

비수용액 에틸렌디아민 중에서의 전위차 중화 적정 연구

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Potentiometric Neutralization Titration of Acid-Base in Anhydrous Ethylenediamine

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요 약. 비수용액 에틸렌디아민 중에서 산-알칼리의 전위차 중화 적정 이론을 고찰하여 실험한 결과 이론과 잘 일치하였다.

ABSTRACT. Equilibria equations, applicable to solvent of low dielectric constant, were derived for potentiometric neutralization titration. Effects of salt and solvent were studied in potentiometric neutralization titration using ethylenediamine as solvent. Good agreement was observed between theory and experimental results.

INTRODUCTION

Although a large number of practical applications¹⁻⁷ of neutralization titrations have been developed using ethylenediamine as solvent, no careful physical and chemical studies of the equilibria involved have yet been made, because of the lack of adequate theory for their interpretation and lack of ion-pair formation constants of acids and salts.

In order to make accurate calculations of the effect of electrolyte concentration on cell potentials and neutralization titration curves, it is necessary to know the following factors: (1) ion-pair association constants of all possible combination of cations, and anions, (2) activity coefficients, (3) the autoprotolysis constant of

ethylenediamine, and liquid junction potentials, if they are present. In addition, it is necessary to have a stable, reproducible reference electrode and indicator electrode. These considerations have been applied to potentiometric titrations as discussed in this paper.

EXPERIMENTAL

Preparation and Pretreatment of Platinized Platinum Electrode. A platinum wire wound around a sintered glass tube was coated with platinum black by electrolytic reduction of a 2 % solution of chloro-platinic acid containing a small quantity of lead acetate using a current density of 200 mA for 3 minutes.⁸ After electrolysis the electrodes were cathodized in H₂SO₄ (1:1) solution, rinsed several times with conductivity

water, and stored in dilute hydrochloric acid solution.

Before being used in ethylenediamine, the platinized platinum electrodes were washed with distilled water, rinsed with purified acetone, dried by air, and stored in anhydrous ethylenediamine solution containing an acid. With the platinized platinum electrode, reproducible results were obtained after the following pre-treatment:

(1) polarographic current-voltage curve was recorded using the platinum electrode as the polarized electrode.

(2) The potential between anodization and cathodization, i. e, the point at which the zero current line was crossed, was measured from the current-voltage curve.

(3) The potential of the electrode was held at this potential (usually about +0.6 volts versus the zinc amalgam-zinc chloride reference electrode) for five to ten minutes.

Reference Electrode⁹ and cell. The zinc amalgam zinc chloride reference electrode was prepared by contacting two-phase zinc amalgam with ethylenediamine saturated with zinc chloride, saturated with sodium chloride. Three-compartment cell for potentiometric titrations was used as shown in *Fig. 1*.

Emf measurements. The hydrogen electrode half-cell was filled and assembled in dry box under nitrogen atmosphere. The solutions were saturated immediately with nitrogen, and half-cell was placed in a thermostat at 25°C until temperature equilibrium was attained. Then, a current of hydrogen was allowed to stream through the solution for about 5 min, before taking emf reading.

Preparation of Sodium Aminoethoxide and Its Autoprotolysis Constant (K_B). 0.7 grams of sodium metal were dissolved in 12~15 ml of purified anhydrous ethanolamine, diluted to

250 ml with distilled ethylenediamine.

The autoprotolysis constant (K_B) of the sodium aminoethoxide was determined by sodium amalgam electrode¹⁰ as shown in *Table 1*.

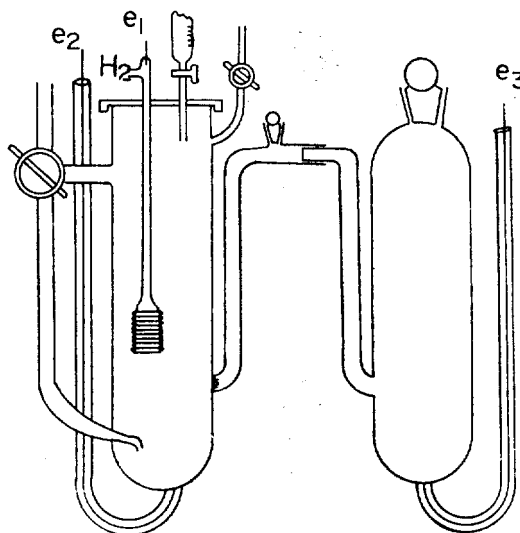


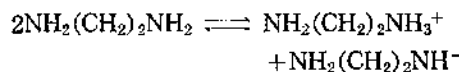
Fig. 1. Three-compartment cell for electrochemical measurements in anhydrous ethylenediamine: ¹¹ e₁, Platinized platinum electrode; e₂, Mercury pool indicator electrode; e₃, Zinc amalgam-zinc chloride reference electrode¹¹

Table 1. Ion-pair formation constant of $K_B(E_{Na-amalgam}$ used, -0.240 volts).

Concentration, (mmole)	E_{obs}	K_B
7.78	0.43000	1.39×10^5
10.50	.45365	1.71×10^5
13.04	.45000	1.60×10^5
19.73	.44500	1.64×10^5
23.09	.44020	1.32×10^5
7.78	.45485	1.37×10^5
10.50	.45105	1.39×10^5
11.79	.45005	1.44×10^5
13.04	.44920	1.50×10^5
14.25	.44885	1.60×10^5
17.64	.44840	1.60×10^5
7.407	.45315	1.31×10^5
9.090	.45225	1.38×10^5
12.280	.44890	1.36×10^5
13.790	.44725	1.136×10^5
10.700	.45075	1.38×10^5

RESULTS and DISCUSSION

1. **Determination of the Factors Used.** The ion-pair formation constants of various acids and salts, K_{HX} , K_{MX} , were reported previously by the author^{11, 13} and other workers.¹⁴ For acid-base neutralization titrations, the over-all association constant of sodium aminoethoxide dissolved in ethylenediamine as a titrant¹⁰ was measured using a sodium amalgam electrode and found to be 1.441×10^5 . Using this value along with data obtained for the titration of HBr a value of 2.3×10^{-16} was calculated for the autoionization constant of the solvent ethylenediamine, (K_s). Data are given in Table 2, conlum 4. The autoionization of ethylenediamine is assumed to be as follows:



2. **Acid-base Titration in Presence of Salts.** Consider the case of an acid, HX, being titrated with base, MOR, in the presence of a large excess of a supporting salt, MX, where X is a common anion. The symbol F is defined as the fraction of the acid neutralized by the base, i. e., $F = \Sigma_B / \Sigma_{HX}^0$, where Σ_B is the analytical concentration of base added.

The before the equivalence point,

$$\Sigma_{HX} = (1-F) \Sigma_{HX}^0 = \Sigma_{HX}^0 - \Sigma_B \quad (1)$$

If MX is present at a much higher concentration, the anion activity, $[X^-]$ may be considered to be governed solely by the supporting electrolyte MX, and may be calculated from the concentration and association constant of MX alone by means of¹⁴

$$[X^-] = \frac{(1 + \Sigma_{MX} K_{MX} f_i^2)^{\frac{1}{2}} - 1}{2K_{MX} f_i}$$

Inserting the equation for $[X^-]$ into the equilibrium expression involving HX allows

Table 2. Autoionization constant K_s of ethylenediamine (Data from titrations of HBr with sodium aminoethoxide after end point).

Acid	Fraction acid titrated	E_{obs}	K_s
1×10^{-2}	1.03	0.23320	4.51×10^{-16}
HBr without NaBr	1.07	.20370	3.32×10^{-16}
NaBr	1.10	.18880	2.66×10^{-16}
	1.16	.17330	2.32×10^{-16}
	1.22	.16520	2.32×10^{-16}
	1.34	.15640	2.52×10^{-16}
	1.46	.15120	2.77×10^{-16}
	1.59	.14840	3.15×10^{-16}
	1.71	.14600	3.42×10^{-16}
	1.83	.14450	
$1 \times 10^{-2} M$	1.06	.23090	2.26×10^{-16}
HBr with 0.1M NaBr	1.13	.20180	1.57×10^{-16}
NaBr	1.19	.18910	1.40×10^{-16}
	1.25	.18170	1.20×10^{-16}
	1.38	.17650	1.70×10^{-16}
	1.50	.17300	1.92×10^{-16}
	1.63	.17055	2.19×10^{-16}
	1.75	.16850	2.40×10^{-16}
	$1 \times 10^{-2} M$	1.05	0.27040
HBr with 1M NaBr	1.08	.25450	1.92×10^{-16}
NaBr	1.15	.23980	2.20×10^{-16}
	1.22	.23150	2.14×10^{-16}
	1.29	.22550	2.20×10^{-16}
	1.37	.22180	2.44×10^{-16}
	1.44	.21900	2.58×10^{-16}
	1.58	.21450	2.89×10^{-16}

the cationic activity to be calculated. Then the expression for $[H^+]$ is represented by the following equation, which does not neglect the dissociation of either HX or MX. The symbol f_i is mean activity coefficients.

$$[H^+] = \frac{\Sigma_{HX} - [H^+]/f_i}{K_{HX}[X^-]} \quad (2)$$

and,

$$[H^+] = (1-F) \Sigma_{HX}^0 \frac{2K_{MX} f_i}{K_{HX}(1 + 4\Sigma_{MX} K_{MX} f_i^2)^{\frac{1}{2}} - K_{HX} + 2K_{MX}} \quad (3)$$

If the salt MX is present at concentration above $10^{-2}M$ and dissociation is neglected, than the expression for hydrogen ion activity simplifies to

$$[H^+] = \frac{(1-F) \Sigma_{HX}^{\circ} (K_{MX})^{\frac{1}{2}}}{K_{HX} (\Sigma_{MX})^{\frac{1}{2}}} \quad (4)$$

$$pH = \log \frac{K_{HX}}{(K_{MX})^{\frac{1}{2}}} + \log \frac{(\Sigma_{MX})^{\frac{1}{2}}}{(1-F) \Sigma_{HX}^{\circ}} \quad (5)$$

It is obvious from equation 5 that the pH decreases with increasing K_{MX} and Σ_{HX}° , and increases as K_{HX} and Σ_{MX}

After the equivalence point, since excess base has been added,

$$[OR^-] = \frac{\Sigma_{MOR} - [OR^-]/f_i}{K_{MOR} [M^+]} \quad (6)$$

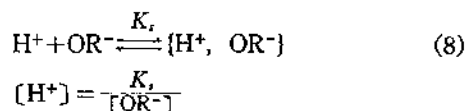
substituting the equation,¹³

$$[M^+] = \frac{(1 + 4 \Sigma_{MX} K_{MX} f_i^2)^{\frac{1}{2}} - 1}{2 K_{MX} f_i}, \text{ in to the}$$

equation 6 becomes,

$$[OR^-] = \frac{2 K_B \Sigma_{MOR} f_i}{K_{MOR} (1 + 4 \Sigma_{MX} K_{MX} f_i^2)^{\frac{1}{2}} - K_{MOR} + 2 K_{MX}} \quad (7)$$

Since the ionization of ethylenediamine is



and following the equivalence point,

$$\Sigma_{HX} = (F-1) \Sigma_{HX}^{\circ}.$$

It follows that

$$[H^+] = \frac{K_i [K_B (1 + 4 \Sigma_{MX} K_{MX} f_i^2)^{\frac{1}{2}} - K_{MOR} + 2 K_{MX}]}{2 (F-1) \Sigma_{MX}^{\circ} K_{MX} f_i} \quad (9)$$

Some typical titration curves calculated for the strong acid, HBr, in the presence of higher concentrations of the common anion salt, NaBr, 0.1M and 1.0M are shown in Fig. 2. In each case the solid lines are theoretical and points

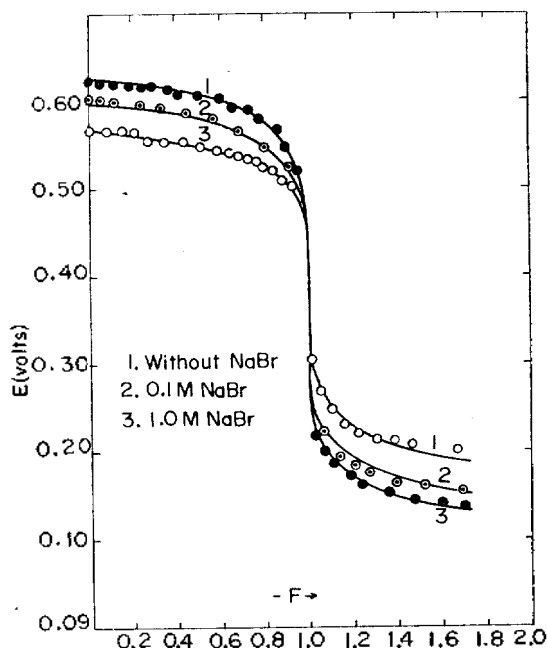


Fig. 2. Titration of HBr in ethylenediamine with sodium aminoethoxide. (Solid lines are theoretical and points are experimental).

$E^{\circ} = 0.792$ volts, $K_{HBr} = 4300$, $K_{NaBr} = 3740$, $K_B = 1.44 \times 10^5$, and $K_i = 2.3 \times 10^{-16}$.

are experimental and have been corrected for volume change* and liquid junction.

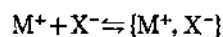
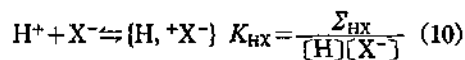
The average value of the standard potential of the platinized platinum hydrogen electrode, E° , obtained prior to the end point of each of the experimental curves, was used to calculate the theoretical curves. The value of E° was +0.793 volts versus the saturated sodium chloride zinc amalgam zinc chloride reference electrode.

To this E° value was added values of the term $-0.0591 \log[H^+]$ calculated by means of Eq. 3 and Eq. 9 with values of f_i estimated from Marshall-Grunwald equation.^{12, 15**}

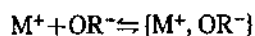
3. Titration of Acids (General). Consider

*Correction before the end point $E_{corr} = E_{obs} + \frac{RT}{nF} \ln \left(\frac{V_i}{V_0}\right)^{\frac{1}{2}}$
 After end point: $E_{corr} = E_{obs} + \frac{RT}{nF} \ln \left(\frac{V_0}{V_i}\right)^{\frac{1}{2}}$
 where, V_0 and V_i are the initial and total volumes, respectively.

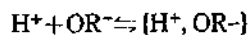
the general and common case in which an acid at a concentration of $10^{-2}M$ or higher is titrated with base, and the only salt present is that formed by neutralization of the acid. The ionic equilibria equations are:



$$K_{MX} = \frac{\Sigma_{MX}}{[M^+][X^-]} \quad (11)$$



$$K_B = \frac{\Sigma_{MOR}}{[M^+][OR^-]} \quad (12)$$



$$K_s = [H^+][OR^-] \quad (13)$$

Before the end point, one obtains from the electroneutrality principle,

$$[H^+] + [M^+] = [X^-] \quad (14)$$

Substituting into this expression the mass action law equilibria for the above reactions gives

$$[H^+]^2 = \frac{\Sigma_{HX} K_{MX}}{K_{HX}^2 \Sigma_{MX} + K_{MX} K_{HX} \Sigma_{MX}^{\circ}} \quad (15)$$

where $\Sigma_{MX} = \Sigma_{HX}^{\circ} - \Sigma_{HX}$, $\Sigma_{HX} = (1-F)\Sigma_{HX}^{\circ}$, and Σ_{HX}° is the original concentration of acid.

The expression for $[H^+]$ prior to the end point is,

$$[H^+] = (1-F)[H^+]_0 \sqrt{\frac{K_{MX}}{K_{MX} + (1-F)(K_{HX} - K_{MX})}} \quad (16)$$

where $[H^+]_0$ is the hydrogen ion activity of the original acid solution before any base is added, $[H^+]_0 = (\Sigma_{HX}^{\circ}/K_{HX})^{\frac{1}{2}}$

After the end point, application of the electroneutrality principle gives,

$$[M^+] = [X^-] + [OR^-] \quad (17)$$

Substitution of the mass action law expression for equations 10, 12, and 17 gives the expression,

$$[OR^-]^2 = \frac{K_{MX}(\Sigma_{MOR})^2}{K_B K_{MX} \Sigma_{MOR} + \Sigma_{MX} K_B^2} \quad (18)$$

After the end point, $\Sigma_{MX} = \Sigma_{HX}^{\circ}$ and $\Sigma_{MOR} = (F-1)\Sigma_{HX}^{\circ}$. Accordingly,

$$[OR^-]^2 = \frac{(F-1)^2 K_{MX} \Sigma_{HX}^{\circ}}{K_B (FK_{MX} - K_{MX} + K_B)} \quad (19)$$

Combining equation 19 and 13, $[H^+]$ may be calculated from the approximate expression,

$$[H^+] = \frac{K_s}{(F-1)} \left[\frac{K_B}{\Sigma_{HX}^{\circ}} \left(\frac{K_B}{K_{MX}} + F - 1 \right) \right]^{\frac{1}{2}} \quad (20)$$

Typical titration curves for HBr, benzoic acid, and phenol are shown in Fig. 3. If K_{MX} for the salt is approximately equal to K_{HX} for the acid, e. g., HBr ($K_{HBr} = 4300$) and NaBr ($K_{NaBr} = 3740$), then equation 16 reduces to $[H^+] = (1-F)[H^+]_0$. Thus, $[H^+]$ varies directly with the concentration of unreacted acid present, and the curve before the equivalence point resembles that of a strong acid in water. The slope of a plot of E_{obs} versus F is $0.0257(1/1-F)$.

At or near the equivalence point, where $F \rightarrow 1$, the slope should approach an infinite value indicating the end point. Similar titrations can be obtained for acids such as nitric and benzoic acids, when the sodium salts are formed. However, since the sodium salt of benzoic acid is more associated than the acid, as the titration proceeds the concentration of dissociated anions decreases, causing the acid to dissociate to a greater extent. The increasing degree of dissociation counteracts somewhat the effect of decreasing the acid concentration as the titration proceeds, causing the slope of the titration curve to be more horizontal as shown in Fig. 3, curve 2.

On the other hand, for phenol the association

**Mean activity coefficient,

$$-\log f_i = \frac{8.02\sqrt{\mu}}{(1+18.1\sqrt{2\mu})^3}$$

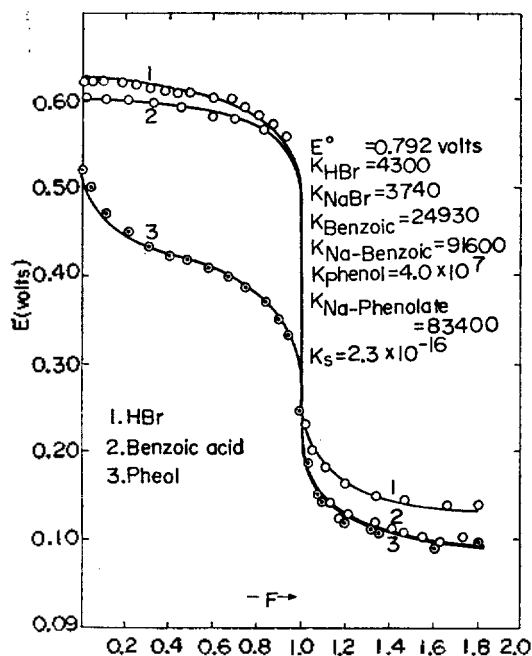


Fig. 3. Titration of HBr, benzoic acid, and phenol in ethylenediamine with sodium aminoethoxide (Solid lines are theoretical and points are experimental).

constant is much greater than that of sodium phenolate, e. g., phenol ($K_{\text{phenol}}=4.0 \times 10^7$) and sodium phenolate ($K_{\text{Na-phenolate}}=83400$), and equation 16 simplifies to,

$$[H^+] = (1-F)[H^+]_0 \left(\frac{K_{MX}}{K_{MX} + FK_{HX}} \right)^{\frac{1}{2}} \quad (21)$$

Since K_{HX} is large compared to K_{MX} , $[H^+]$ will depend strongly on F , when F is small and finite. With increasing small values of F , $[H^+]$ will decrease sharply, resulting in a titration curve similar to a typical weak-acid titration curve in water as shown in Fig. 3 curve 3. The

slope of $[H^+]$ versus F , divided by $[H^+]_0$, should approach the value $K_{HX}/2K_{MX}$ when F is less than 0.1, and should approach the value K_{MX}/K_{HX} as $F \rightarrow 1$.

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