	0.1755	0.3963	0.1570
0.4202	0.1704	0.4220	0.1841	0.4284	0.1760	0.4337	0.1588
0.4530	0.1708	0.4548	0.1842	0.4614	0.1763	0.4512	0.1595
0.4823	0.1711	0.4706	0.1840	0.4645	0.1762	0.4668	0.1600
0.4863	0.1709	0.4842	0.1845	0.4907	0.1768	0.4774	0.1607
0.5127	0.1710	0.4969	0.1842	0.4908	0.1767	0.4962	0.1612
0.5420	0.1713	0.5263	0.1845	0.5203	0.1770	0.5068	0.1615
0.5749	0.1719	0.5594	0.1848	0.5535	0.1772	0.5401	0.1630
0.6121	0.1719	0.5970	0.1850	0.5912	0.1778	0.5781	0.1648
0.6544	0.1725	0.6400	0.1853	0.6344	0.1782	0.6218	0.1662
0.7030	0.1730	0.6896	0.1856	0.6844	0.1788	0.6727	0.1685
0.7594	0.1732	0.7476	0.1867	0.7431	0.1798	0.7326	0.1710
0.8256	0.1740	0.8163	0.1868	0.8127	0.1802	0.8043	0.1750
0.9045	0.1742	0.8989	0.1874	0.8966	0.1812	0.8915	0.1774

Table 1 - Activity coefficient of NaCl in the NaCl-$Ca(NO_3)_2$-H_2O system

I = 0.5		I = 1.0		I = 2.0		I = 3.0	
$y_{Ca(NO3)2}$	$-\log \Upsilon_{NaCl}$	$y_{Ca(NO3)2}$	$-\log \Upsilon_{NaCl}$	$y_{Ca(NO3)2}$	$-\log \Upsilon_{NaCl}$	$y_{Ca(NO3)2}$	$-\log \Upsilon_{NaCl}$
Temp. = 45°C							
0.0984	0.1697	0.0953	0.1825	0.0995	0.1728	0.0959	0.1454
0.1792	0.1701	0.1741	0.1835	0.1810	0.1750	0.1751	0.1516
0.2467	0.1711	0.2402	0.1844	0.2489	0.1768	0.2415	0.1562
0.3039	0.1721	0.2965	0.1851	0.3065	0.1782	0.2980	0.1606
0.3530	0.1726	0.3451	0.1858	0.3558	0.1798	0.3466	0.1637
0.3957	0.1732	0.3874	0.1862	0.3986	0.1808	0.3890	0.1672
0.4331	0.1737	0.4245	0.1868	0.4361	0.1818	0.4262	0.1698
0.4661	0.1740	0.4574	0.1872	0.4593	0.1828	0.4563	0.1722
0.4863	0.1741	0.4810	0.1874	0.4692	0.1828	0.4591	0.1723
0.4955	0.1753	0.4868	0.1875	0.4856	0.1833	0.4825	0.1740
0.5127	0.1744	0.5073	0.1877	0.4986	0.1848	0.4885	0.1745
0.5420	0.1748	0.5367	0.1882	0.5150	0.1842	0.5119	0.1763

0.5749	0.1753	0.5697	0.1886	0.5482	0.1853	0.5452	0.1788
0.6121	0.1757	0.6070	0.1890	0.5861	0.1862	0.5831	0.1816
0.6544	0.1762	0.6495	0.1896	0.6295	0.1875	0.6266	0.1845
0.7030	0.1770	0.6985	0.1900	0.6799	0.1888	0.6772	0.1885
0.7594	0.1776	0.7554	0.1910	0.7390	0.1905	0.7366	0.1930
0.8256	0.1785	0.8225	0.1919	0.8094	0.1925	0.8075	0.1990
0.9045	0.1790	0.9026	0.1929	0.8947	0.1949	0.8935	0.2052

These γ± values at each ionic strength and all the temperatures studied were fitted to the Harned equation6,

$$\log \gamma_A = \log \gamma^0_A - \alpha_{AB}\, y_B \qquad (3)$$

Where, γoA is the activity coefficient of pure NaCl solution at the same ionic strength as the mixture.ThelogγA vsγBplots are strait lines. The resulting Harned coefficient (αAB) values are listed in Table 2. The activity coefficient data at 25o were further analysed using the Pitzer equations7,8

Table 2 - Harned Coefficients for the NaCl-$Ca(NO_3)_2$-H_2O System

I/mol.kg^{-1}	**logΥ^o_A**	**α_{AB}**	**RMSDx10^4**
	T = 25ºC		
0.5	-0.1667	-0.0068	1.816
1.0	-0.1823	-0.0092	2.692
2.0	-0.1749	-0.0269	1.468
3.0	-0.1465	-0.0397	2.379
	T = 35ºC		
0.5	-0.1671	-0.0081	1.47
1.0	-0.1811	-0.0068	1.93
2.0	-0.1710	-0.0115	1.003
3.0	-0.1409	-0.0412	2.602
	T = 45ºC		
0.5	-0.1686	-0.0117	2.816
1.0	-0.1816	-0.0123	1.359
2.0	-0.1699	-0.0279	2.523
3.0	-0.1389	-0.0733	3.760

Table3- Osmotic coefficients in NaCl-$Ca(NO_3)_2$-H_2O at 25ºC

y_B	**I = 0.5**	**I = 1.0**	**I = 2.0**	**I = 3.0**
1.0	0.8472	0.8399	0.8413	0.8579
0.9	0.8592	0.8562	0.8662	0.8898
0.8	0.8695	0.8698	0.8865	0.9153
0.7	0.8785	0.8815	0.9035	0.9364
0.6	0.8864	0.8917	0.9182	0.9546

0.5	0.8936	0.9008	0.9311	0.9708
0.4	0.9001	0.9090	0.9427	0.9859
0.3	0.9061	0.9165	0.9536	1.0004
0.2	0.9117	0.9235	0.9039	1.0148
0.1	0.9170	0.9301	0.9739	1.0294
0.0	0.9220	0.9363	0.9839	1.0446

in order to avoid the precipitation of salts after the addition of NaCl solution.

$$Ln\gamma_M = Z^2_M F + \Sigma_a m_a (2B_{Ma} + ZC_{Ma}) + \Sigma_c m_c (2\theta_{Mc} + \Sigma_{ma}\Psi_{Mca}) + \Sigma\Sigma_{a<a'} m_a m_{a'} \Psi_{Maa'} + |Z_M| \Sigma_c \Sigma_a m_c m_a C_{ca} \quad (4)$$

$$Ln\gamma X = Z^2_X F + \Sigma_C m_C (2B_{cX} + ZC_{cX}) + \Sigma_a m_a (2\theta_{Xa} + \Sigma m_c \Psi_C Xa) + \Sigma\Sigma_{C<C'} m_C m_{C'} \Psi_{CC'X} + |Z_X| \Sigma_c \Sigma_a m_c m_a C_{ca} \quad (5)$$

where, $F = -A_\phi \left(\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b} \ln(1+bI^{1/2}) \right) + \Sigma_c \Sigma_a m_c m_a B'_{ca} + \Sigma\Sigma_{C<C'} m_C m_{C'} \theta'_{CC'} + \Sigma\Sigma_{a<a'} m_a m_{a'} \theta'_{aa'}$ (6)

$$B_{ca} = \beta^o_{ca} + \beta^1_{ca}\, g(\alpha I^{1/2})$$

$$B'_{ca} = \beta^1_{ca}\, g'(\alpha I^{1/2})/I$$

$$\theta_{ij} = {}^s\theta_{ij} + {}^E\theta_{ij}(I) \quad (7)$$

Where all other symbols have their usual significance.

The Pitzer coefficients at 25oCfor the pure salts are taken from the literature 4,8,9 and listed below:

$\beta^0_{NaCl}=0.075373, \beta^1_{NaCl} = 0.277031, C^\phi_{NaCl} = 0.001407$

$\beta^0_{Ca(NO3)2}=0.17030, \beta^1_{Ca(NO3)2}=2.021, C^\phi_{Ca(NO3)2} = -0.0069$

$\beta^0_{CaCl2} = 0.30534, \beta^1_{CaCl2} = 1.7083, C^\phi_{CaCl2} = 0.002153$

$\beta^0_{NaNO3} = 0.0068, \beta^1_{NaNO3} = 0.1783, C^\phi_{NaNO3} = -0.00072$

The values of the Pitzer mixing parameters are given below 5,10

$S_{\theta NaCa}=0.070$ $S_{\theta ClNO3} = 0.0164$

$\psi_{NaCaCl} = -0.014$ $\psi_{NaCaNO3} = -0.004$

$\psi_{ClNO3Na} = -0.076$ $\psi_{ClNO3Ca} = -0.017$

These Pitzer parameters were used to calculated the osmotic coefficients of the NaCl-Ca(NO3)2-H2O system and the results are listed in Table 3. The activity coefficients of Ca(NO3)2 in this system at 25oC were also calculated and the values are given the Table 4.

Table 4 - Mean Activity Coefficients of $Ca(NO_3)_2$ in the System

$NaCl$-$Ca(NO_3)_2$-H_2O at 25°C

I = 0.5		I = 1.0		I = 2.0		I = 3.0	
y_B	-log ϒ	y_B	-log ϒ	y_B	-log ϒ	y_B	-log ϒ
0.0000	0.3440	0.0000	0.3858	0.0000	0.4041	0.0000	0.3929
0.0965	0.3335	0.0953	0.3725	0.0958	0.3876	0.0996	0.3735
0.1760	0.3262	0.1741	0.3635	0.1749	0.3770	0.1811	0.3614
0.2427	0.3209	0.2402	0.3571	0.2412	0.3700	0.2491	0.3541
0.2994	0.3170	0.2965	0.3526	0.2977	0.3653	0.3067	0.3498
0.3482	0.3142	0.3451	0.3494	0.3463	0.3624	0.3560	0.3476
0.3906	0.3121	0.3874	0.3472	0.3887	0.3606	0.3989	0.3466
0.4278	0.3105	0.4245	0.3455	0.4259	0.3597	0.4363	0.3465
0.4608	0.3093	0.4574	0.3445	0.4588	0.3593	0.4486	0.3467
0.4837	0.3086	0.4732	0.3440	0.4697	0.3593	0.4694	0.3471
0.4902	0.3084	0.4868	0.3437	0.4882	0.3593	0.4747	0.3473
0.5101	0.3079	0.4995	0.3434	0.4960	0.3594	0.4988	0.3481
0.5394	0.3072	0.5289	0.3430	0.5254	0.3599	0.5042	0.3483
0.5724	0.3074	0.5620	0.3429	0.5585	0.3608	0.5375	0.3501
0.6096	0.3062	0.5995	0.3429	0.5961	0.3624	0.5755	0.3529
0.6521	0.3062	0.6424	0.3436	0.6392	0.3650	0.6193	0.3574
0.7008	0.3065	0.6919	0.3450	0.6889	0.3689	0.6704	0.3630
0.7575	0.3073	0.7496	0.3473	0.7470	0.3747	0.7306	0.3719
0.8241	0.3091	0.8179	0.3513	0.8158	0.3833	0.8027	0.3852
0.9036	0.3122	0.8998	0.3576	0.8985	0.3962	0.8905	0.4050

The excess free energies (ΔmGE) of the mixture were calculated using the equation11,

$$\Delta_m G^E = Y_A[\ln(\gamma_A/\gamma^0_A)+(\phi_A - \phi_m)]+Y_B[\ln(\gamma_B/\gamma^0_B)+(\phi_B - \phi_m)] \quad (8)$$

$$Y_A=\nu_A y_A m_A RT; Y_B=\nu_B y_B m_B RT \quad (9)$$

Where ϕA and ϕB are osmotic coefficients of the pure components at the same ionic strength as the mixture and ϕ is the osmotic coefficient of the mixture, and all other symbols have their usual significance. The resulting values are listed in Table 5. Thus, these Sθ and ψ values along with other Pitzer parameters are able to represent well, the thermodynamic data of the system at 25oC.

Table 5 - Excess Free Energies for the system

$NaCl-Ca(NO_3)_2-H_2O$ at 25ºC (Joules /kg of Water)

y_B	I = 0.5	I = 1.0	I = 2.0	I = 3.0
0.1	-1.5284	-3.9138	-10.3439	-20.4813
0.2	-2.7101	-6.9004	-17.9299	-34.8619
0.3	-3.5476	-8.9813	-22.9308	-43.7224
0.4	-4.0436	-10.1784	-25.5177	-47.6443
0.5	-4.2009	-10.5128	-25.8639	-47.2089

Conclusions:

Pitzer formulism made use to describe the properties of concentrated electrolyte mixtures.Trends of activity coefficients of pure andmixed electrolyte solutions explained.The differences in activitycoefficient arise due tothe effect of different electrolytes are explained.

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