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Physical Properties of Aqueous Mixed Electrolyte Solutions Of $CaCl_2$ In $CaCl_2$ - $MgCl_2$ - Arginine - H_2O at 35^0C

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Abstract

Aqueous solutions of multi component electrolytes solutions are analogues to natural brines encountered in water pollution control, oceanography and petroleum drilling. A thorough knowledge of the thermodynamic properties of these solutions is useful in understanding the behavior of these solutions. Therefore, in present work the activity coefficient (γ) of NaCl in several aqueous quaternary electrolyte mixtures were determined using the Na ion selective electrode by EMF method at temperatures viz., 25oC over an ionic strength. This experimental activity coefficient data were analyzed using the Pitzer equations. With a view to ascertain the validity of Pitzer equations for mixed electrolyte solutions.

INTRODUCTION

Thermodynamics provide two strong, possibly unique advantages. First for its broad range of applicability, as it is used in a large variety of scientific disciplines like physics, engineering, earth sciences and life sciences. Second because it is integrated science concerned with bulk properties it can provide useful answers to scientific problems with a minimum set of experimental data points. As a result there is a growing literature describing how chemical thermodynamics can be used to uniform process for old and new biological products for industry and medicine. A particular application of chemical thermodynamics concerns separation of biochemical's (amino acids) for this purpose we need the activity coefficient data for determining this data we need to understand not only the physical nature of aqueous amino acids but also the intermolecular forces between the amino acids and the salts in the electrolytes solutions. It is this integrative coarse-grained feature of thermodynamics that makes is attractive for describing some of the overall features of thermodynamics.

The mean activity coefficient of one electrolyte in the presence of other electrolyte(s) are being determined with renewed interest now a days all over the world. Aqueous electrolyte solutions and their thermodynamic properties play an important role in understanding the behavior of amino acids[1-4], natural waters such as sea and lake water, environmental pollution waters, industrial solutions[5-7]. The specific ion interaction principle which postulated the existence of short range interactions among the ions of unlike charge was enunciated by Bronsted[8-10] and was applied to dilute solutions by Guggenheim[11-13]. Modification to this principle was suggested by Scatchard[14-15] who took into the consideration the interactions among the like charge ions as well. Scatchard et al[16] have subsequently extended and elaborated the Guggenheim equation in several ways by considering all possible interactions of ions in solutions leading to very complex formulae for activity coefficients and osmotic coefficients. Bromley[17] also, proposed single parameter equations for activity coefficients and osmotic coefficients. Pitzer and Bremer[18] extended the Guggenheim equations and developed a single and complex set of multicomponent electrolyte solutions. These Pitzer[19] equations have an electrostatic term of Debye-Huckel type plus a virial coefficients series.Recently, the concentration and temperature dependence on thermodynamic properties of electrolyte solutions has been of much concern in different fields. Of all the thermodynamic properties, of these single and multicomponent electrolytes solutions the activity coefficients and osmotic coefficients received the maximum attention. In the present work we have used the Pitzer model to describe thermodynamic properties.

The present work consists of Experimental determination of Activity Coefficient of aqueous NaCl in quaternary mixtures containing *NaCl - $MgCl_2$-Glycine - H_2O and* Evaluation of Pitzer ion interaction parameters of experimentally determined Activity Coefficients data in order to find Activity coefficient of other components.

MATERIAL AND METHODS

In this description of Na ion selective electrode potentiometer, reagents used preparation of Ag /AgCl reference electrode and preparation of solutions is given.
The cell arrangement used is as follows:

Na Ion Selective Electrode NY_2 (m_b) + Amino Acid	NaX (or) Mx +	Ag/AgCl Electrode

Where M=Na^+
Y=X=Cl^-, Na, Mg

The E.M.F's were measured using Keithly 5 1\2 digit electrometer. The experimental procedure of measuring the Emf's has been described. The method of estimating the activity coefficient in mixed electrolyte solutions from the experimentally measured Emf's values is given. The calibration of Na ion Selective electrode at 25^0C was done to evaluate the values of E_o and Nernst slope.

Treatment of Data

The emfs of sodium ion-selective electrode vs the *Ag/AgCl* electrode in NaCl-$MgCl_2$ solution is given by the relation.

$$E_{MX-NY_2} = E_0 + k \log (a_M a_X + K a_N^{1\backslash 2} a_X + K' a_N^{1/2} a_Y + K'' a_M a_Y)$$

The K′ and K′′ terms are omitted because the cell is reversible to ′X′ ion only. The K term could be neglected in the final calculation because the emfs recorded in the fourth set (≅ - 40mV) are very low as compared to the emfs obtained (≅125mV) in the 1st, 2nd and 3rd sets.
first equation reduces to

$$E_{MX-NY_2} = E_0 + k \log (a_M a_X + K a_N^{1\backslash 2} a_X)$$

Where k′ is the Nernst slope i.e., k= 2.303 RT/nF, K is the selectivity coefficient of the ion selective electrodes the N^{2+} ions and E_o is the emf due to the NaCl solution at unit activity. In pure NaClX solution a_N =0 and therefore equation-108 becomes

$$E_{MX} = E_0 + k \log a_M a_X$$

In pure NY solution a_M = 0 and thus,

$$E_{NY} = E_0 + k \log K a_N^{1/2} a_Y$$

$$K^2 = \frac{1}{a^3_{NY_2}} \cdot \exp[4.606 (E_{NY_2} - E_0)/k]$$

For the calibration run in the first set at each ionic strength, the Emfs of the aqueous *NaCl* solutions were measured. The pure electrolytes activity coefficients of *NaCl* were taken from literature. The selectivity coefficient (K) values for all seconds salt solutions and the all the ionic strengths studied were in the range of 10^{-5} to 10^{-4}.

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RESULTS AND DISCUSSION

The experimental results are presented in the form of tables. The experimental data of quaternary mixtures are discussed. The osmotic and Harned coefficients were calculated using the Pitzer ion interaction parameters estimated for these systems at constant total ionic strength of 0.1 to 3.0 mol. kg^{-1} at 25ºC.

Table: 1 Activity coefficients of NaCl in the NaCl-MgCl$_2$- Arginine -H$_2$O System at 35ºC.

Conc. NaCl mol. kg^{-1}	Conc.MgCl$_2$ mol. kg^{-1}	Conc. Glycine mol. kg^{-1}	EmF Volts.	y_B	logγ_{NaCl}	γ $_{NaCl}$
			I = 0.5			
0.5000	0.0000	0.0000	0.1176	0.0000	-0.1172	0.7634
0.4475	0.0525	0.0525	0.1150	0.1051	-0.1162	0.7651
0.4050	0.0950	0.0950	0.1125	0.1899	-0.1151	0.7671
0.3698	0.1302	0.1302	0.1103	0.2603	-0.1147	0.7679
0.3403	0.1597	0.1597	0.1083	0.3194	-0.1145	0.7681
0.3152	0.1848	0.1848	0.1064	0.3697	-0.1146	0.7680
0.2935	0.2065	0.2065	0.1047	0.4131	-0.1139	0.7692
0.2746	0.2254	0.2254	0.1030	0.4509	-0.1141	0.7690
0.2579	0.2421	0.2421	0.1015	0.4841	-0.1141	0.7690
0.2432	0.2568	0.2568	0.1000	0.5136	-0.1142	0.7688
0.2301	0.2699	0.2699	0.0987	0.5399	-0.1142	0.7688
0.0517	0.4483	0.4483	0.0610	0.8967	-0.1165	0.7646
0.0936	0.4064	0.4064	0.0761	0.8127	-0.1163	0.7650
0.1284	0.3716	0.3716	0.0841	0.7451	-0.1154	0.7667
0.1577	0.3423	0.3423	0.0893	0.6845	-0.1151	0.7671
0.1828	0.3172	0.3172	0.0929	0.6331	-0.1147	0.7678
0.2044	0.2956	0.2956	0.0957	0.5912	-0.1144	0.7684
0.2232	0.2768	0.2768	0.0979	0.5535	-0.1142	0.7687
0.2398	0.2602	0.2602	0.0997	0.5203	-0.1142	0.7687
0.2545	0.2455	0.2455	0.1012	0.4909	-0.1141	0.7689
I = 1.0						
1.0000	0.0000	0.0000	0.1513	0.0000	-0.1354	0.7321
0.8995	0.1005	0.1005	0.1489	0.1005	-0.1321	0.7378
0.8173	0.1827	0.1827	0.1467	0.1827	-0.1304	0.7406
0.7489	0.2511	0.2511	0.1446	0.2511	-0.1283	0.7442
0.6910	0.3090	0.3090	0.1427	0.3090	-0.1277	0.7452
0.6415	0.3585	0.3585	0.1410	0.3585	-0.1264	0.7475
0.5986	0.4010	0.4010	0.1393	0.4014	-0.1263	0.7476
0.5610	0.4390	0.4390	0.1378	0.4390	-0.1255	0.7490
0.5279	0.4721	0.4721	0.1363	0.4721	-0.1251	0.7497
0.4985	0.5015	0.5015	0.1349	0.5015	-0.1249	0.7500
0.4722	0.278	0.278	0.1336	0.5278	-0.1245	0.7507
0.1059	0.8941	0.8941	0.0964	0.8941	-0.1245	0.7507
0.1915	0.8085	0.8085	0.1113	0.8085	-0.1245	0.7507
0.2621	0.7379	0.7379	0.1192	0.7379	-0.1245	0.7507
0.3214	0.6786	0.6786	0.1242	0.6786	-0.1245	0.7507
0.3719	0.6281	0.6281	0.1278	0.6281	-0.1245	0.7507

0.4153	0.5847	0.5847	0.1305	0.5847	-0.1243	0.7511
0.4532	0.5468	0.5468	0.1326	0.5468	-0.1243	0.7511
0.4864	0.5136	0.5136	0.1343	0.5136	-0.1245	0.7507
0.5159	0.4841	0.4841	0.1358	0.4841	-0.1249	0.7500

RESULTS AND DISCUSSION

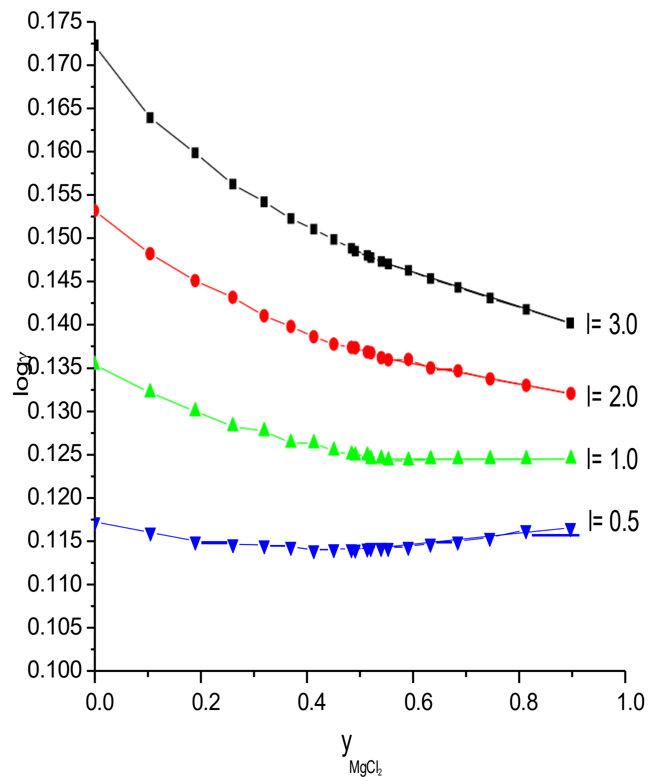
The experimentally determined activity coefficient data of NaCl in these mixtures were fitted to the Harned equations.

$$\log\gamma_A = \log\gamma^o_A - \alpha_{AB} y_B - \beta_{AB} y^2_B$$

Where α_{AB} and β_{AB} are Harned coefficients. When the plot of $\log\gamma_A$ v/s y_B is nearly linear for any system, then the β_{AB} value is very small and can be neglected, then the Harned equations can be written as

$$\log\gamma_A = \log\gamma^o_A - \alpha_{AB} y_B$$

These Harned coefficients α_{AB} and β_{AB} values which are function of the ionic strength and temperature are useful in calculating the γ_{NaCl} values in the mixtures of any given ionic strength fraction (y_B) i.e., at any given composition.



Graph1: Variation of –log $CaCl_2$ with y $_{MgCl2}$ at 35^0C in the system NaCl-$MgCl_2$-arginine-H_2O.

The activity coefficient data is further analyzed using the Pitzer equations for multicomponent electrolyte solutions and Pitzer interaction parameters viz; binary interaction parameter (S_θ) and ternary interaction parameter(φ) values are evaluated.

The results obtained in the present work have been summarized to reveal the trends in the activity coefficients. The effect of added cations, anions and amino acids on the activity coefficients of NaCl is discussed.

The trends in the activity coefficients values of NaCl in the quaternary systems will be explained on the basis of the crystallographic radii, charge densities and activity coefficients of the pure electrolytes. The activity coefficients of

NaCl in the quaternary systems studied shows that the activity coefficient also depend on the amino acid used.Thus, the experimental data measured in the present work on several mixed electrolyte systems is analyzed using the Pitzer equations to demonstrate the usefulness of the thermodynamic properties of the aqueous electrolytes solutions in several fields of practical importance.

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