Ionic Interactions in Organic Electrolyte Solutions. Activity Coefficients for {Sodium Chloride + Sodium Malonate}{aq} at 298.15 K

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ABSTRACT

Activity coefficients of NaCl and Na_2Mal (Sodium Malonate) in their aqueous mixtures, $NaCl + Na_2Mal + H_2O$ at 298.15 K, were determined from emf measurements of galvanic cells. The measurements were carried out at stoichiometric ionic strengths of 0.025, 0.05, 0.075, 0.1, 0.25, 0.5, 0.75, 1, 2, and 3 mol kg^{-1} and at series of ionic-strength fractions $y_B = 3m_B/(m_A + 3m_B)$ within each of these ionic strengths. The results obtained were analysed by the Harned rule, Pitzer ($^S\theta_{ClMal} = 0.0380$ kg mol^{-1}; $\psi_{NaClMal} = -0.0257$ kg^2mol^{-2}) and Lim (HOLL) equations.

Key Words: Mixed Electrolytes/ Activity Coefficients/ Sodium Chloride/ Sodium Malonate.

INTRODUCTION

The knowledge of the activity coefficients of electrolytes is essential for an accurate interpretation of some properties of these electrolytes in solution. The use of sodium malonate (Na_2Mal) in polarographic research on stability constants of complexes that is being carried out in our department, and the lack of information about the behaviour of unsymmetrical mixed-electrolyte solutions with organic dibasic anions [1] led us to study this organic electrolyte. In a previous paper [2] we report the activity coefficients of Na_2Mal in aqueous solutions; in the present, we study the aqueous mixture with NaCl. Because the mixing-electrolyte is unsymmetrical the higher

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order electrostatic terms must be into account to explain the behaviour of this system [3,4].

The values of the activity coefficients here presented, were obtained from the emf measurements of the cell:

$$Na-glass \,|\, NaCl(m_A), Na_2Mal(m_B), AgCl(s) \,|\, Ag \qquad (1)$$
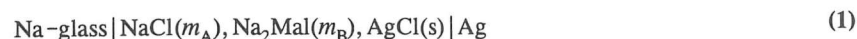
(where m_i represents the molality of i) combined with a reference [1]:

$$Na-glass \,|\, NaCl(m_R), AgCl(s) \,|\, Ag \qquad (2)$$

to eliminate the asymmetry potential of the Na-glass electrode used [5,6]. In cell (2), m_R was always equal to the total ionic strength of the cell (1), i.e.:

$$m_R = m_A + 3m_B \qquad (3)$$

EXPERIMENTAL

Chemicals and Solutions

NaCl, Merck *pro analysi*, was dried in vacuo at 150 °C for 48 hours before use. Na$_2$Mal Merck *pro synthesis*, were used as described elsewhere [1,2].

All mixed electrolyte solutions were obtained from stock aqueous solutions of both NaCl and Na$_2$Mal, which were prepared by weighting the corresponding solute and the conductivity-grade water.

Electrodes, Cells and Apparatus

Na-glass electrodes and the silver-silver chloride electrodes, cells and apparatus used have been described elsewhere [1,7]. The experimental error was less than ± 0.10 mV (i.e. ± 0.0008 in log γ) [1].

RESULTS AND DISCUSSION

The difference in emf between work cell (1) and the reference cell (2), can be expressed as:

$$\Delta E = E_1 - E_2 = k \log \left[\frac{\left(m_R \gamma_R^0\right)^2}{(m_A + 2m_B) m_A \gamma_A^2} \right] \qquad (4)$$

where $k = \ln(10)\, RT/F = 59.158$ mV, and A represents NaCl, and B Na$_2$Mal. γ_A and γ_A^0 stand for the ionic mean activity coefficients of NaCl in the mixed electrolyte and the *pure* solution at $m_R = I = m_A + 3m_B$ concentration, respectively.

Equation (4) can be rearranged as:

$$\log \gamma_A = \log \gamma_A^0 - (1/2) \log \left[(m_A + 2m_B) m_A / m_R^2 \right] - \Delta E / (2k) \qquad (5)$$

From Equation (5) the experimental ionic mean activity coefficient values for NaCl in the mixed-electrolyte solutions can be obtained. γ_A^0 values have been taken from the literature [8]. The values for $-\log \gamma_A$ are summarized in Table 1 at each composition of the mixed electolyte studied.

Harned's Rule

The activity coefficients for NaCl were fitted by the Harned equation [9]:

$$\log \gamma_A = \log \gamma_A^0 - \alpha_A I_B - \beta_A I_B^2 \qquad (6)$$

which relates the logarithm of such activity coefficients to the Na$_2$Mal ionic strength in the mixture, when the total ionic strength remains constant. The values found for the parameters $\log \gamma_A^0$ and α_A are given in Table 2 with the standard deviations of the fit. Since the deviations are within the experimental error, these data follows the Harned Rule ($\beta_A = 0$).

Pitzer's Equations

The Pitzer equation for the electrolyte A (NaCl) can be written as [10,11]:

Table 1. Activity Coefficients in the mixed electrolyte system: $NaCl + Na_2Mal + H_2O$.

I/mol kg^{-1}	y_B	$-\log \gamma_A^b$	$-\log \gamma_B^c$	$-\log \gamma_B^d$
0.02497	0.	0.0652	0.1360	0.1337
0.02497	0.4000	0.0673	0.1340	0.1330
0.02497	0.7000	0.0689	0.1330	0.1326
0.02497	0.9500	0.0694	0.1324	0.1323
0.02497	1.	0.0700^a	0.1323	0.1323
0.05000	0.	0.0852	0.1789	0.1762
0.05000	0.2500	0.0858	0.1771	0.1754
0.05000	0.5000	0.0865	0.1757	0.1748
0.05010	0.7503	0.0862	0.1748	0.1745
0.05000	1.	0.0869^a	0.1740	0.1740
0.07500	0.	0.0985	0.2078	0.2048
0.07500	0.2500	0.0991	0.2056	0.2039
0.07499	0.5001	0.1107	0.2257	0.2248
0.07500	0.7500	0.1001	0.2029	0.2026
0.07500	1.	0.1008^a	0.2023	0.2023
0.1000	0.	0.1085	0.2298	0.2268
0.1000	0.2501	0.1091	0.2275	0.2257
0.1000	0.5001	0.1107	0.2257	0.2248
0.1000	0.9500	0.1119	0.2240	0.2240
0.1000	1.	0.1122^a	0.2240	0.2240
0.2500	0.	0.1423	0.3064	0.3037
0.2500	0.1999	0.1434	0.3042	0.3025
0.2500	0.4000	0.1461	0.3026	0.3016
0.2500	0.6000	0.1480	0.3015	0.3011
0.2502	0.7994	0.1492	0.3011	0.3010
0.2500	0.9500	0.1504	0.3011	0.3011
0.2500	1.	0.1511^a	0.3011	0.3011
0.5000	0.	0.1665	0.3679	0.3657
0.5000	0.2000	0.1699	0.3661	0.3648
0.5000	0.6000	0.1760	0.3648	0.3645
0.4999	0.8000	0.1782	0.3652	0.3652
0.4999	0.9500	0.1830	0.3660	0.3660
0.5000	1.	0.1827^a	0.3664	0.3664

Table 1. Continued.

I/mol kg^{-1}	y_B	$-\log \gamma_A^b$	$-\log \gamma_B^c$	$-\log \gamma_B^d$
0.7500	0.	0.1777	0.4034	0.4013
0.7499	0.2000	0.1827	0.4024	0.4013
0.7499	0.4001	0.1857	0.4022	0.4018
0.7500	0.6000	0.1906	0.4028	0.4029
0.7502	0.7998	0.1956	0.4043	0.4045
0.7500	1.	0.1995^a	0.4065	0.4065
1.000	0.	0.1828	0.4274	0.4254
1.000	0.2000	0.1891	0.4273	0.4266
1.001	0.5997	0.2014	0.4297	0.4302
1.000	0.8000	0.2063	0.4322	0.4327
1.000	0.9500	0.2118	0.4346	0.4348
1.000	1.	0.2130^a	0.4355	0.4355
2.000	0.	0.1754	0.4745	0.4731
2.000	0.2002	0.1876	0.4784	0.4793
1.999	0.6002	0.2149	0.4884	0.4910
2.000	0.8000	0.2264	0.4947	0.4965
2.000	0.9500	0.2381	0.4999	0.5005
2.000	1.	0.2406^a	0.5018	0.5018
3.000	0.	0.1464	0.4876	0.4836
3.000	0.1999	0.1677	0.4952	0.4928
3.000	0.4000	0.1876	0.5033	0.5022
3.000	0.6000	0.2072	0.5120	0.5116
3.009	0.8008	0.2271	0.5213	0.5213
3.000	1.	0.2472^a	0.5308	0.5308

a: from Harned's Rule; b: experimental; c: from Pitzer's eq.; d: from Lim (HOLL) eq.

Table 2. Parameters ot the Harned Equation for NaCl.

I/mol kg^{-1}	$-\log \gamma_A^0$	α_A/kg mol^{-1}	σ/mV
0.025	0.0653	0.18$_5$	0.04
0.05	0.0854	0.029	0.05
0.075	0.0986	0.0296	0.01
0.1	0.1085	0.0371	0.04
0.25	0.1424	0.0348	0.03
0.5	0.1664	0.0327	0.12
0.75	0.1777	0.0291	0.07
1.	0.1830	0.0300	0.06
2.	0.1750	0.0328	0.09
3.	0.1471	0.0334	0.07

In all cases $\beta_A = 0$.

$$\ln(\gamma_A/\gamma_A^0) = -\left[4B_A - B_B - \theta_{ClMal} + I\left(4B_A' - B_B' - \theta_{ClMal}' + 5C_A^\phi - C_B^\phi/\sqrt{2} - \psi_{NaClMal}\right)\right]m_B \quad (7)$$
$$-\left[B_B' - 3B_A' + 3\theta_{ClMal}' - (7/2)C_A^\phi + C_B^\phi/\sqrt{2} + 2\psi_{NaClMal}\right]m_B^2$$

where:

$$B_i = \beta^{(0)} + (2\beta^{(1)}/\alpha^2 I)\left[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})\right] \quad (8.a)$$

and,

$$B_i' = (2\beta_i^{(1)}/\alpha^2 I^2)\left[-1 + (1 + \alpha I^{1/2} + (1/2)\alpha^2 I)\exp(-\alpha I^{1/2})\right] \quad (8.b)$$

The value assumed for α is 2.0 kg$^{1/2}$mol$^{-1/2}$ [8]. The values of the parameters $\beta_i^{(0)}$, $\beta_i^{(1)}$ and C_i^ϕ for the *pure* electrolytes are given in Table 3. From these values those for θ and ψ were obtained by least-squares method, assuming the mixing parameter θ to be constant [10] and therefore, $\theta'=0$. These values are presented in Table 4 with the standard deviation, in mV, of this fitting and which would be obtained if θ and ψ are zero. The figure found for the standard deviation, 0.17, which is higher than the experimental error, demands an improved fitting.

Pitzer [3,4] has proved that is essential to consider the higher-order electrostatic terms to study unsymmetrical mixture properly. According to this author, the parameter θ can be expressed as:

$$\theta_{ClMal} = {}^S\theta_{ClMal} + {}^E\theta_{ClMal} \quad (9.a)$$

in which ${}^S\theta$ arises from all the short-range forces, and ${}^E\theta$ from the higher-order electrostatic terms. Similarly, the value of θ' is:

$$\theta_{ClMal}' = {}^S\theta_{ClMal}' + {}^E\theta_{ClMal}' = {}^E\theta_{ClMal}' \quad (9.b)$$

in which ${}^S\theta'$ has been omitted because it is negligible (${}^S\theta$ is constant). These ${}^E\theta$ and ${}^E\theta'$ were calculated from the expressions [1,4]:

$$^E\theta = (z_{Cl}z_{Mal}/4I)\left[J(x_{ClMal}) - (1/2)J(x_{ClCl}) - (1/2)J(x_{MalMal})\right] \quad (10.a)$$

and,

Table 3. Pitzer parameters for pure solutions of NaCl and Na$_2$Mal.

Electrolyte	$\beta_i^{(0)}$/kg mol^{-1}	$\beta_i^{(1)}$/kg mol^{-1}	C_i^ϕ/kg^2 mol^{-2}	max. m	Reference
NaCl	0.0754	0.2770	0.00140	6	[8]
Na$_2$Mal	0.1401	1.340	0	1	[2]

Table 4. Summary of the Pitzer parameters values in the mixed electrolyte system NaCl+Na$_2$Mal+H$_2$O.

${}^E\theta = {}^E\theta' = 0$			${}^E\theta \neq {}^E\theta' \neq 0$		
θ_{ClMal}	$\psi_{NaClMal}$	σ/mV	${}^S\theta_{ClMal}$	$\psi_{NaClMal}$	σ/mV
0^a	0^a	0.99	0^a	0^a	0.22
−0.10691	0.01990	0.17	0.03788	−0.02580	0.12

a: fixed value; θ: kg mol^{-1}; ψ: kg^2 mol^{-2}

Table 5. Summary of the values calculated for the higher-order electrostatic terms.

I/mol kg^{-1}	$-{}^E\theta_{12}$/kg mol^{-1}	${}^E\theta_{12}'$/kg^2 mol^{-2}
0.025	0.74560	11.7341
0.05	0.56265	4.7083
0.075	0.47360	2.7246
0.1	0.41775	1.8381
0.25	0.27615	0.51087
0.5	0.19952	0.18946
0.75	0.16439	0.10532
1.	0.14310	0.06919
2.	0.10213	0.02500
3.	0.08370	0.01372

$$^E\theta'_{ClMal} = -(^E\theta_{ClMal}/I) + (z_{Cl}z_{Mal}/8I^2)\big[x_{ClMal}J'(x_{ClMal}) - (1/2)x_{ClCl}J'(x_{ClCl}) \\ - (1/2)x_{MalMal}J'(x_{MalMal})\big]$$ (10.b)

where $x_{ij} = 6z_iz_jA_\phi I^{1/2}$, A_ϕ is the Debye-Hückel coefficient for the osmotic coefficient [8,12], and z_i, z_j are the valence of the ions. The functions $J(x_{ij})$ and $J'(x_{ij})$ are given by the equations of Pitzer [4,13]. The values of these $^E\theta$ and $^E\theta'$ parameters are summarized in Table 5 at the different values of ionic strength. The values for $^S\theta$ and ψ were obtained by a least-squares method. The values thus found are also presented in Table 4.

As can be seen from the values in Table 4, if only the higher-order electrostatic terms are take into account ($^S\theta=0$ and $\psi=0$), the standard deviation figure found, 0.22 mV, is much smaller (by a factor of 4.5) than that obtained when these electrostatic terms were ignored, 0.99 mV. Therefore, it can be concluded that the main factor which must be considered, is that of these higher-order terms. Finally, the best standard deviation value is obtained when all parameters are considered not to be zero. This value, 0.12 mV, is of the same order as that of the experimental error.

From the knowledge of $^S\theta$ and ψ, the activity coefficient values for Na$_2$Mal in the mixed-electrolyte solution, γ_B, were calculated by the Pitzer equation [4,13]:

$$\ln\gamma_B = \ln\gamma_B^0 + (m_A/3)\Big\{4B_A - (2/3)B_B + 2\theta_{ClMal} + I[4B_A' - (2/3)B_B' + 2\theta'_{ClMal} \\ + (8/3)C_A^\phi + (4/3)\psi_{NaClMal}]\Big\} + (m_A^2/3)\big[2B_A' - (2/3)B_B' - 2\theta'_{ClMal} \\ + (4/3)C_A^\phi - (\sqrt{2}/6)C_B^\phi - (1/3)\psi_{NaClMal}\big]$$ (11)

The values for $-\log\gamma_B$ are summarized in the fourth column in Table 1.

Lim (HOLL) Equation

The activity coefficients of a binary electrolyte mixture, MX + M$_2$Y (with a common cation) can be given by the following equations [14,15]:

$$\ln(\gamma_A/\gamma_A^0) = (y_B/2)\big[g_0 + g_0'I(1-y_B) + g_1I(2-3y_B) - \Phi\big]$$ (12)

and

where $g_0' = \partial g_0/\partial I$, and Φ [14]:

$$\ln(\gamma_B/\gamma_B^0) = (1-y_B)I\big[g_0 + g_0'Iy_B + g_1I(1-3y_B) + \Phi\big]$$ (13)

$$\Phi = \big[(1-\phi_B) - 2(1-\phi_A)\big](1/I)$$ (14)

In the higher-order limiting-law (HOLL) method the parameters, g_n, were forced to satisfy the higher-order limiting-law and the consistency condition [15]. The following variation of g_0 with respect to I can be suggested [15], keeping in mind the higher order limiting law for unsymmetrical mixing ($g_0 \to \ln I$ as $I \to 0$) and the observations of Scatchard and Prentiss [16,17]:

$$g_0 = \lambda\ln I + \mu I + \nu I^{3/2}$$ (15.a)

and, therefore:

$$g_0' = (\lambda/I) + \mu + (3/2)\nu I^{1/2}$$ (15.b)

g_1 is necessarily an I-independent constant in order to satisfy the cross-differential condition [15]. The values obtained from the fitting of experimental results are given in Table 6, together with the corresponding standard deviation.

From the knowledge of λ, μ, ν and g_1, the activity coefficient values for Na$_2$Mal in the mixed-electrolyte, γ_B, were calculated by the equation (13). The values for $-\log\gamma_B$ are summarized in the last column in Table 1.

Trace activity coefficients

Finally, in Figure 1, the trace values $\log\gamma_A^{tr}$ and $\log\gamma_B^{tr}$, are plotted against $I^{1/2}$ together with those of the *pure* electrolytes, $\log\gamma_A^0$ and $\log\gamma_B^0$. First, it can be seen that γ_A^0 is higher than γ_A^{tr}, whereas γ_B^0 is smaller than γ_B^{tr}. The fact that at high ionic strength the difference between γ_i^{tr} and γ_i^0 increases, could be interpreted in terms of an increase in the ionic pairs (Na-Mal)$^-$ formation, with the corresponding decrease in the free Na$^+$ ions in the solution. The formation of ion pairs are more favoreced in Na$_2$Mal solutions than in Na$_2$Succ (Succ=succinate) ones [2,18].

Table 6. Summary of the Lim-HOLL parameters values.

$\lambda/\text{kg mol}^{-1}$	$\mu/\text{kg}^2 \text{ mol}^{-2}$	$\nu/\text{kg}^{5/2} \text{ mol}^{-5/2}$	$g_1/\text{kg}^2 \text{ mol}^{-2}$	σ/mV
0.05815	−0.08381	0.02467	−0.00021	0.10
0.05829	−0.08334	0.02439	0^a	0.10

a: fixed value.
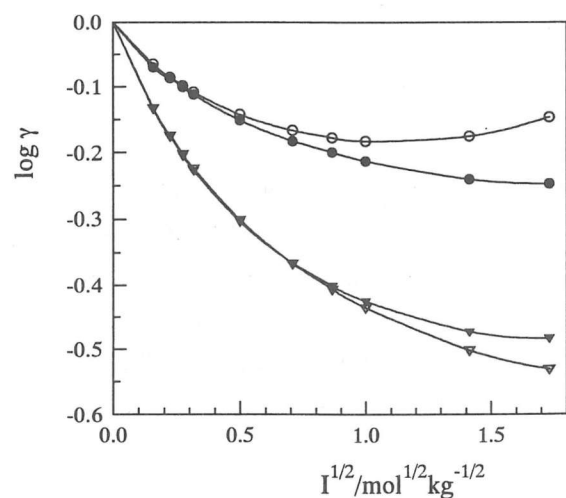
Figure 1. Plot of log γ against $I^{1/2}$ for the mixture $NaCl+Na_2Mal+H_2O$:

○ NaCl pure soln.

● NaCl traces.

▽ Na_2Mal pure soln.

▼ Na_2Mal traces.

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