

ACTIVITY COEFFICIENTS OF ELECTROLYTES

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(Received 14 December 1981, after revision 11 March 1982)

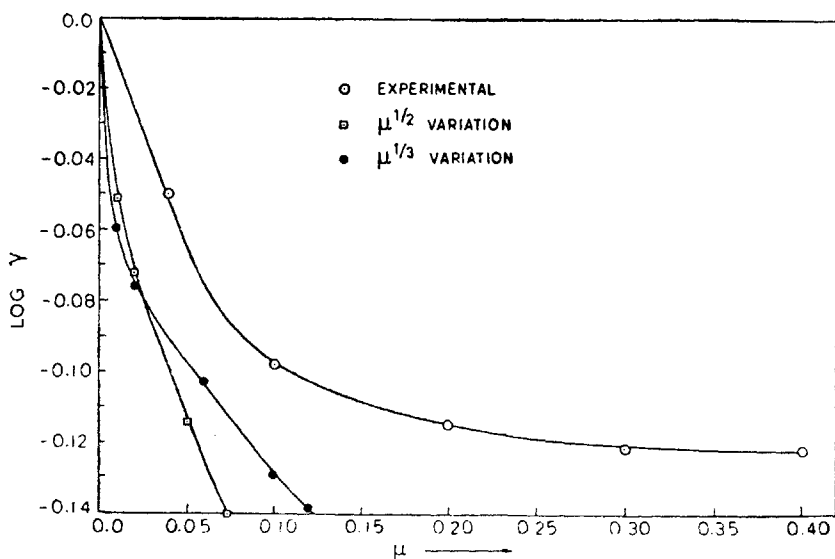
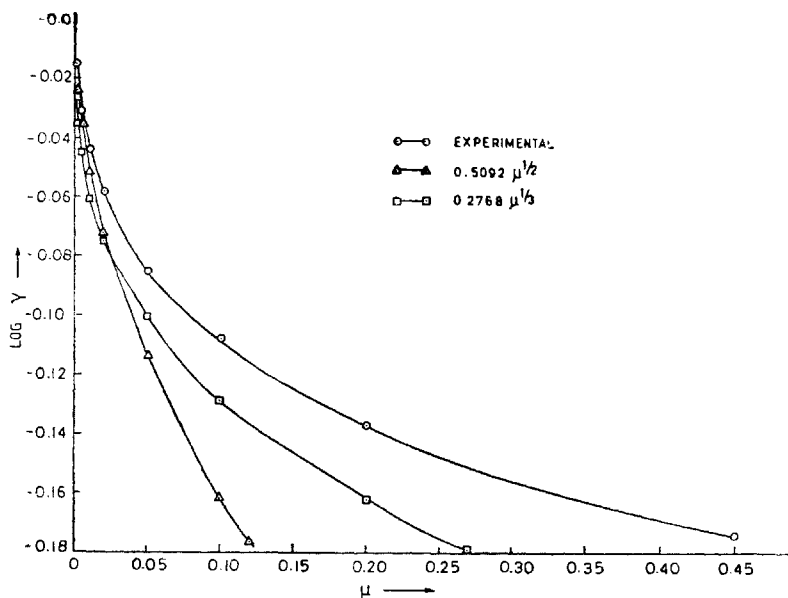
The ion lattice concept is extended to the solution of electrolytes. It is shown that the experimental values of activity coefficients of dilute solutions conform more to the cube root law than to the square root law. At high concentration there is the opposite effect of ion compression which should be calculated separately. An empirical constant may explain the experimental curves for various electrolytes. In brief, the cube root law (using the Madelung constant for crystals) explains the observations for the intermediate and low concentrations, but for higher concentrations a term inversely proportional to concentration becomes important.

Keywords : Activity Coefficients; Electrolytes; Lattice; Madelung Constant; Size of Ions in Solution

INTRODUCTION

THE activity coefficients (γ) of electrolytes in solution can be experimentally inferred in various ways. There is a marked lack of theoretical understanding of these measurements especially at intermediate or high concentrations. Theoretically derived values, half-a-century ago are said only to reflect the asymptotic behaviour at very low concentrations (molality μ less than 0.001). The Debye and Huckel theory (1923) has been modified by a correction factor in the denominator $1/(1 + 0.94 \sqrt{\mu})$, which reduces the magnitude of $\log \gamma$ by about 25 per cent at molality 0.1 and by 50 per cent at molality 1.0, but the logarithm will not change sign, while the observed values change sign at molalities around 2 to 6. Bjerrum (1926) suggested association of ions which causes true molality to change and Robinson and Stokes (1948) under the assumption of hydration of ions have given an expression containing empirical hydration number to fit an observed drop in the magnitude of the logarithm. The theoretical formula using the Huckel term and the appropriate hydration number does not usually reflect the experimental trend throughout the range. One tries to fit the data by an expression containing two arbitrary coefficients (Moelwyn-Hughes, 1965).

Following Huckel's theory it can be shown that the asymptotic behaviour very nearly corresponds to $\mu^{1/2}$ dependence for very low concentrations. In Fig. 1, we have plotted the experimental values for HCl vs. μ . In the same plot are shown the curves $0.5094 \mu^{1/2}$ and $0.2768 \mu^{1/3}$. The former is the expected variation as per Debye-Huckel Theory and the latter expression indicating $\mu^{1/3}$ variation as deduced

FIG. 1. $\text{Log } (\gamma)_{\text{HCl}}$ vs. μ .FIG. 2. $\text{Log } (\gamma)_{\text{NaCl}}$ vs. μ .

in this paper. One notices that both the theoretical curves deviate materially from experimental data, however the latter curve is a better approximation to the experimental trend at intermediate concentrations.

In Fig. 2, we have plotted $\log \gamma$ for NaCl vs. μ , and also on the same graph are indicated the curves $0.5094 \mu^{1/2}$ and $0.2768 \mu^{1/3}$. The striking observation is the rapid

divergence at higher values of μ rather than the asymptotic convergence at low concentration and the $\mu^{1/3}$ variation is better indicative of the trend from $\mu = 0.01$ to $\mu = 0.5$. The experimental observations used here are given in most text-books of physical chemistry (e.g., Moore : *Physical Chemistry*—Prentice Hall, 1972, p. 444).

ELECTROSTATIC ENERGY FOR AN ION IN SOLUTION

Once it is accepted that ions of electrolytes exhibit dissociation, the interionic forces will limit each ion to its allotted volume in the solution and as a first approximation, it can be considered as having on the average a fixed lattice position for static effects like calculation of the electrostatic energy of a single ion, in the field of all other ions, which will be equated to $2.303 \text{ kT} \log \gamma$, (since the extra electric free enthalpy per ion is $\text{kT} \ln \gamma$). Such a calculation has been carried out for crystal lattices e.g., Heyes (1981). In the case of solutions we have to replace the lattice constant by the separation of ions in the solution depending on the concentration, and to replace the dielectric constant of the vacuum by that of water, if that is the solvent. Using the expression by Seitz (1940), for two-atom ionic crystals, the electrostatic energy, per ion out of $2N$ ions where N is the number of molecules in the entire sample, is $-1/2(Ae^2/\epsilon.a.)C$, where A , the Madelung constant is 2.2018, n is of the order 8 in the factor $C = (1 - 1/n)$ which is the correction for short range repulsion between any two ions, ϵ is 78 for water (it should decrease by few per cent for each mole of solute). a is the intermolecular separation and is given by $(1000/N\mu)^{1/3}$, where N is the avagadro's number and μ is the molality of the solution. Substituting the numerical value we get $\log \gamma = -0.2768 \mu^{1/3}$. This approach seems to fit the data better for a much larger range of dilutions and also leads to a natural extension for higher concentrations.

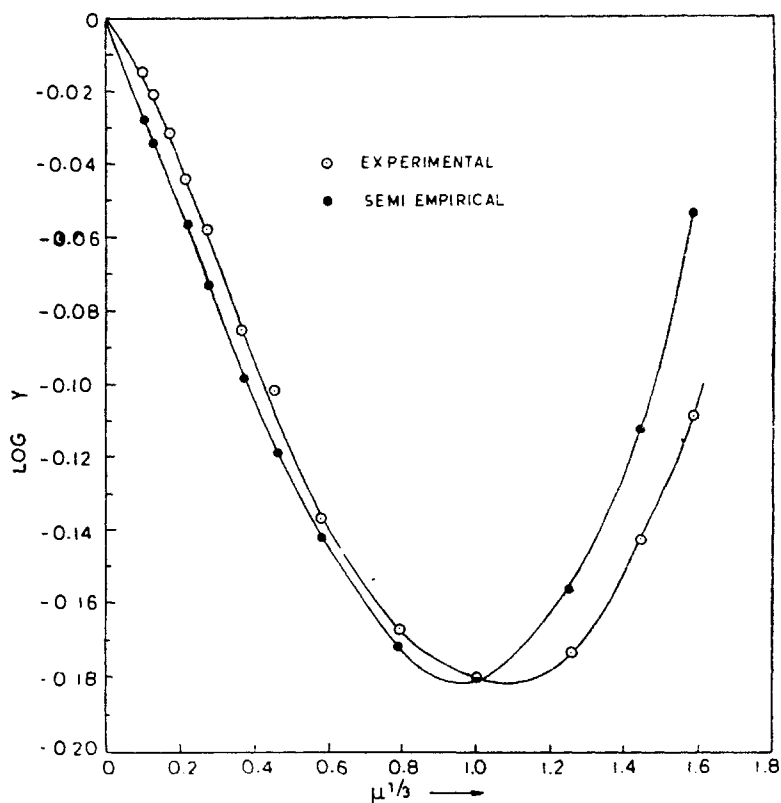
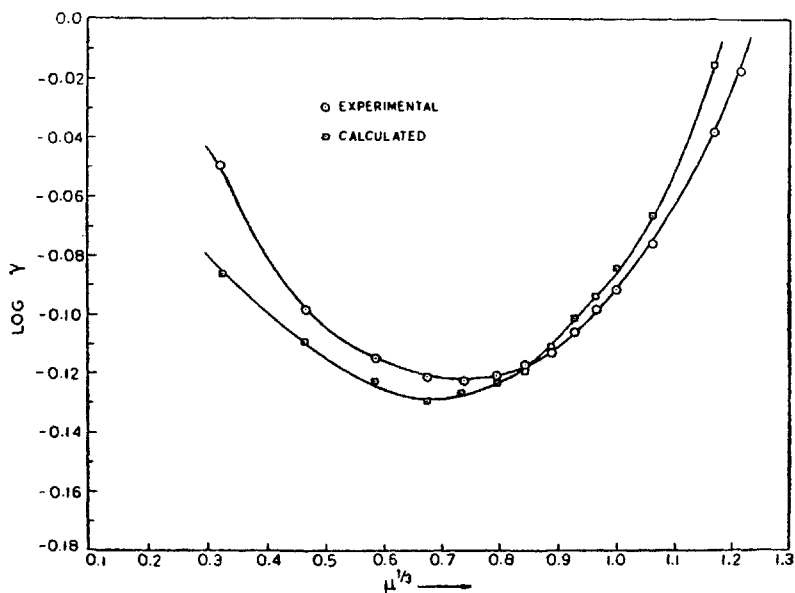
SIZE OF IONS IN SOLUTION

An ion has to be squeezed on account of neighbouring ions, into a limited space. For NaCl at $\mu = 4$, and if a is the lattice constant (inter-molecular distance), the allotted linear dimension (radius) for sodium ion is $0.44a = 3.15\text{\AA}$. The sodium ion will suffer a squeeze so that the probability of the outermost electron to be outside this space is reduced below about 10^{-6} depending on the size of the sample. The electrostatic energy required for this 'ionic' compression will be inversely proportional to the allotted space, i.e., will be proportional to the concentration.

Combining the Madelung term with the ionic compression term discussed here, the activity coefficient γ is given by :

$$\log \gamma = -0.2768 \mu^{1/3} + B\mu$$

In Fig. 3, we have plotted experimental points for NaCl vs. $\mu^{1/3}$, and also drawn a calculated curve following above expression matching it at the minimum of the experimental curve, which is possible using $B = 0.0964$. In Fig. 4, the matching curve has been drawn for data for HCl and some hopeful match is seen when a new constant $B' = 2B = 0.1928$ is used. The double magnitude of the constant for HCl may be

FIG. 3. $\text{LOG } (\gamma)_{\text{NaCl}}$ vs. $\mu^{1/3}$.FIG. 4. $\text{LOG}_{10} \gamma_{\text{HCl}}$ vs. $\mu^{1/3}$.

related to the cations being only protons (point charges) which do not experience any compression, and cause polarization of the chloride ions to a greater extent.

CONCLUSION

A semi-empirical relationship is given for the calculation of the activity coefficients which is based on an extension of Madelung type electrostatic energy in lattices. An additional term is required due to electrostatic squeezing of ions. The modified relation is suggested to be $\log \gamma = -A\mu^{1/3} + B\mu$. The value of A for two atom electrolytes is 0.2768 and can be determined theoretically for other electrolytes. The value of B from experimental data for HCl is found to be twice that for NaCl.

ACKNOWLEDGEMENT

Thanks are due to the colleagues in the Physics Department for helpful discussions.

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