

Thermodynamics of Electrolyte Solutions: Activity Coefficients of NaCl in NaCl + MnCl₂ + H₂O System at 25°C

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The EMF values of a cell consisting of sodium ion-selective electrode and silver-silver chloride electrode have been measured to find the activity coefficients of NaCl in its mixtures with aqueous MnCl₂ at 25°C and total ionic strengths of 0.5, 1.0, 2.0 and 3.0. The Harned coefficients have been evaluated by fitting the activity coefficient data to the equation:

$$\log \gamma_A = \log \gamma_A^0 - \alpha_{AB} \gamma_B - \beta_{AB} \gamma_B^2$$

The data have been also fitted to the Pitzer equations and the corresponding binary and ternary interaction parameters are reported.

Recently, activity coefficients of aqueous electrolyte solutions and mixed electrolyte solutions have been extensively studied¹⁻⁵ because such data are useful in the fields of petroleum drilling, industrial processing, water pollution control and oceanography. However, the ternary mixtures of aqueous alkali metal halides with transition metal halides have not received much attention. Roy *et al.*⁶ and Downes⁷ have estimated the activity coefficients of HCl in the system HCl + MnCl₂ + H₂O. But, only isopiestic data are available⁸ for the system NaCl + MnCl₂ + H₂O. Hence, in the present study the mean ionic activity coefficients of NaCl in the system NaCl + MnCl₂ + H₂O have been estimated by EMF measurements method at 25°C and total ionic strengths 0.5, 1, 2 and 3.

Materials and Methods

Deionised, doubly distilled water was used for preparing all the solutions. Analytical grade sodium chloride (GR, S Merck) and manganous chloride (AR, Glaxo) were used without further purification. The solutions were standardised volumetrically using AgNO₃. All the solutions were prepared by weight. Also, all titrations and dilutions were made using weight burettes.

The cell consisted of a Na ion-selective electrode (Elico, India) and an Ag-AgCl electrode in a mixture of NaCl and MnCl₂ solutions placed in a double-walled glass vessel whose temperature was maintained constant by circulation of water from a thermostat. The Ag/AgCl electrodes were prepared as described by Ives and Janz⁹. The potentials were measured with a Keithly 5½ digit electrometer/multimeter after processing the signals with a unit gain amplifier of input impedance $\approx 10^{12} \Omega$. The accuracy

of the EMF measurements was ± 0.1 mV. The electrodes were allowed to stand in a mixture of 0.01 M NaCl while not in use, and were properly conditioned for use in mixed electrolyte solutions. Electrodes were standardised at all the ionic strengths studied.

At each ionic strength, in the first set, the potentials of the Na electrode vs Ag-AgCl electrode were measured and these potentials were plotted against $\log a_{\text{NaCl}}$. The activity coefficients of pure NaCl solutions at 25°C were taken from the literature (NBS data)¹⁰. The pH of the solutions were in the range 3.8-5.5 and these pH values are well above the pH limits suggested by the manufacturer for the Na ion-selective electrode. At every ionic strength the electrodes were allowed to stand in the solutions for about 30-45 min before taking the initial reading, so as to allow attainment of the equilibrium.

The EMF values of Na ion-selective electrode vs Ag/AgCl electrode in NaCl-MnCl₂ mixtures are given by the relation:

$$E_{\text{NaCl-MnCl}_2} = E_o + k \log (a_{\text{Na}} a_{\text{Cl}} + K a_{\text{Mn}}^{1/2} a_{\text{Cl}}) \quad \dots (1)$$

where k is the Nernst slope and K is the selectivity coefficient of Na electrode for Mn²⁺ ions.

In pure NaCl solution, i.e., when $a_{\text{Mn}} = 0$,

$$E_{\text{NaCl}} = E_o + k \log a_{\text{Na}} a_{\text{Cl}} \quad \dots (2)$$

In pure MnCl₂ solutions $a_{\text{Na}} = 0$ and, therefore,

$$E_{\text{MnCl}_2} = E_o + k \log K a_{\text{Mn}}^{1/2} a_{\text{Cl}} \quad \dots (3)$$

or

$$K^2 = (1/a_{\text{MnCl}_2}^3) \exp [4.606 (E_{\text{MnCl}_2} - E_o)/k] \quad \dots (4)$$

At each ionic strength the EMF data obtained in the calibration run (the first set) was fitted to Eq. 2 and E_o and k values were evaluated using least squares

Table 1—Mean Activity Coefficients of NaCl in NaCl + MnCl₂ + H₂O System at 25°C

<i>I</i> = 0.5		<i>I</i> = 1		<i>I</i> = 2		<i>I</i> = 3	
<i>y</i> _B	−log γ _{NaCl}	<i>y</i> _B	−log γ _{NaCl}	<i>y</i> _B	−log γ _{NaCl}	<i>y</i> _B	−log γ _{NaCl}
0.0911	0.1620	0.0923	0.1713	0.0935	0.1719	0.0960	0.1515
0.1670	0.1617	0.1690	0.1632	0.1710	0.1701	0.1752	0.1535
0.2312	0.1581	0.2338	0.1574	0.2363	0.1658	0.2981	0.1571
0.2862	0.1565	0.2891	0.1536	0.2920	0.1702	0.3468	0.1580
0.3338	0.1565	0.3371	0.1514	0.3402	0.1678	0.3892	0.1600
0.3755	0.1578	0.3789	0.1470	0.3822	0.1669	0.4887	0.1625
0.4123	0.1604	0.4486	0.1442	0.4192	0.1672	0.4978	0.1610
0.4450	0.1641	0.5042	0.1455	0.4520	0.1686	0.5272	0.1623
0.5006	0.1647	0.4915	0.1397	0.5077	0.1658	0.5603	0.1675
0.4949	0.1675	0.5178	0.1427	0.5082	0.1655	0.5979	0.1717
0.5505	0.1751	0.5472	0.1433	0.5376	0.1663	0.5979	0.1687
0.5833	0.1745	0.5800	0.1409	0.5706	0.1642	0.6408	0.1657
0.6202	0.1793	0.6591	0.1389	0.6079	0.1663	0.6904	0.1657
0.7101	0.1877	0.7073	0.1433	0.6504	0.1628	0.7483	0.1746
0.8305	0.2011	0.7632	0.1425	0.7561	0.1640	0.8169	0.1680
0.9074	0.2123	0.8286	0.1501	0.9029	0.1626	0.8992	0.1727
		0.9062	0.1458	0.9490	0.1610	0.9469	0.1725
		0.9508	0.1525				

procedure. Next, selectivity coefficient values for MnCl₂ were determined by substituting the EMF data obtained in the second set, i.e., with pure MnCl₂ solution, in Eq. 4. The activity coefficients of manganese chloride were taken from the literature (NBS data)¹¹. The values of the selectivity coefficients (*K*) at all the ionic strengths were $< 1 \times 10^{-4}$. Therefore, the second term within brackets on the right hand side of Eq. 1 was neglected. The third set consisted of the EMF measurements with aqueous mixtures of NaCl-MnCl₂. For this set the potentials were first measured with pure NaCl solutions and then aliquots of MnCl₂ solution were added. Next, starting with pure MnCl₂ solution, aliquots of NaCl solution were successively added. The overlapping portion between these two experiments was used to test the reproducibility and accuracy of the measurements. Also, all the three sets were repeated at least twice to get consistent and reproducible results.

The cell EMF values for NaCl + MnCl₂ + H₂O mixtures are described by the relation,

$$E_{\text{NaCl-MnCl}_2} = E^{\circ} + k \log a_{\text{Na}} a_{\text{Cl}} \quad \dots (5)$$

But

$$a_{\text{Na}} = m_{\text{Na}} \gamma_{\pm} = m_{\text{A}} \gamma_{\pm}$$

and

$$a_{\text{Cl}} = m_{\text{Cl}} \gamma_{\pm} = (m_{\text{A}} + 2m_{\text{B}}) \gamma_{\pm}$$

where γ_{\pm} is the mean ionic activity coefficient of NaCl. Substituting these relations in Eq. 5, we get

$$E_{\text{NaCl-MnCl}_2} = E^{\circ} + k \log m_{\text{A}} (m_{\text{A}} + 2m_{\text{B}}) \gamma_{\pm}^2$$

or

 Table 2—Harned Coefficients of NaCl in NaCl-MnCl₂-H₂O System at 25°C

<i>I</i>	log γ _{NaCl} ^o	α	β	RMSD ^a × 10 ³
0.5	−0.1667	−0.0650	0.1298	2.16
1	−0.1823	−0.1304	0.1030	1.80
2	−0.1749	−0.0299	0.0207	1.79
3	−0.1466	0.0438	−0.0176	2.37

^aRoot mean square deviation

$$\gamma_{\pm}^2 = (1/m_{\text{Na}} m_{\text{Cl}}) \exp \{2.303 (E_{\text{NaCl-MnCl}_2} - E^{\circ})/k\} \quad \dots (6)$$

Thus, the activity coefficients of NaCl in aqueous NaCl-MnCl₂ mixtures were calculated by substituting in Eq. 6 the cell EMF ($E_{\text{NaCl-MnCl}_2}$) values along with the E° and *k* values estimated in the calibration set.

Results and Discussion

The experimental mean activity coefficients of NaCl at all the ionic strengths studied are summarised in the Table 1, at different values of *y*_B where,

$$y_{\text{B}} = 3m_{\text{MnCl}_2} / (m_{\text{NaCl}} + 3m_{\text{MnCl}_2}) \quad \dots (7)$$

The log γ_± vs *y*_B plots are shown in Fig. 1. These γ_± values at each ionic strength, were fitted to the Harned equation¹²:

$$\log \gamma_{\text{A}} = \log \gamma_{\text{A}}^{\circ} - \alpha_{\text{AB}} y_{\text{B}} - \beta_{\text{AB}} y_{\text{B}}^2 \quad \dots (8)$$

where $\gamma_{\text{A}}^{\circ}$ is the activity coefficient of pure NaCl at the same ionic strength as the mixture. The values of Harned coefficients, i.e., α_{AB} and β_{AB} are listed in

Table 3— s_0 and ψ Values Obtained from the Activity Coefficient Data of NaCl in NaCl + MnCl₂ + H₂O at 25°C

I	$s_{0\text{NaMn}}$	ψ_{NaMnCl}	RMSD $\times 10^3$	RMSD $\times 10^2$ with $s_0 = 0.9517$ $\psi = -0.6623$	RMSD $\times 10^2$ with $s_0 = 0.082$ $\psi = -0.017$
0.5	-1.696	5.143	2.29	3.91	1.70
1.0	-0.1177	1.037	1.89	2.28	3.10
2.0	0.0991	0.0089	1.47	3.48	0.60
3.0	0.0288	-0.0274	2.49	6.33	1.76

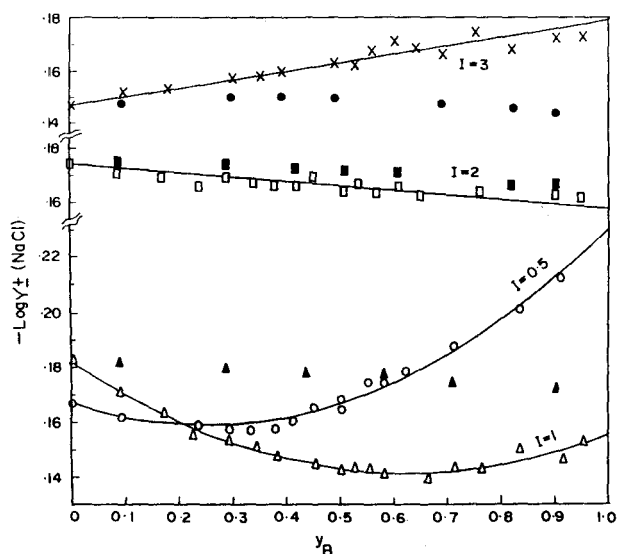

 Fig. 1—Plot of $\log \gamma_{\pm \text{NaCl}}$ versus y_{MnCl_2} [Downes⁸ data at $I=1$, Δ ; $I=2$, \blacksquare ; at $I=3$, \bullet]

Table 2. All the calculations were done using a Vax Computer.

The activity coefficient data were also fitted to the recently developed Pitzer equations¹³⁻¹⁵. The NBS data^{10,11} on the activity coefficients of pure NaCl and MnCl₂ solutions were fitted to the Pitzer equations¹³⁻¹⁵. The values of the Pitzer coefficients are given below:

$$\beta_{\text{NaCl}}^0 = 0.07537; \beta_{\text{NaCl}}^1 = 0.2770; C_{\text{NaCl}}^\dagger = 0.001407$$

$$\beta_{\text{MnCl}_2}^0 = 0.3356; \beta_{\text{MnCl}_2}^1 = 1.456; C_{\text{MnCl}_2}^\dagger = -0.02351$$

The activity coefficients of aqueous NaCl in constant ionic strength mixtures of NaCl-MnCl₂ are also described by the Pitzer equation¹⁶.

From Fig. 1 it is evident that our data are in good agreement with the activity coefficient data of Downes⁸ at $I=2$. Also, at $I=1.0$ our data show the same trend as those of Downes⁸ even though the numerical agreement is not so close. The experimental activity coefficient data were fitted to the Pitzer equation¹⁶ and the binary interaction coefficient ($s_{0\text{NaMn}}$) and the ternary interaction coefficient (ψ_{NaMnCl}) were evaluated at each ionic strength. These values are listed in Table 3.

 Table 4—Osmotic Coefficients in the Mixture NaCl + MnCl₂ + H₂O System at 25°C

y_{NaCl}	$I=0.5$	$I=1.0$	$I=2.0$
0	0.853	0.876	0.945
0.1	0.882	0.909	0.946
0.2	0.902	0.930	0.941
0.3	0.919	0.942	0.933
0.4	0.925	0.949	0.925
0.5	0.930	0.959	0.920
0.6	0.932	0.950	0.920
0.7	0.932	0.948	0.925
0.8	0.930	0.944	0.937
0.9	0.926	0.940	0.956
1.0	0.922	0.936	0.984

 Table 5—Excess Free Energies of Mixing for the NaCl-MnCl₂ System at 25°C

y_{NaCl}	$\Delta_m G^E$ (J kg ⁻¹ of water)		
	$I=0.5$	$I=1.0$	$I=2.0$
0.2	13.0	52.7	121
0.4	45.3	138	279
0.6	55.0	150	268
0.8	36.2	86.7	129

Also, the activity coefficient data at all the four ionic strengths were fitted into a single least-squares programme and common s_0 and ψ values were evaluated. These s_0 and ψ values are 0.9517 and -0.6623 respectively. The corresponding RMSD values are also listed in Table 3. Pitzer¹⁶ analysed the isopiestic data reported by Downes⁸ and obtained the values of $s_0 = 0.082$ and $\psi = -0.017$. The RMSD values corresponding to these s_0 and ψ values are also listed in the last column of Table 3. A comparison of the RMSD values listed in the last two columns of Table 3 shows that these two sets of s_0 and ψ values are equally good.

The s_0 and ψ values ($s_0 = 0.9517$ and $\psi = -0.6623$) were used to calculate the osmotic coefficients of the mixture at various compositions using the Pitzer equations¹⁴ (Table 4). These osmotic coefficients agree within about $\pm 1.0\%$ with the experimental values reported by Downes⁸.

The excess free energies of the mixtures were calculated using the equation,

$$\Delta_m G^E = Y_A [\ln(\gamma_A/\gamma_A^0) + (\phi_A - \phi_M)] + Y_B [\ln(\gamma_B/\gamma_B^0) + (\phi_B - \phi_M)]$$

where all the symbols have their usual significance¹⁷. These excess free energies of mixing are listed in Table 5. Thus, these common s_0 and ψ values are able to represent the thermodynamic data of the system up to an ionic strength of 2.0.

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