Determination of activity coefficient from conductometry data

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Abstract

Interactions between ions are so strong that the approximation of replacing activities by molalities is valid only in very dilute solutions and in precise work activities must themselves be used. In this study values of activity coefficients for acetic acid were obtained at different concentrations by the method of iteration using a program written in C.

1 Introduction

The dissociation of acetic acid occurs according to the following equation

$$\begin{array}{cccc} CH_3COOH & \rightleftharpoons & CH_3COO^- & + H^+ \\ c(1-\alpha) & \rightleftharpoons & c(\alpha) & c(\alpha) \end{array}$$

c is the initial concentration of AcOH
α is the rate of dissociation.
Activity of positive species, a_+ , is cf_+ where f_+ is the activity coefficient. Activity coefficient of AcOH is taken to be 1. The dissociation constant for the above reaction is given by

$$K_a = \frac{(a_{CH_3COO^-})(a_{H^+})}{a_{CH_3COOH}}$$

$$K_a = \frac{c(\alpha)^2 f_+ f_-}{1-\alpha} \tag{1}$$

If the equivalent conductance of the solution at concentration c is Λ and at c=0 is Λ_0 then

$$\alpha = \frac{\Lambda}{\Lambda_0} \tag{2}$$

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The quantity $f_{\pm}$,the mean activity coefficient,for a species of type $A^{+}B^{-}$ is defined as

$$f_{\pm}^{2} = f_{+}f_{-} \tag{3}$$

The activity coefficient, at very low concentrations can be calculated from the **Debye-Hückel Limiting Law** as

$$\log f_{\pm} = -|z_{+}z_{-}|AI^{\frac{1}{2}} \tag{4}$$

z_{+} and z_{-} are the charges on the positive and negative ions
$A = 0.509$ for an aqueous solution at $25^{0}C$
I is the ionic strength of the solution:

$$I = \frac{1}{2}\sum_{i} c_i z_i^2 \tag{5}$$

Using equations (1)-(5) we obtain

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \frac{\Lambda c f_{\pm}^{2}}{K_a \Lambda_0^2} \tag{6}$$

2 Experiment and Computation

2.1 Materials and Methods

50 mL of water was taken in a 100 mL beaker. Each time 0.5 mL acetic acid was added to water and the conductivity of the solution was measured. The equivalent conductance values were calculated for each concentration of acetic acid.

2.2 Iteration algorithm

Instead of simply doing a linear fit, we implemented the following algorithm, which enabled us to get not only Λ_0 and Ka but also the values of $f\pm$ for different concentrations.

1. Take all the values of $f_{\pm}$ to be 1 initially.
2. Arbitrarily fix the initial values of Λ_o and k_a to 0.
3. Calculate an array of values of $\frac{1}{\Lambda}$ and $\Lambda c {f_{\pm}}^2$ using experimental data and current values of $f_{\pm}$.
4. Fit the calculated values to $\frac{1}{\Lambda} = \frac{1}{\Lambda_o} + \frac{1}{K_a {\Lambda_o}^2}\Lambda c {f_{\pm}}^2$.
5. Determine the values of Λ_o and K_a.
6. Calculate values of $f_{\pm}$ using the formula $f_{\pm} = -A\sqrt{\frac{\Lambda c}{\Lambda_o}}$.

7. If old and new constants differ by more than 0.0001 % then goback to 3 else continue.

8. Plot the final values of $log(f_{\pm}) vs \sqrt{c}$.

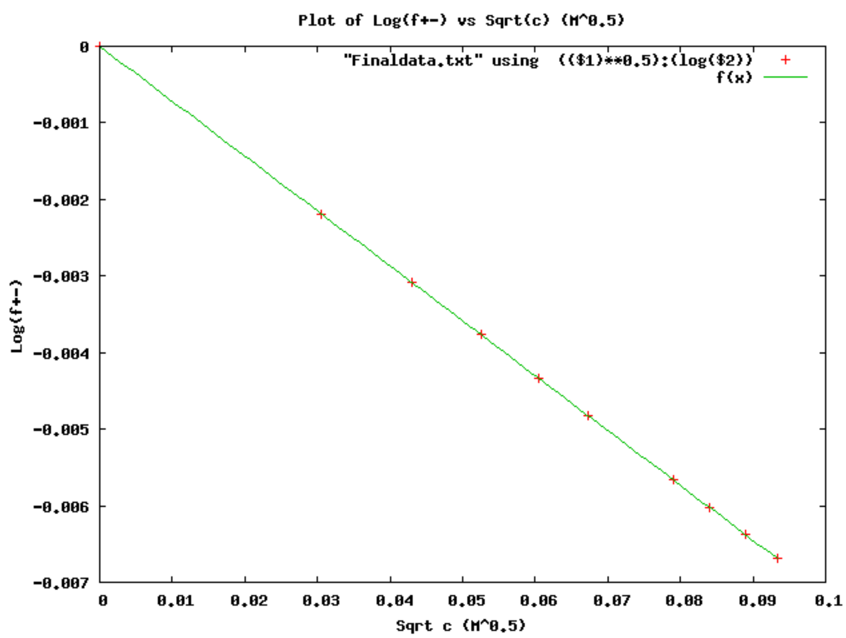
3 Results and Conclusions

The $f\pm$ values were obtained at different concentrations of acetic acid. The value of Λ_0 was also obtained.

Table 1.1 Data obtained with and without assuming activity coefficient = 1

	With assumption $f_{\pm}^2 = 1$	**Without the assumption(Computed)**
Λ_0	196.46	201.65
K_a	$8.67 * 10^{-5}$	$8.1 * 10^{-5}$

The accuracy of our fitting program can be easily estimated from the graph shown below. The values of $log f_{\pm}$ were plotted against the concentration of acetic acid.



The close agreement of the values shown in Table 1.1 is due to very low concentrations of acetic acid in solution emphasising that the electrostatic interactions between ions in solution is sensitive to their concentration. The lower the concentration the more the solution tends to ideality.

4 Future Work

When the ionic strength of the solution is too high for the limiting law (4) to be valid, the activity coefficient can be estimated from the *extended Debye-Hückel law*. The distance of closest approach of the ions in solution can also be estimated with its help. Another approach for estimating the activity coefficient is to set up a theory for the dependence of the activity coefficient of the solvent on the concentration of the solute and then using the *Gibbs-Duhem Equation*.

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6 Reference

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