

## 에틸렌디아민 非水溶液中에서의 1 : 1염의 活性係數

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## Activity Coefficients of Uni-univalent Electrolytes in Anhydrous Ethylenediamine

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**요 약.** 非水溶液 에틸렌디아민中에서, K-Hg, KI(C<sub>1</sub>) || (C<sub>2</sub>)KI, Hg-K의 濃淡電位를 構成하여, 電位差法으로 電位差를 測定하여, Debye-Hückel型의 活性係數式으로 計算한 理論値와 比較한 結果 Marshall-Grunwald 式이 잘 適用되었다.

**Abstract.** The dependence of ionic activity and electrode potential upon electrolyte concentration in ethylenediamine includes the effects of ion-pair formation involving all possible combinations of cations and anions represent in the solution and includes the ion-atmosphere effects of dissociated ions. For calculating activity coefficients, Debye-Hückel limiting law, extended Debye-Hückel equation, and Marshall Grunwald equation were used in comparison of experimental and calculated plots of the electromotive force of the cell versus the logarithm of concentration. The fit of the experimental points to the theoretical curves was improved in case of the Marshall-Grunwald equation.

### Introduction

No careful study of activity coefficients or their calculation by Debye-Hückel types equation has yet been made in ethylenediamine over an appreciable concentration range. In ethylenediamine with such a low dielectric constant, solutions of electrolytes may be expected to deviate greatly from ideality because of ion-pair formation and enhanced longer range ion atmosphere effects.

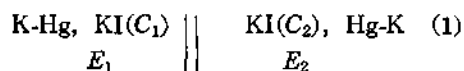
Reference to the derivations of the equation used in analysing conductance data by the Fuoss Kraus<sup>1</sup> procedure, which of low dielectric constant, reveals that the activity coefficients were usually calculated by means of an extended form of the Debye-Hückel equation. In their report, parameter  $a$  used to be about 4~5 Å for most alkali metal salts in ethylenediamine. On the other hand, in the studies of ethylenediamine, Hillard and Schmidt<sup>2</sup> used the Debye-Hückel limiting law in concentration with the

Fuoss-Krous procedure. Because their final plots were either linear, or very nearly so. Bruckenstein and Mukherjee<sup>3</sup> used also the limiting law to calculate activity coefficients. One promising approach that appeared to be directly applicable to ethylenediamine solutions was that of Marshall and Grunwald<sup>4</sup>, who derived and tested the equation for calculating the activity of HCl in mixed aqueous dioxane solutions with a dielectric constant as low as 10.

In the present work, the electromotive force of concentration cell with minimized liquid junction potentials was measured by potentiometric method. In comparison of experimental and calculated plots of the electromotive force of cell versus the logarithm of concentration, the Marshall and Grunwald equation was improved considerably the fit of theoretical calculation curve.

### Theoretical

Using two electrodes reversible to the same ion constituent, it is possible to set up and measure potentials of concentration cells with transference. A typical cell of this kind, which would be useable in ethylenediamine could be made up of two-phase potassium amalgam in contact with ethylenediamine containing a potassium salt at two different concentrations, e. g.,



This cell has an electrolyte-electrolyte boundary, more commonly referred to as a "liquid junction", between two solutions of the same salt at different concentrations. The electromotive force of the cell given above would be the difference between  $E_1$  and  $E_2$ , at 25° C,

$$\begin{aligned} \Delta E &= E_1 - E_2 \\ &= 0.059 \log a_{K^+} - 0.059 \log a'_{K^+} + E_j \quad (2) \end{aligned}$$

On the other hand, equilibria involving uni-univalent electrolytes and the effects of ion-pair formation on electrode potentials in anhydrous ethylenediamine have been studied in detail by Schaap and co-workers<sup>5</sup>, Bruckenstein<sup>3</sup> and the author<sup>6</sup>. The associate ion-pair can be treated as neutral species in equilibrium with the free ions,



The law of mass action can be applied to give

$$K_{MX} = \frac{\{M^+, X^-\}}{(M^+)(X^-)} = \frac{a_{MX} f_{MX}}{a_M^+ a_X^- f_M^+ f_X^-} \quad (4)$$

where  $K_{MX}$  is the thermodynamic association constant. All ion-pairs are enclosed in brace and the square brackets denote stoichiometric concentration. Assuming the activity coefficients of the uni-valent ions to be equal and considering  $f_{MX}=1$ , the equation becomes

$$K_{MX} = \frac{\sum_{MX} - a_M^+ / f_M^+}{(a_M^+)^2 (f)^2} \quad (5)$$

Therefore, the activity of the cation or anion in ethylenediamine is given by the expression

$$(M^+) = (X^-) = \frac{(1 + 4 \sum_{MX} K_{MX} f_i^2)^{1/2} - 1}{2 K_{MX} f_i} \quad (6)$$

Accordingly, equation 2 will be

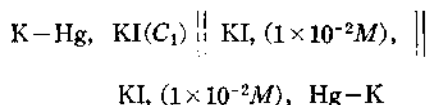
$$\Delta E = E_j + 0.059 \log \frac{(\sqrt{1 + 4 \sum_{MX} K_{MX} f_i^2} - 1) f_i'}{(\sqrt{1 + 4 \sum_{MX} K_{MX} f_i'^2} - 1) f_i} \quad (7)$$

where,  $K_{MX}$  and  $\sum_{MX}$  are the ion-pair association constant and total analytical concentration of KI in ethylenediamine, respectively. Equation 7 can be used for calculated and experimented values of activity coefficients if the liquid junction potentials,  $E_j$  can either be calculated or eliminated.

### Experimental

**Preparation Potassium Amalgam.** The potassium amalgam was prepared by electrolysis of potassium hydroxide in methanol using a mercury cathode and a platinum screen anode. The product is two-phase amalgam (mercury saturated with potassium), which is washed with methanol to remove excess potassium hydroxide and is preserved under dry petroleum ether.

**Concentration Cell.** Three-compartment cell<sup>6</sup> for electrochemical measurements in anhydrous ethylenediamine was used:



**E. m. f. Measurements.** The potassium amalgam electrode half-cell was filled and assembled in dry box under nitrogen atmosphere. The solutions were saturated immediately with nitrogen and cell was placed in thermostat at 25 °C until temperature equilibrium was attained. Then, a current of nitrogen was allowed to stream through the solution for about 5 min. before taking the electromotive force reading, *e. m. f.* values then were recorded every 5 to 10 min. by potentiometer.

### Results and discussion

**Choice of Activity Coefficients.** The various equations which have been used for calculating activity coefficients in solvents of low dielectric constant are given in *Table 1*.

Although the limiting law is convenient, it probably over-corrects, especially at higher concentrations. The term  $(1 + \delta\sqrt{\mu})$  in the denominator of the extended Debye-Hückel equation in *Table 1*, decreases the correction, but introduces the arbitrary parameter, *a*, the distance of closest approach. In this case, it was assumed that the sizes of the solvated ions are larger in ethylenediamine than in water and thus we chose the value of about 5 Å for a typical distance of closest approach for alkali metal salts in ethylenediamine, compared to 3~4 Å in water.

In the Marshall-Grunwald equation,<sup>4</sup> the ion-size parameter in ethylenediamine is taken to be the Bjerrum critical ion-pairing distance,  $a=q=22 \text{ \AA}$ , which may be calculated. The values of the mean activity coefficient,  $f_{\pm}$ , are obtained by successively solving the equation  $C_i^2 = (\sum_{MX} - C_i) / K f_{\pm}^2$  until the values of  $C_i$  and  $f_i$  changed insignificantly. The symbol  $C_i$  represents the concentration of the dissociated

Table 1. Debye Huckel types equations for activity coefficients

	Formula-in H <sub>2</sub> O	Formula in en	Parameter <i>a</i> (Å)
Debye Hückel limiting law	$-\log f_i = AZ^+Z^- \sqrt{\mu}$	$-\log f_i = 8.02 \sqrt{\mu}$	—
Extended Debye Hückel equation	$-\log f_i = \frac{\beta \sqrt{\mu}}{1 + \delta \sqrt{\mu}}$	$-\log f_i = \frac{8.02 \sqrt{\mu}}{1 + 4.12 \sqrt{\mu}}$	5
Marshall Grunwald equation	$-\log f_i = \frac{\beta \sqrt{\mu}}{(1 + \delta \sqrt{\mu})^{2/3}}$	$-\log f_i = \frac{8.02 \sqrt{\mu}}{(1 + 18.1 \sqrt{\mu})^{2/3}}$	22

$$\beta = (0.4343 \frac{e^2}{2DkT}) (8\pi N e^2 / 1000 D k T)$$

$$\delta = (a) (8\pi N e^2 / 1000 D k T)$$

$$D = 12.5; T = 298^\circ \text{C}; N = \text{Avogadro number};$$

$$k = \text{Boltzmann}; \mu = \text{Ionic strength}.$$

ion.

Activity coefficients calculated for uni univalent electrolytes in ethylenediamine using the Debye-Hückel limiting law, the extended Debye-Hückel equation, and the Marshall-

Grunwald equation are shown in Fig. 1 as a function of the total stoichiometric concentrations of the electrolyte,  $\Sigma_{MX}$ , and in Fig. 2 as a function of  $K_{MX}$ , the ion-pair association constant.

**Liquid Junction Potential.** Liquid junction

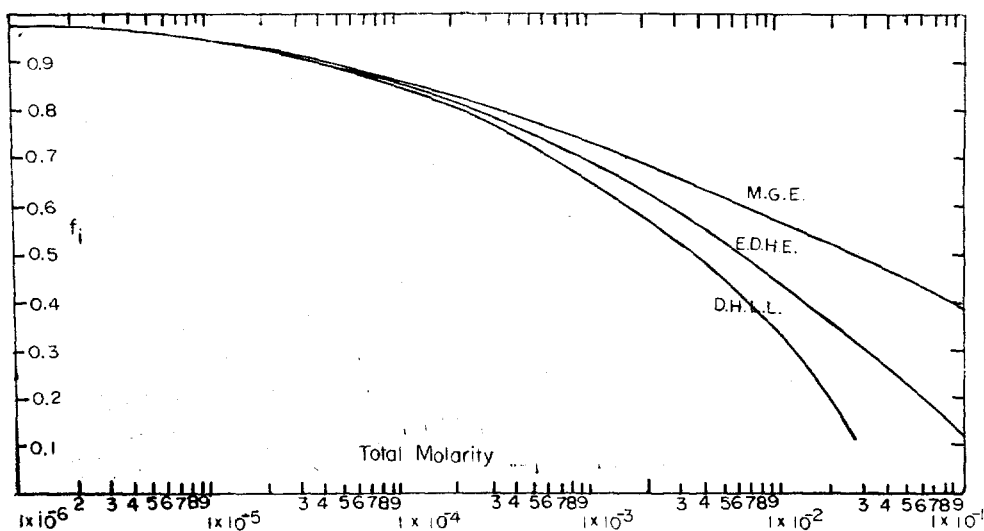


Fig. 1. Activity coefficients for MX ( $K_{MX}=50,000$ ) in ethylenediamine calculated by means of the D. H. L., E. D. H. E., and M. G. E., as function of total stoichiometric molarity of electrolyte present

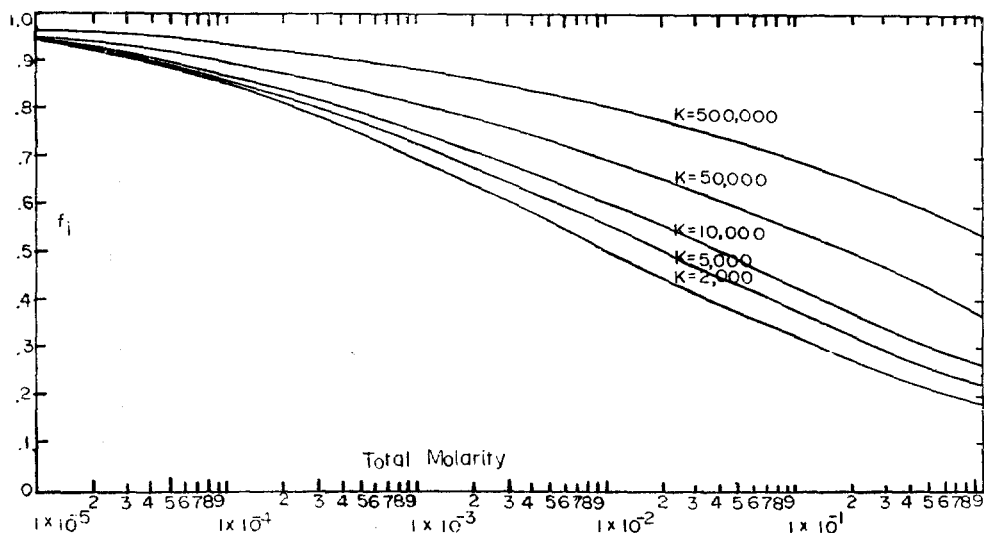


Fig. 2. Activity coefficients for 1:1 electrolytes in ethylenediamine calculated by means of the Marshall-Grunwald equation as a function of total stoichiometric molarity of electrolyte present and a function of the ion pairing association constant of the electrolyte

Table 2. *E. M. F.* of the cell and dependence of the choice of activity coefficients.

Concentrations (C <sub>1</sub> )	<i>E</i> <sub>obs.</sub>	M. G. E.	<i>E</i> <sub>theor.</sub>	
			<i>f</i> <sub>±=1</sub>	D. H. L. L.
K-Hg, KI(C <sub>1</sub> ),    KI(1×10 <sup>-2</sup> M), Hg-K				
9.91 10 <sup>-5</sup> M	77.27 mV.	80.44 mV.	77.4 mV.	80.62 mV.
1.96 10 <sup>-4</sup>	65.70	66.39	63.62	66.18
2.91 10 <sup>-4</sup>	58.70	58.84	56.04	59.64
3.85 10 <sup>-4</sup>	53.30	53.77	50.87	53.97
5.66 10 <sup>-4</sup>	46.80	46.77	44.01	47.76
7.407 10 <sup>-4</sup>	41.10	43.15	40.04	43.06
9.091 10 <sup>-4</sup>	38.04	38.66	35.97	39.96
1.071 10 <sup>-3</sup>	35.55	36.06	33.30	37.07
1.453 10 <sup>-3</sup>	30.20	31.04	28.72	32.28
1.660 10 <sup>-3</sup>	27.85	30.20	26.28	30.30
2.479 10 <sup>-3</sup>	21.80	22.84	20.32	24.14
3.279 10 <sup>-3</sup>	17.12	18.22	16.13	19.94
4.839 10 <sup>-3</sup>	11.00	12.55	10.34	14.39
6.349 10 <sup>-3</sup>	6.50	8.43	6.41	11.05
7.813 10 <sup>-3</sup>	3.55	5.45	3.45	8.30
9.231 10 <sup>-3</sup>	0.55	3.18	1.13	6.01
1.061 10 <sup>-2</sup>	1.62	1.13	0.78	5.61
1.194 10 <sup>-2</sup>	2.95	0.47	2.55	2.82
1.412 10 <sup>-2</sup>	5.36	2.83	4.87	3.91
1.571 10 <sup>-2</sup>	6.76	4.48	6.37	1.31
2.418 10 <sup>-2</sup>	12.77	10.48	12.20	
2.970 10 <sup>-2</sup>	15.30	13.35	14.98	
4.366 10 <sup>-2</sup>	20.70	18.69	20.15	
7.083 10 <sup>-2</sup>	25.00	25.22	26.60	
9.726 10 <sup>-2</sup>	28.13	29.51	30.49	
1.230 10 <sup>-1</sup>	29.40	32.35	33.87	
1.480 10 <sup>-1</sup>	29.00			
1.961 10 <sup>-1</sup>	30.00			
2.638 10 <sup>-1</sup>	25.50			
3.706 10 <sup>-1</sup>	22.00			
4.567 10 <sup>-1</sup>	22.00			

potentials in Galvanic cells are a recurrent problem. From the Nernst formula<sup>7</sup> for liquid junction between two different solutions of

the same electrolyte, it shows that the nearer the cationic transport number is to 0.5, the smaller is the liquid junction potential. Since the

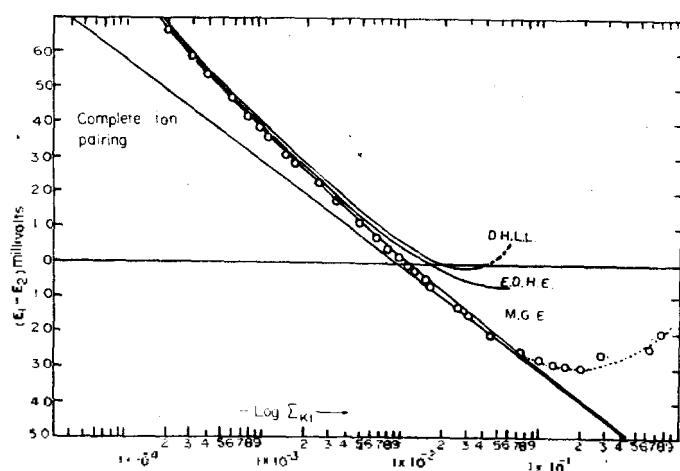


Fig. 3. Concentration cell potentials and choice of activity coefficients

ionic mobilities\* of  $K^+$  and  $I^-$  ions in ethylene diamine have been found to be very nearly equal, potassium iodide was chosen for the potentiometric measurements in a concentration cell, so that the liquid junction potentials would be reduced to negligible values.

**Experimental Data and Calculation.** The experimental data are summarized in Table 2 and compared with the potentials calculated using activity coefficients predicted by the Debye-Hückel limiting law, the Marshall-Grunwald equation, and the case where the

\* Unpublished results: The association constant and limiting conductance for KI is to be,  $K_{MX}=3150$ ,  $\lambda_0^+=71.9$ ,  $\lambda_0^*=35.4$ ,  $\lambda_0^-=36.5$ , respectively.

activity coefficients are assumed 1.0 at all concentrations.

The calculation curves are shown in Fig. 3.

The points are experimental and solid lines are theoretical. As shown by general shape of the concentration dependence in Fig. 3, Marshall-Grunwald equation is to be preferred. However, the limiting law probably overcorrects, especially at higher concentrations of potassium iodide.

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