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Conductance of KCl-Glycerol Solutions: Test of the Fuoss Paired Ion Model

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The electrical conductance of KCl in glycerol solutions has been measured at concentrations between 1.5 mol m^{-3} and 353 mol m^{-3} at 22°C . The results are compared with the Fuoss paired ion model and fits to the data are obtained assuming a Gurney co-sphere having a radius in the approximate range $6 \times 10^{-10} \text{ m}$ to $9 \times 10^{-10} \text{ m}$. The model leads to an estimate of ionic association which is less than that given by the theory of Bjerrum.

KEYWORDS Glycerol, KCl, solution, conductance, electrolyte.

1 INTRODUCTION

It is generally accepted that the electrical conductivities of strong electrolytes in aqueous solution vary with concentration in a manner which is described well by the Debye-Huckel-Onsanger theory in the limit of low concentration. As a result interest is now centred on extending understanding to higher concentrations and to solvents other than water. In this context glycerol is an interesting solvent because in many respects it is similar to water, in that it is a hydrogen bonded liquid of relatively simple polar molecules which has a high relative permittivity ($\epsilon_r \approx 40$) and is a good solvent for common salts: however glycerol stands out from other common solvents in having a relatively very high viscosity at room temperature and also in having a Walden product which, for alkyl halides, is higher than in any other common

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solvent. By Walden product we mean, as usual, the product $\Lambda^\infty \eta$, where Λ^∞ is the molar conductivity of solution extrapolated to infinite dilution and η is the viscosity of the pure solvent.

There have been many attempts to extend the Debye-Huckel-Onsanger theory so as to apply to higher concentrations and these are reviewed elsewhere:^{1,2} we choose the Fuoss³ paired ion model as representing a commonly used recent attempt. There have been two previous analyses of the concentration dependence of molar conductivity of KCl-glycerol solutions, by Heigemann⁴ and by Accascina and Petrucci.^{5,6} This work showed quite good agreement with the limiting formula of Debye-Huckel-Onsanger, but did not extend to concentration above about 17 mol m^{-3} . We present data extending up to a concentration, c , of about 350 mol m^{-3} and are thus able to test the Fuoss equation in this regime.

2 RESULTS AND DISCUSSION

The conductance measurements were made using an AC technique in a cryostat designed primarily for a study of the temperature dependence from 50°C to about -90°C , and the experimental details are described elsewhere.⁷ The glycerol was Aldrich gold label and was distilled to reduce traces of water. Further details on the purity, as indicated by viscosity and conductivity measurements, are also described elsewhere.⁷

In Figures 1-4 our data at $T = 295.15 \text{ K}$ is compared with the Onsanger formula and with various curves based on the Fuoss theory for different parameter values. In Fuoss's theory the effects of ion-solvent and ion-ion interactions (including ionic association) enter through two adjustable parameters R and α having the following interpretations. R is the radius of the Gurney cosphere, i.e. the radius of 'the little spherical portion of a solvent which encloses the ion and is somewhat modified by the presence of the ion'. α is a dimensionless ratio defined by classifying each ion into one of three categories as follows, according to the magnitude of r the distance from the centre of the ion to the centre of the nearest ion of opposite sign. If $r > R$ then the ion is 'unpaired'; otherwise the ion is said to be 'paired', and paired ions are further subdivided into two types. If r is so small that a paired ion and its neighbour behave temporarily as a neutral pair contributing nothing to the conductivity of the solution then the ion is said to belong to a 'contact pair'; this critical distance of approach is assumed to be smaller than R . The remaining paired ions, with larger values of r , are

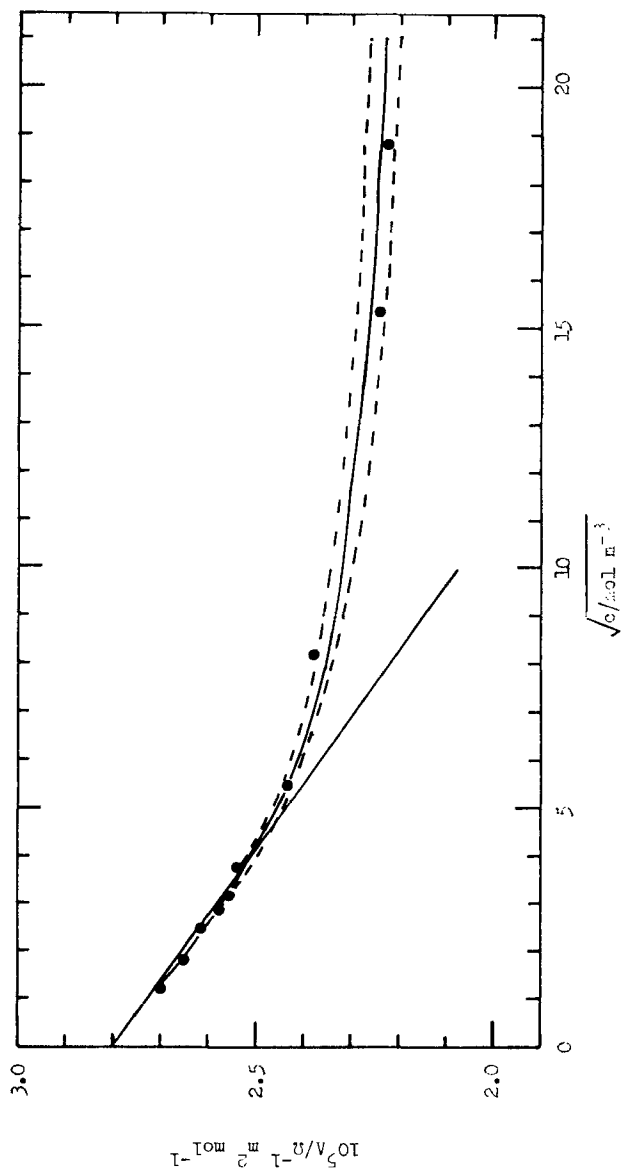


Figure 1 The molar conductance of KCl in glycerol solutions at 22°C plotted against \sqrt{c} . The curves are calculated from the Fuoss equation for $R = 0.3$ nm; (a) $\alpha = 0.11$, (b) $\alpha = 0.16$, (c) $\alpha = 0.21$. The straight line is calculated from the Debye-Hückel-Onsager theory. The curves end at the highest concentration at which Fuoss applied his theory.

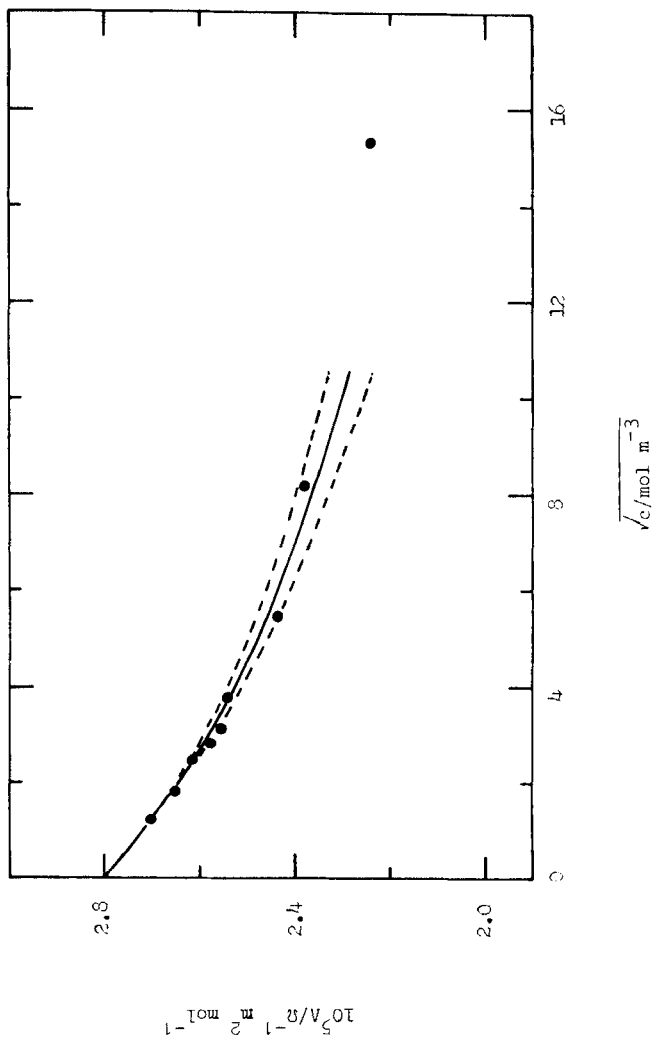


Figure 2 As Figure 1, but with $R = 0.6 \text{ nm}$, (a) $\alpha = 0.39$, (b) $\alpha = 0.44$, (c) $\alpha = 0.49$.

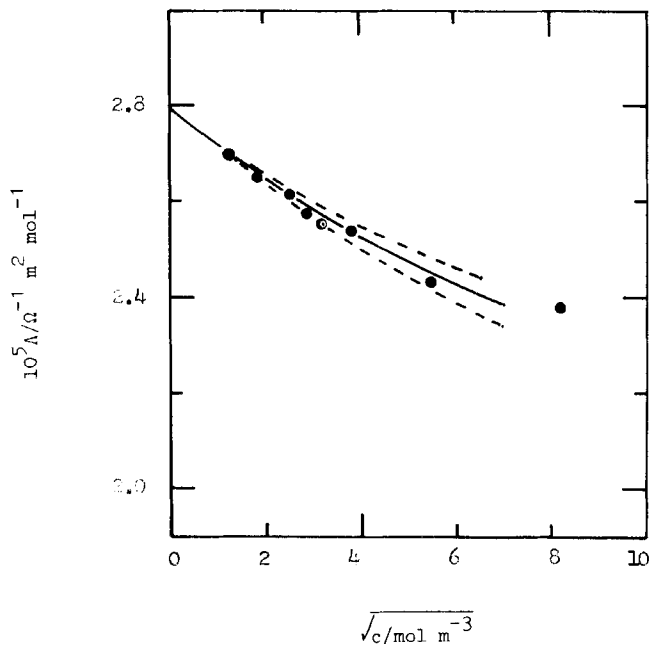


Figure 3 As Figure 1, but with $R = 0.9$ nm; (a) $\alpha = 0.37$ nm, (b) $\alpha = 0.42$, (c) $\alpha = 0.47$.

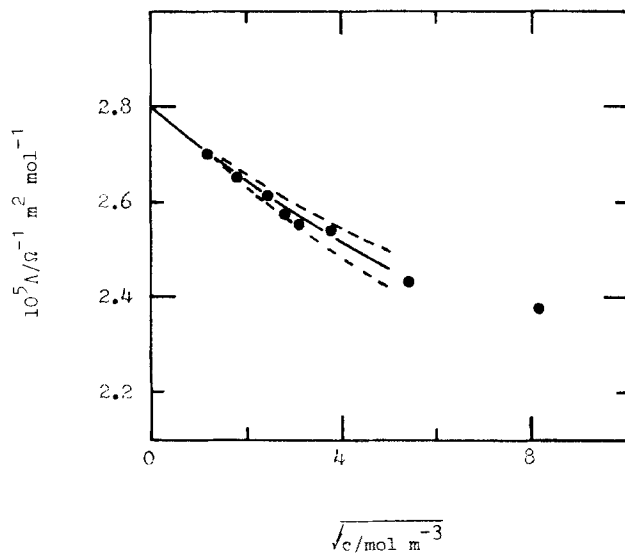


Figure 4 As Figure 1, but with $r = 1.2$ nm; (a) $\alpha = 0.33$, (b) $\alpha = 0.38$, (c) $\alpha = 0.43$.

said to belong to 'solvent separated pairs'. α is the fraction of paired ions that belong to contact pairs, and α enters the theory as a parameter independent of concentration. For given values of the six system parameters R , α , T , ϵ_r , η , and Λ^∞ the Fuoss theory determines Λ as a function of c . However, the result was not originally given as a single explicit formula employing these variables, and the calculation of Λ is not entirely straightforward. We adopted the following procedure, suitable for a 1:1 electrolyte and using SI units.

From Eqs 1.13, 1.9, 4.12-4.14 of Fuoss³ we may derive the following implicit expression for γ , the concentration dependent fraction of ions which are unpaired.

$$\gamma = 1 - \frac{\gamma^2 4\pi N_0 R^3 c}{3(1 - \alpha)} \exp \left[\frac{\beta/R}{1 + R\sqrt{8\pi\beta N_0 \gamma c}} \right]$$

where

$$\beta = e^2/(4\pi\epsilon_0\epsilon_r kT),$$

e is the electronic charge, N_0 is the Avogadro constant, k is Boltzmann's constant, and ϵ_0 is the permittivity of vacuum. For given values of the six system parameters, γ can be found by iteration for a specified concentration. Thence the modified Debye-Huckel parameter κ defined by Fuoss as

$$\kappa = \left(\frac{2N_0 c \gamma e^2}{\epsilon_0 \epsilon_r kT} \right)^{1/2}$$

can be determined. The molar conductivity at a given concentration may now be evaluated explicitly from

$$\Lambda = p\Lambda^\infty \{1 - A\tau + B\tau^2 + C\tau^3\}$$

where the following are dimensionless quantities dependent on concentration,

$$p = 1 - \alpha(1 - \gamma)$$

$$t = \kappa R$$

$$\tau = \beta\kappa/2$$

$$W = \frac{2N_0 e^2 \gamma^{1/2}}{3\pi\eta\Lambda^\infty\beta}$$

$$A = \frac{W}{1+t} + \frac{1}{3(1+t)\left(1 + \frac{t}{\sqrt{2}}\right)\left(1 + \frac{1}{\sqrt{2}}\right)}$$

$$B = 4FH2(t) + (W/8)H_2(t) - WH_1(t) + \left(\frac{2-3W}{6}\right)\ln_e t$$

$$C = 8FH3(t).$$

In the above, the parameter W has to do with the hydrodynamic terms in the theory and has been introduced by us as more convenient than the parameter β_0 used by Fuoss; the quantities $FH_2(t)$, $FH_3(t)$, $H_1(t)$ and $H_2(t)$ are functions of t defined by Fuoss through various polynomials for different ranges of value of t , and we reproduce them as an appendix so that the present paper becomes self-contained.

In Figures 1-4 we show the theoretical dependence of Λ on \sqrt{c} , for various values of R and α , compared with our data and using the values $\Lambda^\infty = 2.8 \times 10^{-5} \text{ S m}^2 \text{ mol}^{-1}$, $\epsilon_r = 42$, $\eta = 1.2 \text{ Pa s}$, $T = 295.15 \text{ K}$. It will then be seen that a reasonable fit to our data can be obtained at each value of R provided α is chosen appropriately.

A least squares fit for α at various set values of R gave the best fit values shown in Table 1:

R/nm	0.3	0.6	0.9	1.2
α	0.16	0.44	0.42	0.38

In order to give a feeling for the precision of these values of α we have included in Figures 1-4 some graphs for values of α differing from the best values by 0.05. It can be seen that the quality of fit varies very little as the value of R is changed, as was noticed by Fuoss himself for solvents with $\epsilon_r \leq 25$. Although the standard deviation of the 3 Å fit was slightly higher, the other fits gave standard deviations which were not significantly different from each other. However following Fuoss we may make a rough estimate of R as follows. The volume per molecule in glycerol is equal to the volume of a cube of edge 0.5 nm, and the sum of the crystallographic radii of K^+ and Cl^- ions is approximately 0.3 nm; hence by addition we estimate $R \sim 0.8 \text{ nm}$. This value of R corresponds, from our data, to a value of α between 0.42 and 0.44.

From these values of R and α one can deduce the value of γ at various concentrations and thence evaluate p , the fraction of ions that contribute to the conduction process. The results are shown in Figure 5 for R equal to 0.6 nm and 0.9 nm. Also shown is the degree of dissociation, p_B , that is predicted by the well-known early theory of Bjerrum,^{8,9} using a 'closest distance of approach' of two ions equal to 0.3 nm. These graphs show that the effects of ion association are less pronounced on the Fuoss model than on the Bjerrum model, and in fact the parameter γ rather than p approaches the Bjerrum value p_B at low concentrations.

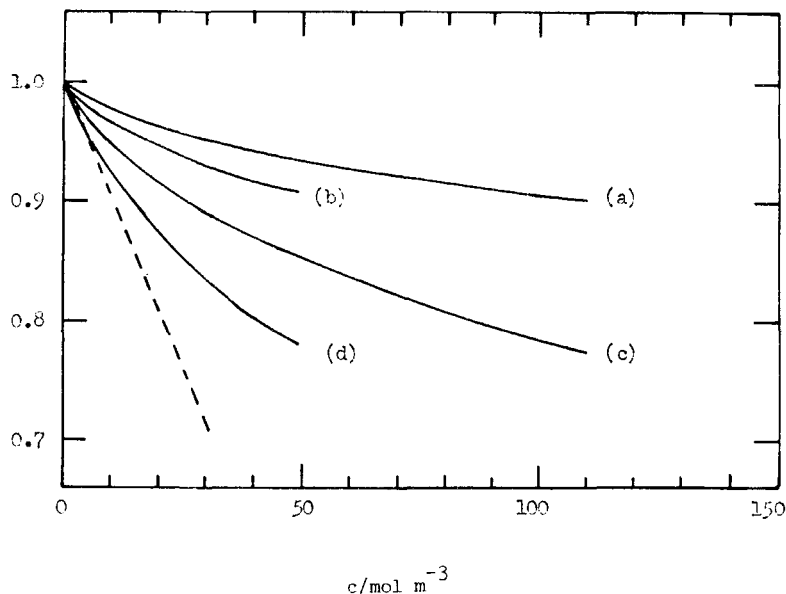


Figure 5 Calculated values of the Fuoss parameters p and γ plotted versus concentration. (a) p versus c for $R = 0.6$ nm, (b) p versus c for $R = 0.9$ nm, (c) γ versus c for $R = 0.6$ nm, (d) γ versus c for $R = 0.9$ nm. $\alpha = 0.44$ for $R = 0.6$ nm, $\alpha = 0.42$ for $R = 0.9$ nm. The dashed line is derived from the Bjerrum theory.

3 CONCLUSION

Conductance data on glycerol show that the Fuoss model can be used to fit the data up to the limits set by his model. However, the fit is insensitive to the value of R over the approximate range 0.6 to 1.2 nm. If one uses a physically plausible value of $R \approx 0.8$ nm, then the other parameters of the theory can be deduced from the data and hence the fraction of ions contributing to the conductivity process at various concentrations. This fraction is found to be considerably higher than in the Bjerrum model.

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Appendix

The functions $FH2(t)$, $FH3(t)$, $H_1(t)$ and $H_2(t)$ are defined by Fuoss through the following polynomials for various ranges of the dimensionless variable t up to $t = 0.8$

$$FH2(t) = 0.13842 - 0.25289 t + 0.16281 t^2 - 0.044868 t^3 \quad (0 \leq t \leq 0.4)$$

$$FH2(t) = 0.13558 - 0.23739 t + 0.14034 t^2 - 0.041583 t^3 \quad (0.4 \leq t \leq 0.8)$$

$$FH3(t) = 0.0084869 - 0.029776 t + 0.045001 t^2 - 0.026344 t^3 \quad (0 \leq t \leq 0.4)$$

$$FH3(t) = 0.0067047 - 0.017767 t + 0.018269 t^2 - 0.0068686 t^3 \quad (0.4 \leq t \leq 0.8)$$

$$H_1(t) = 0.19295 - 0.18508 t - 0.32106 t^2 + 0.40243 t^3 \quad (0 \leq t \leq 0.4)$$

$$H_1(t) = 0.20742 - 0.31145 t + 0.06461 t^2 \quad (0.4 \leq t \leq 0.8)$$

$$H_2(t) = -2.6851 + 18.438 t - 35.735 t^2 + 28.476 t^3 \quad (0 \leq t \leq 0.3)$$

$$H_2(t) = -2.0722 + 12.452 t - 15.804 t^2 + 6.0045 t^3 \quad (0.3 \leq t \leq 0.6)$$

$$H_2(t) = -1.0425 + 6.9012 t - 5.8121 t^2 \quad (0.6 \leq t \leq 0.8)$$