purified by crystallization from chloroform. The infrared absorption spectrum was determined, using freshly crystallized material in paraffin oil paste, with a Perkin Elmer infrared spectrometer, Model 12 C, with 67° calcium fluoride prism.

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An Observation on the Parameter $\alpha$ of the Debye-Hückel Formula

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The writer has investigated the dissociation of acetic acid in water solutions of strong 1–1 electrolytes. In this report part of the results obtained is presented.

The investigation was carried out by a method developed by Kilpi 1. The method is based on potentiometric titration of a weak acid with a strong hydroxide, and from the buffer capacity determined at one of the inflexion points of the titration curve the corresponding dissociation constant can be calculated. Eleven different salts were used as electrolytes. The concentrations used are expressed in moles of salt per liter of solution.

From the observations it was found that the negative logarithm of the dissociation constant, $pK$ of acetic acid is an additive
quantity. This was deduced from the in-
varieties of
\[ pK_{KCl} - pK_{NaCl} = pK_{KNO_3} - pK_{NaNO_3} \]
and
\[ pK_{NaClO_4} - pK_{NaBr} = pK_{LiClO_4} - pK_{LiBr} \]
which were found to be true in all cases investigated and being dependent separa-
tively on the anions and cations of the co-
electrolyte at constant molarity. In the
equations the indices refer to the salt, in the
solution of which the measurement was
performed.

This observation is in good agreement
with the specific interionic attraction
theory of Brönsted.\(^2\) Recently Olson and
Simonson\(^3\) have reported on works which
have led them to the conclusion, that only
the oppositely charged ions influence each
other. Combining these two observations,
that of Olson and Simonson and of mine,
it was possible to alter the orthodox semi-
empirical Debye-Hückel formula applied
to weak acids into the following form
\[ pK = pK_0 - \left( \frac{0.5062 \sqrt{I}}{1 + a_{H^{-}} V I} + \frac{0.5062 \sqrt{I}}{1 + a_{Ac^{+}} V I} \right) + BI \]  \(1\)
where \(a_{H^{-}}\) means the parameter, which
characterizes the coulombic influence of the
ions of the co-electrolyte upon the
H-ions and \(a_{Ac^{+}}\) the parameter, which
characterizes the coulombic influence of the
cations of the co-electrolyte upon the
acetate ions. The following results were
obtained at 25°C.

<table>
<thead>
<tr>
<th>Ionic Electrolyte strength</th>
<th>pK</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl 0.999</td>
<td>4.5605</td>
<td>0.2008</td>
</tr>
<tr>
<td>KCl 2.693</td>
<td>4.8285</td>
<td></td>
</tr>
<tr>
<td>LiCl 0.999</td>
<td>4.4439</td>
<td>0.1400</td>
</tr>
<tr>
<td>LiCl 2.693</td>
<td>4.5835</td>
<td></td>
</tr>
</tbody>
</table>

Using these values and that for \(pK_0 =
4.7570\), determined by Harned and Ehlers\(^4\),
the term B in the fourth column was
calculated assuming in the orthodox man-
ner that \(a_{H^{-}} = a_{Ac^{+}}\).

Introducing these results into the equation
(1) four equations were obtained. Subtracting
from each other those having the same value for I,
the result was two equations with two variables. When
solved, the following values were obtained:
\(a_{Ac(K)} = 1.755; a_{Ac(Cl)} = 1.104\)
and further \(a_{H(Cl)} = 1.377\). When calculated in
the usual manner (\(a_{H^{-}} = a_{Ac^{+}}\)), one gets the
values \(a_{KCl} = 1.550, a_{LiCl} = 1.230\).

The table above includes pK-values at
several ionic strengths in KCl-solution cal-
culated by the usual manner and in the
way presented in this paper. The table
indicates, that the method of calculation
does not influence the results.

A more detailed report on the work and
on the results obtained will be published
in the near future in the form of an aca-
demic dissertation.

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