INTRODUCTION

Ion Chromatography is a unique technique combining the powerful separating ability of ion exchange resins with conductivity detection. For most ions, linearity of response is observed over a wide range of concentrations. Generally, deviations from linearity occur with temperature changes or equilibration processes taking place within the analyzed solution. The theory of conductivity and the mathematical considerations involved are quite complex. The following discussion will focus on the aspects of conductivity applicable to IC which, when combined with good analytical practice, will assure the widest range of linearity and best quantitative results.

I. Basic Conductance Laws in Solution

The total electrical conductance of a solution depends upon the type and concentration of all ions present. It is not a specific function of any ionic species. Electrical current is carried by both cations and anions in solution. The equivalent conductance of a salt \( M^{+}\cdot X^{-} \) is, therefore, expressed as the sum of equivalent ionic conductances of the cation \( M^{+} \) and anion \( X^{-} \):

\[
\Lambda_{M^{+}\cdot X^{-}} = \Lambda_{M^{+}} + \Lambda_{X^{-}}
\]

Conductance of:

<table>
<thead>
<tr>
<th>Cation</th>
<th>Anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt</td>
<td></td>
</tr>
<tr>
<td>( \Lambda_{M^{+}\cdot X^{-}} )</td>
<td>( \Lambda_{M^{+}} + \Lambda_{X^{-}} )</td>
</tr>
</tbody>
</table>

This equation represents the law of independent migration first described by Kohlrausch in 1876. It is truly valid only at infinite dilution \( \Lambda^{o} = \Lambda_{M^{+}} + \Lambda_{X^{-}} \). In a dilute solution containing a mixture of electrolytes, the specific conductance is proportional to the sum over all ions of the equivalent conductance of each ion multiplied by its normality:

\[
\kappa = \sum \frac{N_{i} \lambda_{i}}{1000}
\]

\( \lambda^{o} \) values for most ions in water lie in the range 30–80 \( \mu \)S/cm equivalent. Two notable exceptions to this are conductance of solvated proton \( H_{2}O^{+} \) and hydroxyl \( OH^{-} \) ions, for which \( \lambda_{proton} = 350 \) and \( \lambda_{OH^{-}} = 192 \). The exceptionally high mobilities of \( H^{+} \) and \( OH^{-} \) ions are due to a unique transport mechanism available to these ions in water. Specifically, a shift of hydrogen bonds in the water structure produces a charge transfer to the place distant from the original ion without the necessity to move the ions themselves.

The high conductance of \( H^{+} \) and \( OH^{-} \) ions is utilized to advantage in IC. Ions of interest are detected in their corresponding acid or hydroxide form, allowing for the most sensitive means of conductimetric detection (resulting from \( H^{+} \) or \( OH^{-} \) contribution in the measured current). In single column systems, the presence of \( OH^{-} \) or \( H^{+} \) ions in the eluant would dramatically increase the background conductivity, precluding sensitive detection. Thus, single column systems may not utilize the most sensitive type of detection. The result of this is that in the single column techniques the detection limits are at least an order of magnitude higher. Please refer to Section III of this discussion for additional pH effects in the nonsuppressed systems.

II. Temperature Effect on Conductance

Temperature increases cause ion conductance increases at infinite dilution. The equation below describes this relationship:

\[
\lambda_{i}^{o} = \lambda_{25}^{o} e^{k(t-25)}
\]

where \( \lambda_{i}^{o}, \lambda_{25}^{o} \) are values of equivalent conductance at infinite dilution for temperature \( t \), and 25°C respectively. The factor \( k \) is constant for a given ion and solvent. The value of temperature coefficient \( k \) for most ions is close to 0.02 at 25°C. In other words, equivalent conductance of an ion increases by approximately 2% per degree C. This effect is minimized in suppressed IC where background conductivity is reduced to approximately 25 \( \mu \)S. Remember, however, that drastic temperature changes will result in both baseline drift and a change of response of species of interest. Due to higher background conductivities in single column methods, judicious temperature control is a prerequisite for a successful analysis. As summarized in Table I, the higher the background conductivity, the more pronounced the temperature effect on the analysis. For a background conductivity of 300 \( \mu \)S, a 1°C temperature change will result in background conductivity variation of 6 \( \mu \)S, corresponding to 60% on a 10 \( \mu \)S scale. Such a variation of background conductivity would preclude a successful analysis of, for example, 1 pp Cl\(^{-}\), which gives a response of approximately 3 \( \mu \)S. This type of determination is still possible in chemically suppressed Ion Chromatography.
III. Degree of Dissociation and its Significance

The degree of dissociation, $\alpha$, represents the fraction of total solute which is free to carry electrical current. It depends both on the concentration of solute and type of solvent. When dissociation is complete, the value of $\alpha$ reaches unity. The departure of the value of $\alpha$ from unity may be attributed to two phenomena:

A. Influence of Analytes on Dissociation

1. Weak Acids or Bases. Many species, such as weak acids or bases and certain salts, are not completely ionized. In other words, these species in solution exist partially in the form of unionized molecules, regardless of the possibility of ion-pair formation described in Sect. 2. These species, therefore, will not exhibit linearity of detector response for a wide range of concentrations because the numbers of ions capable of carrying an electrical current will vary with concentration. A typical example of this is in the determinations of ammonia, for which the $pK_a = 9.2$ for the pair $\text{NH}_4^+/\text{NH}_3$.

For these weakly dissociated species, the linearity range will vary and depend on the $pK_a$. For most of these ions, linearity will be observed at low ppb (mg/L) levels where the dissociation is essentially complete. It is recommended that for quantitation, a set of standard solutions closely approximating the sample concentration be used. The standards should be prepared in such a manner as to bracket the sample concentration. In addition, it is common knowledge that the degree of dissociation of weak acids or bases is dependent on a concentration of a common ion in solution. Examples of such analyses are determination of $\text{NH}_4^+$ in the presence of large excesses of $\text{Na}^+$ or $\text{PO}_4^{3-}$ in a brine (NaCl) solution. In these analyses, standards should closely approximate concentrations of both ions in order to minimize the difference in the detector response due to the effect of $\text{Na}^+$ on the dissociation of $\text{NH}_4^+$ and $\text{H}^+$ on the dissociation of $\text{H}_2\text{PO}_4^-$. In any event, matrix matching is good analytical practice.

In a similar fashion then, the eluting band of a strongly acidic or basic analyte should cause dissociation suppression of the background carbonic acid in IC. Typically, under standard anion conditions, the concentration of carbonic acid is $3.5 \times 10^{-3} \text{M}$. In practice, the suppressed dissociation has only a negligible effect on the decrease in the contribution of $\text{H}^+/\text{HCO}_3^-$ ions to the background conductivity. The error resulting from this is essentially zero with proper calibration. In single column techniques, the use of acidic or basic eluants is further restricted. In order to secure sufficient eluting power, a relatively strong acid (i.e., dissociated) would have to be utilized. In addition to extremely high background conductance and related effects described previously, the situation becomes quite complex. The relative acidity of eluting ion versus analyte ion determines the dissociation and, thus, detection of species. If HCl is used as eluant for weakly acidic species (e.g., NO$_2^-$, acetate, etc.), dissociation is almost completely suppressed, thus precluding detection without chemical eluant suppression.

Note: This type of analysis is conducted routinely in the ICE mode after eluant suppression.

2. Ion–Ion Interactions. As a result of electrostatic attraction between ions in solution, ions of opposite signs may temporarily form "ion-pairs." These "ion-pairs" have individually limited lifetime; however, at any instant due to continual interchange of ions in solution, the total number of free ions capable of carrying a current is lower than the simple concentration relationship. Several species may be then completely ionized, e.g., salts, but not necessarily completely dissociated. At high dilutions (below $10^{-4} \text{M}$) ion-ion interactions become virtually negligible and solutes are both completely ionized and dissociated. Ion-pairing formation (or ion association) is favored for small-sized or high-valence ions in a low dielectric constant medium. The ion size referred to is the "effective" size of an ion existing in solution and includes the solvation sphere. The thickness of the ionetric atmosphere approaches $10^4 \text{cm}$. It decreases with increasing concentration and increasing valence of ions present in the electrolyte.

In the concentration range usually analyzed in IC, the ion-pair or ion-association formation may be neglected and does not cause deviations from linearity of response. In this case, the initial concentration of eluting ions, as a result of complete dissociation of salts, is decreased from approximately $10^{-3} \text{M}$ (standard anion eluant: $0.0018 \text{M} \text{Na}_2\text{CO}_3/0.0017 \text{M} \text{NaHCO}_3$) to approximately $10^{-2} \text{M}$ due to suppressor reactions which generate weakly dissociated $\text{H}_2\text{CO}_3$ ($pK_a = 6.3$). In other words, in this instance only, $\text{H}^+/\text{HCO}_3^-$ ions in the concentration range of $10^{-3} \text{M}$ contribute to the total ionic content of the analyte band, thus minimizing interactions within the band. Conversely, in single column techniques, completely dissociated salts used as eluants, at approximately $10^{-3} \text{M}$ concentrations, are present throughout the system and contribute $10^{-2}$ to total ionic content of the effluent. This fact restricts the linear operating range of single column techniques because of increased possibility of ion-ion interactions within the analyzed electrolyte (see diagram). Please refer to Section V for further discussion of this phenomenon.

### Table I. Temperature Effect on Background Conductivity

<table>
<thead>
<tr>
<th>Background Conductivity</th>
<th>Background Changes per 1°C</th>
<th>Impact on Readings on 10 μS Scale (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>± 0.5</td>
<td>5</td>
</tr>
<tr>
<td>100</td>
<td>± 2.0</td>
<td>20</td>
</tr>
<tr>
<td>200</td>
<td>± 4.0</td>
<td>40</td>
</tr>
<tr>
<td>300</td>
<td>± 6.0</td>
<td>60</td>
</tr>
</tbody>
</table>

Note: This assumes no temperature compensation. Actual values will depend upon the ability to control temperature effects.
B. Influence of Solvent on Dissociation

The nature of the solvent can play an important part in controlling solute dissociation and, thus, will determine solute conductance. In many cases it was discovered that the higher the dielectric constant of the solvent, the lower the electrostatic forces between the ions and, therefore, the higher the dissociation (dielectric constant of water is 78.6, dioxane is 2.2). In many solvents, the ability of a molecule of solvent to form a complex ion with a proton accounts for high dissociation and results in high conductance. This phenomenon explains high conductance of acidic compounds in oxygen containing solvents like alcohols, ethers or ketones. It is important, therefore, to bear in mind that if organic solvent is added to the eluant, the detector response will change for both weakly and strongly dissociated species.

Note: Selectivities of the chromatographic process may also change. Although little information on the use of mixed organic-aqueous solvents in IC is presently available, a lower linearity range and lower sensitivity should be expected due to generally lower dissociation.

IV. Conductance of Strong Electrolytes at High Concentrations

The decrease in the equivalent conductance at high concentrations observed experimentally may be expressed by the Debye-Huckel-Onsager conductance equation:

\[ \Lambda = \Lambda_0 - (A + BA_N) \sqrt{C} \]

This equation assumes complete dissociation of the electrolyte and attributes a decrease in conductance to the decrease in ionic velocity resulting from interionic forces. The constant designated A is dependent on the solvent (dielectric constant, viscosity) and temperature and accounts for electrophoretic retardation in the mechanism of transport. This may be explained by the fact that under the influence of applied potential, the central ion moves in the direction opposite to its solvation sphere (they carry opposite charges) and, therefore, exerts a retarding force on the ion migration. Coefficient B accounts for the asymmetry or relaxation effect. During the movement of the ion, the charge on the solvation sphere surrounding it becomes asymmetrical. For a finite period of time, charge density is greater behind the moving ion than in front of it. This effect causes retardation of the ion movement under the influence of applied potential and, as a result, causes decrease in conductance.

It should be noted that this \( \sqrt{C} \) dependence is only applicable for concentration ranges higher than those typically analyzed by IC where the linear dependence as described by the Kohlrausch law is applicable.

V. Conductance of Mixtures of Electrolytes

Thus far, the process of conduction described assumed that each ionic species drifts independently of one another. This is an oversimplification because it assumes nonexistence of ion-ion interactions. The transference number of an ion \( t_i \) is defined by the equation:

\[ t_i = \frac{\lambda_i N_i}{\sum \lambda_i N_i} \]

and represents the fraction of total current carried by a particular ion in a solution. In mixtures containing an excess of one electrolyte and a small amount of another, a decrease of the transference number of the second electrolyte occurs.

Although, in general, this is observed for higher concentrations than those typically analyzed in IC, again IC offers the advantage of minimizing these effects. As mentioned previously, the suppressed eluant background contributes only \( 10^{-5} \) M range of \( \text{H}^+ / \text{HCO}_3^- \) ions, versus \( 10^{-2} \) M in a single column system. Thus, IC offers the largest fraction of total current carried by the analyte without other ion interferences.

DEFINITIONS

Specific conductance, \( \kappa \), is the conductance across the two opposite faces of a cube of solution, 1 cm on an edge.

Equivalent conductance, \( \Lambda \), is the conductance of 1 gram equivalent of completely dissociated electrolyte, dissolved in 1 cm\(^3\) volume.

These two values are related by the following equation:

\[ \kappa = \frac{\Lambda N}{1000} \]

where N is the normality of the solute, defined as total concentration of positive (or negative) charge produced on dissociation.

![Graph showing linearity and dynamic range of suppressed vs nonsuppressed system](image-url)