

Thermodynamics of electrolyte solutions: Activity and osmotic coefficients of aqueous NaCl in the NaCl-MgCl₂-H₂O system at different temperatures by the EMF method

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MS received 13 March 1989; revised 3 August 1989

Abstract. The activity and osmotic coefficients of aqueous NaCl in the NaCl-MgCl₂-H₂O system at 25, 35 and 45°C and total ionic strengths of 0.5, 1, 2 and 3 were obtained by an EMF method using a sodium ion-selective electrode and an Ag/AgCl electrode. The Harned coefficients and Pitzer binary and ternary interaction coefficients were also determined.

Keywords. Thermodynamics of electrolytes; activity coefficient; sodium chloride; magnesium chloride; potentiometry.

1. Introduction

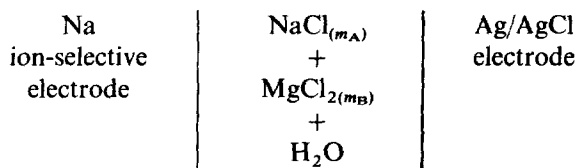
A wide variety of biological and industrial systems and processes involve aqueous electrolyte mixtures. The activity coefficients of NaCl in the NaCl-MgCl₂-H₂O system were obtained at 25°C using the EMF method by Lanier (1965) at ionic strength, $I = 1, 3$ and 6 M and Christenson (1973) at $I = 1$ M. Butler and Huston (1967) did a more detailed study at 25°C from $I = 0.52$ to 5.99 M using sodium amalgam electrodes. The osmotic coefficients of this system were estimated isopiastically at 25°C by Wu *et al* (1968) over the range $I = 1.1$ to 5.9 M and by Platford (1968) over $I = 0.11$ to 8.02 M. An *et al* (1978) measured the vapour pressures covering the ionic strength range of 6.37 to 13.84 at 25°C. Rard and Miller (1987) reinvestigated this system isopiastically at 25°C over the ionic strength range of $I = 0.295$ to crystallization limits. Thus, the activity coefficient data on aqueous NaCl-MgCl₂ mixtures is available mostly at 25°C. Consequently, we decided to investigate this system at $I = 0.5, 1, 2$ and 3 M at three different temperatures, i.e. 25, 35 and 45°C.

2. Experimental

The cell consisted of a sodium ion-selective electrode (Elico: India) and an Ag/AgCl electrode immersed in a mixture of NaCl and MgCl₂ aqueous solutions, placed in a double-walled glass vessel. The temperature was kept constant ($\pm 0.01^\circ\text{C}$) by

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circulating thermostatted water. The cell arrangement was



The Ag/AgCl electrode was prepared according to the standard thermal method described by Ives and Janz (1961). The electrodes were connected to a high impedance unit gain amplifier whose output was measured by a Keithly 5½ digit electrometer (Model: DMM 191). The accuracy of the EMF measurements was ± 0.1 mV.

Analytical grade NaCl (S Merck) and MgCl₂ (S Merck) were used after recrystallization. Stock solutions were prepared with deionised double-distilled water and standardised volumetrically using AgNO₃.

3. Calculations and discussion

Calculations were made as described by Ananthaswamy and Atkinson (1982). The potentials of the cell with NaCl–MgCl₂ are described by the relation

$$E_{\text{NaCl-MgCl}_2} = E_0 + k \log (a_{\text{Na}} a_{\text{Cl}} + K a_{\text{Mg}}^{1/2} a_{\text{Cl}}), \quad (1)$$

where K is the selectivity coefficient of the Na ion-selective electrode for Mg²⁺ ions and k is the Nernst slope. In pure NaCl solutions (1) takes the form

$$E_{\text{NaCl MgCl}_2} = E_0 + k \log a_{\text{Na}} a_{\text{Cl}}. \quad (2)$$

The E_0 and k values were estimated by plotting cell EMF against $\log a_{\text{NaCl}}$. Next, the EMF of the pure MgCl₂ solutions were measured to evaluate the selectivity coefficient (K), which is found to be $\leq 10^{-5}$ at all the temperature and ionic strengths studied. Thus, the term containing K was neglected in (1), so that it could be rearranged thus,

$$\gamma_{\pm}^2 = (1/m_{\text{Na}} m_{\text{Cl}}) \exp \{2.303(E_{\text{NaCl-MgCl}_2} - E_0)/k\}, \quad (3)$$

where γ_{\pm} is the mean activity coefficient of NaCl in an aqueous NaCl–MgCl₂ mixture. The activity coefficient data obtained at $I = 0.5, 1, 2$ and 3 M and at $25, 35$ and 45°C are given in table 1 at different values of y_B where $y_B = 3m_B/(m_A + 3m_B)$. Our γ_{\pm} data at 25°C is in agreement with the data of Rard and Miller (1987) at $I = 0.5$ M, Christenson (1973) at $I = 1$ M, Butler and Huston (1967) at $I = 2$ M, and Lanier (1965) at $I = 3$ M.

These γ_{\pm} values at each ionic strength were fitted using a least-squares technique to the Harned equation (Harned and Owen 1958),

$$\log \gamma_A = \log \gamma_A^0 - \alpha_{AB} y_B, \quad (4)$$

where γ_A^0 is the activity coefficient of pure NaCl at the same ionic strength as the mixture. The Harned coefficient (α_{AB}) values are also listed in table 1.

The γ_{\pm} data at a given temperature (all the four ionic strengths) were fitted into a

Table 1. Activity coefficients of NaCl in the system NaCl–MgCl₂–H₂O.

<i>I</i> = 0.5		<i>I</i> = 1		<i>I</i> = 2		<i>I</i> = 3	
<i>y_B</i>	–log <i>γ</i> _±	<i>y_B</i>	–log <i>γ</i> _±	<i>y_B</i>	–log <i>γ</i> _±	<i>y_B</i>	–log <i>γ</i> _±
25°C; <i>s</i> ₀ = 0.0594; <i>ψ</i> = –0.0128; RMSD* × 10 ⁴ = 1.96							
0.1176	0.1656	0.1193	0.1170	0.1805	0.1726	0.1187	0.1440
0.2105	0.1647	0.2131	0.1792	0.2095	0.1707	0.2122	0.1419
0.2857	0.1641	0.2889	0.1782	0.3465	0.1679	0.2877	0.1401
0.3478	0.1636	0.3514	0.1773	0.3986	0.1669	0.3501	0.1386
0.4000	0.1632	0.4038	0.1767	0.4236	0.1664	0.4020	0.1373
0.4215	0.1630	0.4145	0.1765	0.4430	0.1660	0.4024	0.1373
0.4444	0.1629	0.4403	0.1762	0.4495	0.1658	0.4276	0.1366
0.4767	0.1626	0.4483	0.1761	0.4788	0.1652	0.4469	0.1361
0.4827	0.1626	0.4695	0.1758	0.4813	0.1652	0.4567	0.1359
0.5100	0.1624	0.4867	0.1756	0.5122	0.1646	0.4852	0.1351
0.5161	0.1624	0.5029	0.1754	0.5146	0.1645	0.4899	0.1350
0.5454	0.1622	0.5200	0.1752	0.5440	0.1639	0.5186	0.1343
0.5484	0.1622	0.5413	0.1749	0.5505	0.1638	0.5284	0.1340
0.5714	0.1620	0.5493	0.1748	0.5700	0.1634	0.5479	0.1335
0.5931	0.1619	0.5753	0.1745	0.5951	0.1629	0.5735	0.1328
0.6456	0.1615	0.5861	0.1744	0.6475	0.1618	0.5739	0.1328
0.7084	0.1612	0.6390	0.1737	0.7101	0.1605	0.6270	0.1313
0.7846	0.1608	0.7024	0.1730	0.7861	0.1589	0.6915	0.1295
0.8793	0.1603	0.7797	0.1721	0.8802	0.1569	0.7707	0.1272
		0.8762	0.1711			0.8705	0.1243
	<i>α</i> _{AB} = –0.0008	<i>α</i> _{AB} = –0.0122		<i>α</i> _{AB} = –0.0156		<i>α</i> _{AB} = –0.0170	
	RMSD × 10 ⁴ = 2.77	RMSD × 10 ⁴ = 2.20		RMSD × 10 ⁴ = 1.65		RMSD × 10 ⁴ = 7.75	
35°C; <i>s</i> ₀ = 0.0659; <i>ψ</i> = –0.0131; RMSD × 10 ⁴ = 8.64							
0.1175	0.1663	0.1186	0.1799	0.1128	0.1694	0.1143	0.1392
0.2103	0.1657	0.2120	0.1790	0.2027	0.1682	0.2052	0.1378
0.2854	0.1652	0.2876	0.1783	0.2760	0.1672	0.2792	0.1366
0.3475	0.1649	0.3499	0.1777	0.3370	0.1664	0.3406	0.1357
0.3996	0.1646	0.4022	0.1773	0.3885	0.1657	0.3923	0.1348
0.4257	0.1645	0.4232	0.1771	0.4305	0.1652	0.4217	0.1344
0.4441	0.1644	0.4467	0.1769	0.4326	0.1652	0.4365	0.1341
0.4517	0.1644	0.4491	0.1769	0.4565	0.1649	0.4475	0.1339
0.4810	0.1643	0.4850	0.1766	0.4708	0.1647	0.4768	0.1335
0.4824	0.1642	0.5118	0.1764	0.4859	0.1645	0.5081	0.1330
0.5144	0.1641	0.5184	0.1764	0.5041	0.1643	0.5102	0.1329
0.5158	0.1641	0.5477	0.1761	0.5192	0.1641	0.5375	0.1325
0.5451	0.1640	0.5502	0.1761	0.5335	0.1639	0.5486	0.1323
0.5527	0.1640	0.5736	0.1759	0.5575	0.1636	0.5635	0.1320
0.5711	0.1639	0.5948	0.1758	0.5596	0.1636	0.5932	0.1316
0.5972	0.1638	0.6472	0.1754	0.6019	0.1631	0.6457	0.1307
0.6475	0.1636	0.7098	0.1750	0.6540	0.1624	0.7085	0.1296
0.7119	0.1635	0.7858	0.1746	0.7159	0.1617	0.7847	0.1283
0.7875	0.1633	0.8801	0.1740	0.7908	0.1608	0.8794	0.1267
0.8811	0.1631			0.8832	0.1597		
	<i>α</i> _{AB} = –0.0049	<i>α</i> _{AB} = –0.0076		<i>α</i> _{AB} = –0.0142		<i>α</i> _{AB} = 0.0109	
	RMSD × 10 ⁴ = 3.33	RMSD × 10 ⁴ = 2.78		RMSD × 10 ⁴ = 9.33		RMSD × 10 ⁴ = 1.76	

(continued)

Table 1. (continued)

$I = 0.5$		$I = 1$		$I = 2$		$I = 3$	
y_B	$-\log \gamma_{\pm}$	y_B	$-\log \gamma_{\pm}$	y_B	$-\log \gamma_{\pm}$	y_B	$-\log \gamma_{\pm}$
45°C; $s_{\theta} = 0.0572$; $\psi = -0.0040$; $\text{RMSD} \times 10^4 = 2.98$							
0.1053	0.1681	0.1119	0.1809	0.1170	0.1689	0.1164	0.1378
0.1905	0.1677	0.2012	0.1803	0.2095	0.1682	0.2085	0.1370
0.2610	0.1674	0.2742	0.1799	0.2845	0.1677	0.2833	0.1364
0.3201	0.1672	0.3350	0.1796	0.3465	0.1672	0.3451	0.1359
0.3705	0.1671	0.3864	0.1794	0.3986	0.1669	0.3971	0.1354
0.4139	0.1670	0.4304	0.1792	0.4208	0.1668	0.4005	0.1354
0.4517	0.1669	0.4360	0.1792	0.4430	0.1667	0.4260	0.1352
0.4525	0.1669	0.4620	0.1791	0.4467	0.1666	0.4415	0.1351
0.4787	0.1669	0.4686	0.1791	0.4760	0.1665	0.4550	0.1350
0.4850	0.1668	0.4914	0.1790	0.4813	0.1665	0.4798	0.1348
0.5081	0.1668	0.5019	0.1790	0.5093	0.1663	0.4883	0.1347
0.5144	0.1668	0.5248	0.1789	0.5146	0.1663	0.5131	0.1346
0.5407	0.1668	0.5313	0.1789	0.5440	0.1661	0.5268	0.1345
0.5794	0.1667	0.5574	0.1788	0.5477	0.1661	0.5425	0.1344
0.6231	0.1667	0.5630	0.1788	0.5700	0.1660	0.5685	0.1342
0.6739	0.1666	0.6072	0.1787	0.5924	0.1659	0.5719	0.1341
0.7337	0.1666	0.6590	0.1785	0.6450	0.1656	0.6255	0.1338
0.8052	0.1666	0.7204	0.1784	0.7078	0.1654	0.6901	0.1333
0.8921	0.1667	0.7944	0.1783	0.7842	0.1651	0.7696	0.1328
		0.8854	0.1782	0.8790	0.1648	0.8698	0.1323
	$\alpha_{AB} = -0.0033$	$\alpha_{AB} = -0.0050$		$\alpha_{AB} = -0.0067$		$\alpha_{AB} = -0.0084$	
	$\text{RMSD} \times 10^4 = 3.50$	$\text{RMSD} \times 10^4 = 3.42$		$\text{RMSD} \times 10^4 = 2.00$		$\text{RMSD} \times 10^4 = 2.01$	

* RMSD – root mean square deviation

Table 2. Activity coefficients of NaCl from solubility data and the Pitzer equation for the system NaCl–MgCl₂–H₂O at 25°C.

m_{NaCl}	m_{MgCl_2}	γ_{\pm} (solubility)	γ_{\pm} (calculated)
6.1667	0.0000	1.0047	1.0091
7.1111	0.3750	1.1782	1.1424
7.7388	0.5750	1.3660	1.2547
8.9167	0.7570	1.6302	1.5029
9.6778	0.8335	1.8464	1.6950
10.750	0.9070	3.0172	3.1871

single least-squares program and common s_{θ} and ψ were estimated at 25, 35 and 45°C, which are also listed in table 1. The $s_{\theta} = 0.0594$ and $\psi = -0.0128$ values obtained at 25°C are in good agreement with the values reported by Pitzer and Kim (1974) i.e. $s_{\theta} = 0.07$ and $\psi = -0.01$. Also, the ψ value is in agreement with the value of $\psi = -0.013663$ calculated by Rard and Miller (1987) using all the available isopiestic data upto $I \leq 6.2$ M. Using these s_{θ} and ψ values, the γ_{\pm} values of NaCl can be calculated in this multicomponent electrolyte mixture. Thus, the γ_{\pm} values of NaCl at 25°C could be calculated using the $s_{\theta} = 0.0594$ and $\psi = -0.0128$ in the Pitzer equation for the solubility data (Kournakov and Zemczujnyj 1919) of NaCl in NaCl–

MgCl₂-H₂O mixtures. Also, these γ_{\pm} values of NaCl could be calculated using the solubility data itself by knowing that $\Delta G_s^0 = -2161$ cal/mol (Silvester and Pitzer 1977). These two sets of γ_{\pm} values are listed in table 2 and are in good agreement with an RMSD = 6.209×10^{-2} . The osmotic coefficients and excess free energies of the NaCl-MgCl₂-H₂O mixtures can also be calculated using the appropriate Pitzer equations (Pitzer 1973, 1975; Pitzer and Mayorga 1973; Pitzer and Kim 1974).

Acknowledgements

The authors wish to thank Prof. T Navaneeth Rao and Prof. B Subrahmanyam for many helpful discussions and active assistance. NKR is thankful to the Council of Scientific and Industrial Research for a fellowship.

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