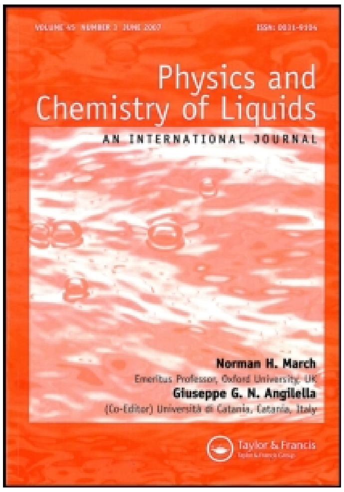

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Mean Ionic Activity Coefficients of Alkali Metals Dissolved in High Dielectric Constant Solvents: A Comparison Between Experimental Data and Fuoss Theoretical Data

M. Kameche[a]; D. C. Champeney[b]; M. C. Blanco[c]; Z. Derriche[d]
[a] Departement de Physique, Faculte des Sciences, Oran, Algerie [b] School of Physics, University of East Anglia, Norwich, UK [c] Departamento de Quimica Fisica, Facultad de Quimica, Universidad de Santiago de Compostela, Spain [d] Departement de Chimie Industrielle, Laboratoire de Physico-Chimie des Materiaux, Algerie

To cite this Article Kameche, M. , Champeney, D. C. , Blanco, M. C. and Derriche, Z.(2002) 'Mean Ionic Activity Coefficients of Alkali Metals Dissolved in High Dielectric Constant Solvents: A Comparison Between Experimental Data and Fuoss Theoretical Data', Physics and Chemistry of Liquids, 40: 1, 9 — 38
To link to this Article: DOI: 10.1080/00319100208086646
URL: http://dx.doi.org/10.1080/00319100208086646

Phys. Chem. Liq., 2002, Vol. 40(1), pp. 9–38

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MEAN IONIC ACTIVITY COEFFICIENTS OF ALKALI METALS DISSOLVED IN HIGH DIELECTRIC CONSTANT SOLVENTS: A COMPARISON BETWEEN EXPERIMENTAL DATA AND FUOSS THEORETICAL DATA

M. KAMECHE[a,*], D. C. CHAMPENEY[b,†], M. C. BLANCO[c]
and Z. DERRICHE[d]

[a]*Département de Physique, Faculté des Sciences, U.S.T.M.B. d'Oran, MN'ouar B.P. 1505, Oran, Algérie;* [b]*School of Physics, University of East Anglia, NR4 7TJ, Norwich, UK;* [c]*Departamento de Quimica Fisica, Facultad de Quimica, Universidad de Santiago de Compostela, Spain;* [d]*Laboratoire de Physico-Chimie des Matériaux, Département de Chimie Industrielle, Faculté des Sciences, U.S.T.M.B. d'Oran, M'Nouar 1505, Algérie*

(Received 25 July 2000)

Ionic association of strong univalent symmetrical electrolytes dissolved in Hydrogen Bonded Solvents (HBS) having high dielectric constants, has been studied in terms of mean ionic activity coefficient. This parameter has been analysed with the Fuoss's Paired Ion Model in the concentration range 0.5–500 mol m^{-3}. The experimental data are consistent with this model. It has been shown that fits to the experimental data could be obtained with fixed values of fraction of contact pairs α and Gurney radius corresponding to the Contact Pair (CP). The results of fractions of free ions γ and conducting ions (p) as a function of concentration are also discussed. Conductimetric pairing constants K_A and Gibbs free energy ΔG are deduced to explain this ionic association. The influence of the dielectric constant of the solvent on the ionic association has been also investigated in this work.

Keywords: Fuoss's theory; Ionic association; Activity; Hydrogen bonding

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[*] Tel.: 213 41 422163, Fax: 213 41 421581, e-mail: kameche@hotmail.com
[†] Corresponding author.

ISSN 0031-9104 © 2002 Taylor & Francis Ltd DOI: 10.1080/00319100290005640

1. INTRODUCTION

Ionic association of electrolyte solutions was the interest of researchers over several years since the end of the nineteenth century until 1980. One amongst of the transport parameters which is convenient to explain this ionic association is the activity. In 1926, Debye and Huckel derived theoretically their famous formula by assuming that the electrolyte dissociates completely (no association). They, therefore, ascribed the decrease of the mean ionic activity coefficient, with increasing concentration, both to the long range Coulombic interactions and short range repulsive interactions.

Moreover, as it is shown in previous experimental works [1, 2] the mean ionic activity coefficient starts to deviate from the Debye-Huckel (D.H.) limiting line at a concentration less than $10\,\mathrm{mol} \cdot \mathrm{m}^{-3}$. This is attributed to the negligence of the short range hard-core repulsive interactions between ions as a consequence of electrostatic association. The latter has been underestimated by the linearised Poisson–Boltzmann approximation employed by Debye and Huckel [3] to describe the distribution of ions. This approximation implies that the electrostatic energy is much less than the thermal energy.

However, when the concentration of the electrolyte solution increases, the short range repulsive force should be taken into account. This means that as the ions approach to each other to form pairs, their sizes and shapes ought to be taken into consideration. This is due to Bjerrum who suggested in 1926, that some ions can be considered to be bound together and therefore do not contribute to the conductance process. Following this, a paired ion model has been proposed by Fuoss [4] who classifies ions in one of the three following categories. The first one concerns an ion which couples its nearest neighbour of opposite sign to form a Contact Pair (CP). The second one concerns an ion whose Gurney cosphere overlaps with that of another ion of opposite sign, as a result of the solvation effect, to form a Solvent Separated Pair (SSP). And finally, the third one concerns an ion which finds no ion of opposite sign in the surrounding of the Gurney cosphere, and is called an unpaired ion.

The D.H. limiting law is well obeyed up a concentration less than $10\,\mathrm{mol\,m}^{-3}$, but does not hold for experimental data beyond this concentration and extending to $500\,\mathrm{mol\,m}^{-3}$. As a matter of fact, we attempt to use the Fuoss Paired Ion Model which takes account of the size of the interacting ions, from a certain concentration. Therefore, we may be able, to reduce the differences between the experimental data and those predicted by the limiting law. Finally, we could understand, for example, the ionic association in some Hydrogen Bonded Solvents (HBS). Such solvents are interesting to investigate because the hydrogen bonding which they formed with the dissolved ions, contribute appreciably to the ion-solvent interaction. The solvents chosen are Glycerol and Ethylene Glycol (EG) because they are similar to Water since they display intermolecular Hydrogen Bonding and have high values of dielectric constants ($\varepsilon_r > 40$).

As far as we know there was no published work in the literature which has tested Fuoss's Model on activity. However, in 1987 Champeney *et al.* [5], found this model suitable to test their experimental data on conductivity.

2. EXPERIMENTAL

Experimental procedure undertaken to deduce mean ionic activity coefficient is described in details in Refs. [1,2]. Nevertheless, we present here, just a brief description of the experimental set up with the aim to make our paper self contained.

Experimental ionic activity coefficients are deduced from measurements of Electro-Motive-Forces (EMF) which are generated in Concentration Cells of solutions of strong univalent electrolytes. The cells are: cell with transference using a liquid junction and cell without transference using the liquid amalgam bridge to link the two half cells. The EMF's were measured using a Solartron 7065 digital voltmeter which has an input resistance greater than 100 GΩ.

Ag/AgCl electrodes were prepared by electrolysis in $100\,\text{mol}\cdot\text{m}^{-3}$ solution of HCl, with a current density of about $0.6\,\text{mA}\cdot\text{cm}^{-2}$. From all the electrodes prepared, one could always, find a pair which displayed a potential difference less than 0.1 mV, when dipping into a solution of KCl of concentration $100\,\text{mol}\cdot\text{m}^{-3}$.

KCl, NaCl and LiCl used throughout the experiment, are Aldrich gold label (more than 99% pure). Glycerol and Ethylene Glycol are also Aldrich gold label solvents having relatively high viscosities, in which traces of water were reduced by distillation.

On account of the high hygroscopic nature of both Ethylene Glycol and Glycerol, solutions were prepared inside a glove box filled with purified Argon gas, in the order to avoid errors arising from traces of water.

The measurements have been made inside a water bath where the temperature was fixed at 25°C.

3. RESULTS AND DISCUSSION

3.1. Mean Ionic Activity Coefficient

Mean ionic activity coefficients are deduced iteratively by combining Nernst equations (1), (2) and the extended D.H. law Eq. (4). The ratio between the EMF's of the most concentrated cells with and without transference, gives the value of the transference number. From the most dilute cell with transference, the transference number is, also deduced from the Nernst equation Eq. (1) where the mean ionic activity coefficients are calculated using D.H. limiting law Eq. (3). Hence, the transference numbers at intermediate concentrations, are deduced by assuming a linear interpolation.

$$|E_{\mathrm{LJ}}| = \frac{2RT}{F}\int_1^2 t_{Li+}\,dLna_{\pm} \tag{1}$$

$$|E_{\mathrm{AMALG}}| = \frac{2RT}{F}Ln\frac{a_{\pm 2}}{a_{\pm 1}} \tag{2}$$

$$Lnf_{\pm} = \frac{-\mathrm{e}^3(2N_0C)^{1/2}}{8\pi(\varepsilon_0\varepsilon_r KT)^{3/2}} \tag{3}$$

$$Lnf_{\pm} = \frac{-\mathrm{e}^3(2N_0C)^{1/2}}{8\pi(\varepsilon_0\varepsilon_r KT)^{3/2}} + AC \tag{4}$$

with

$$a_{\pm} = f_{\pm}C \tag{5}$$

$a_{\pm}$ is the mean ionic activity; $f_{\pm}$ is the ionic activity coefficient; C is the concentration; R is the molar ideal gas constant, F is the Faraday constant; T is the absolute temperature; e is the electronic charge; N_0 is the Avogadro number; ε_0 is the permitivity of the vacuum; ε_r is the relative permitivity of the medium; K is the Boltzman constant and A

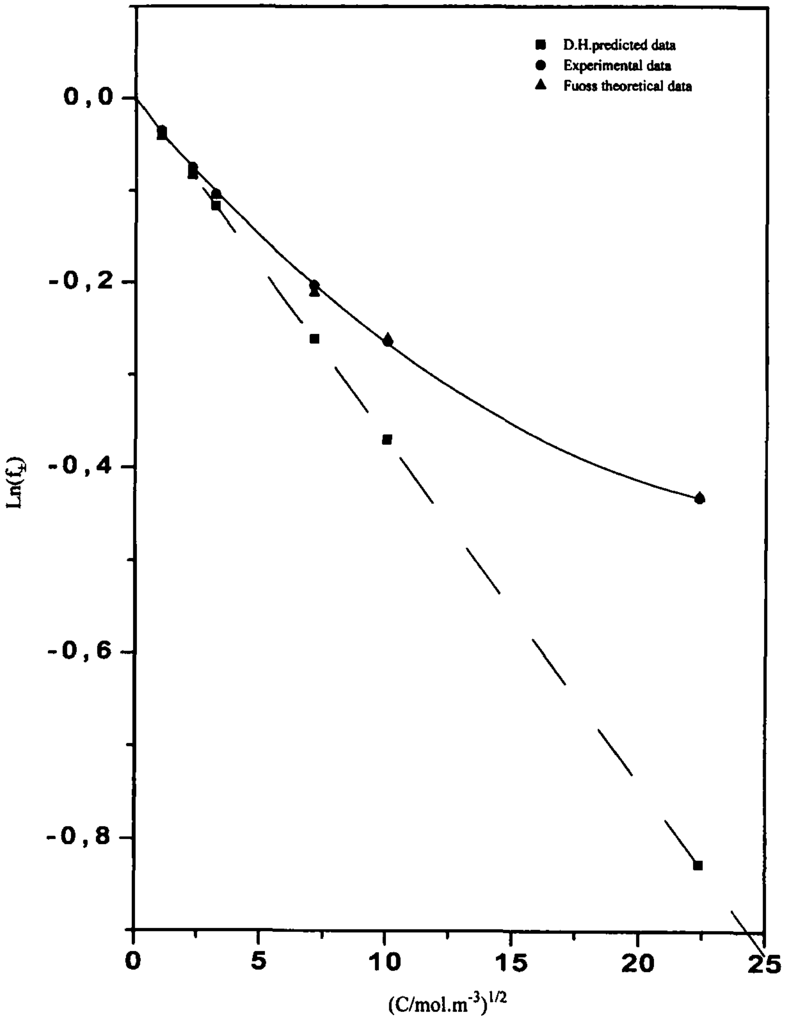

FIGURE 1 Mean ionic activity coefficient of KCl–Water *versus* square root of concentration; $R_G = 0.314\,\text{nm}$, $\alpha = 0.750$.

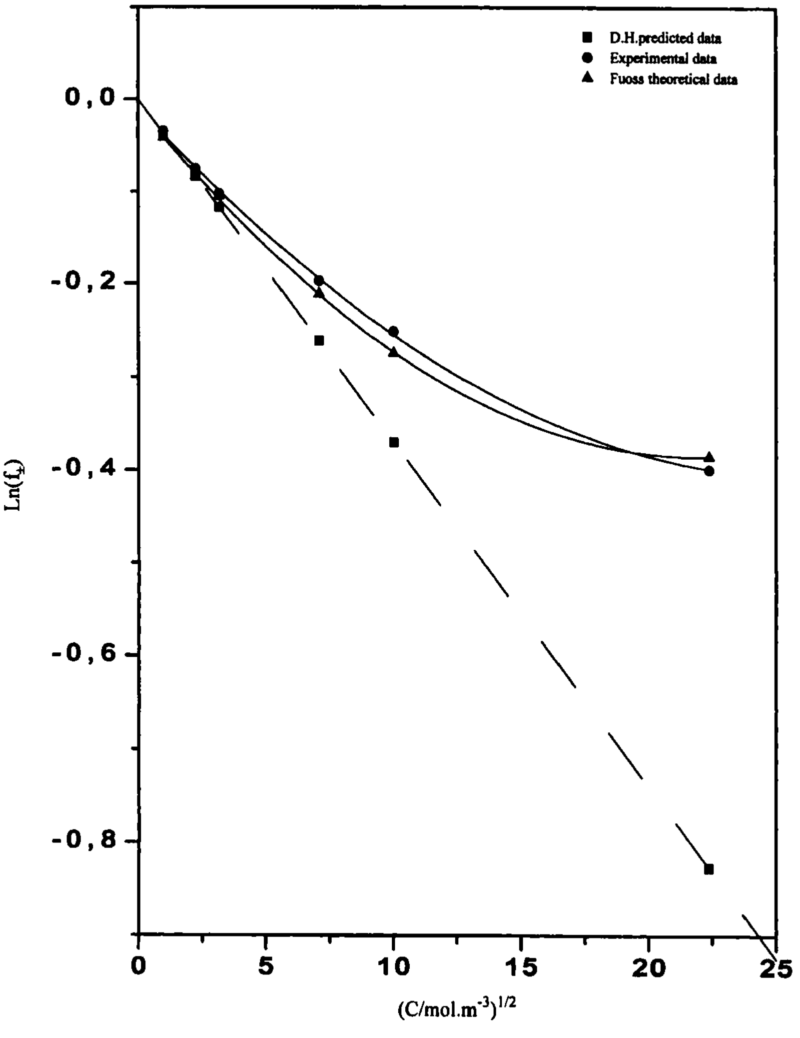

FIGURE 2 Mean ionic activity coefficient of NaCl–Water *versus* square root of concentration; $R_G = 0.276\,\mathrm{nm}$, $\alpha = 0.840$.

is an empirical constant. In Figures 1–8, experimental data lie above the D.H. limiting law, and start to deviate from it earlier at a concentration less than $10\,\mathrm{mol \cdot m^{-3}}$. One can perhaps attribute this to the ionic association with increasing concentration, which

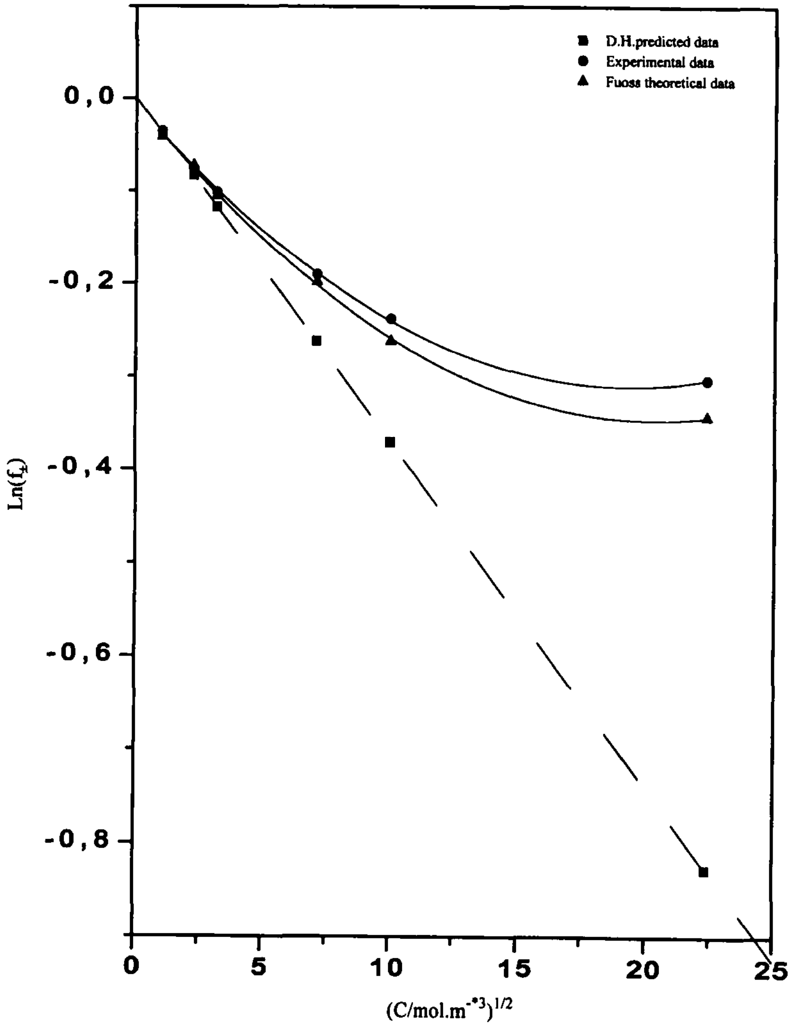

FIGURE 3 Mean ionic activity coefficient of LiCl–Water *versus* square root of concentration; $R_G = 0.259\,\text{nm}$, $\alpha = 0.885$.

counteracts the usual departure from the limiting line. However, by using Fuoss's model [4], we could, always find a theoretical curve which approaches the limiting line from above and fits approximately all the experimental points, provided values of R_{Gurney} (R_G) and α

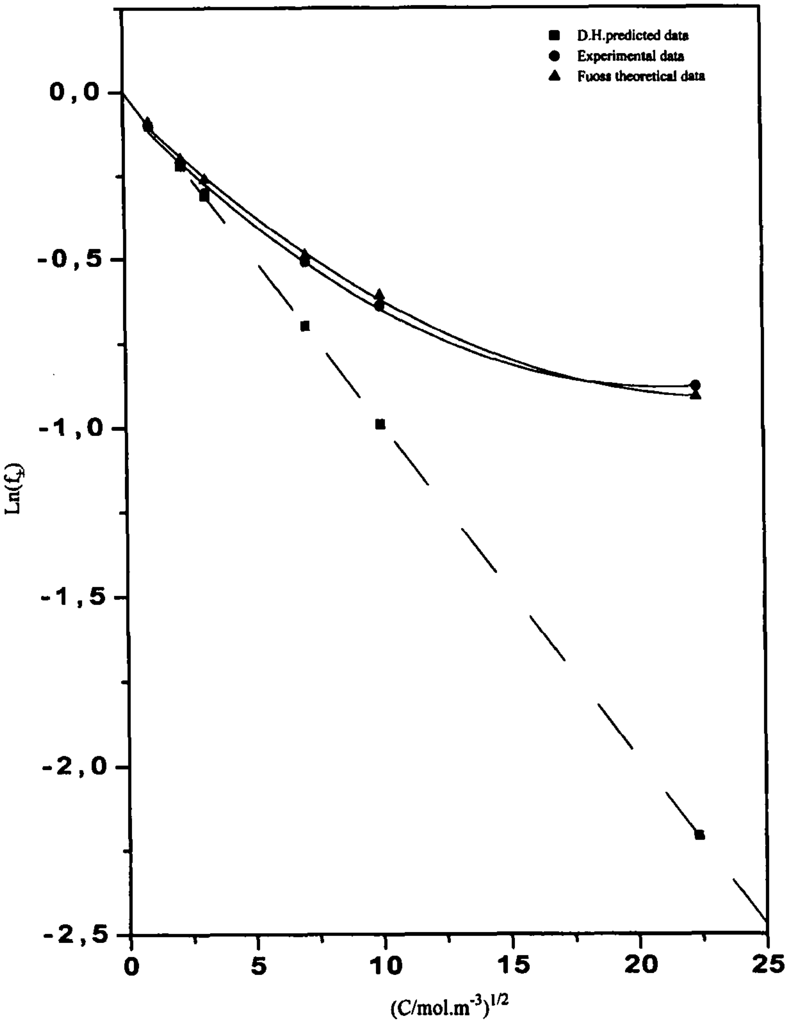

FIGURE 4 Mean ionic activity coefficient of KCl–EG *versus* square root of concentration; $R_G = 0.314$ nm, $\alpha = 0.580$.

are chosen properly. R_G is the radius of the Gurney cosphere and α is the fraction of the Contact Pairs that do not contribute to the conduction process.

Hence, when we increase the concentration of the electrolytic solution, the size of the interacting ions *i.e.*, R_G, and their fraction *i.e.*,

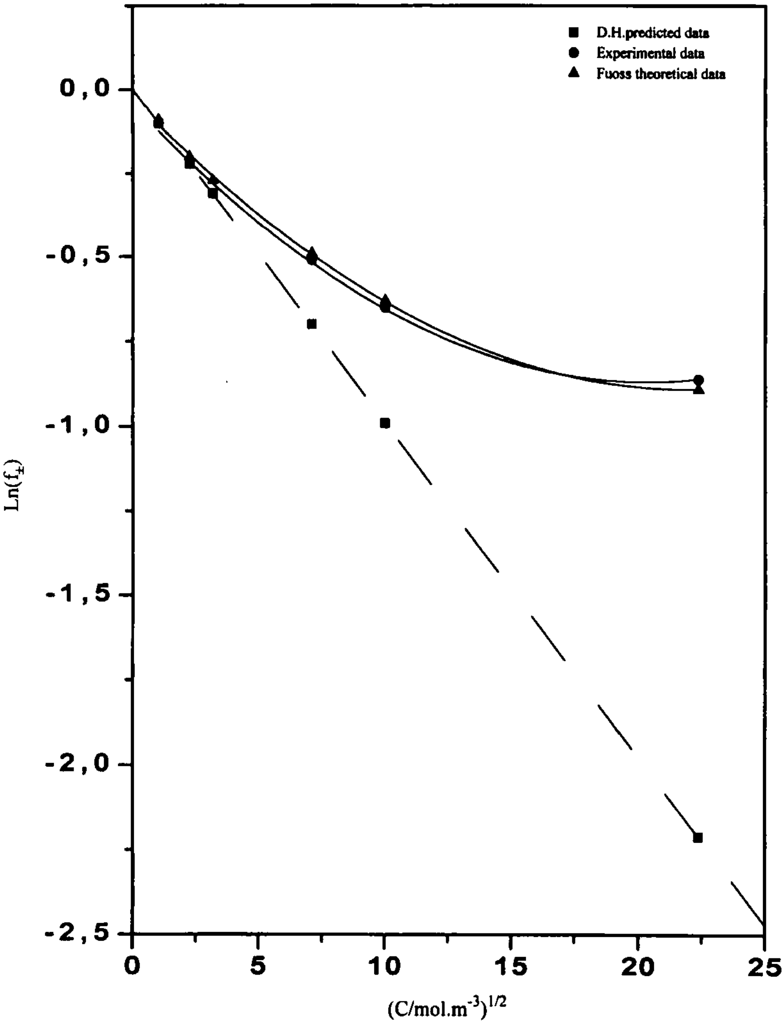

FIGURE 5 Mean ionic activity coefficient of NaCl–EG *versus* square root of concentration; $R_G = 0.276\,\text{nm}$, $\alpha = 0.570$.

κ should be taken into account. As a result the expression of the mean ionic activity coefficient becomes:

$$-Lnf_{\pm} = \frac{\beta\kappa}{2(1+\kappa R_G)} \tag{6}$$

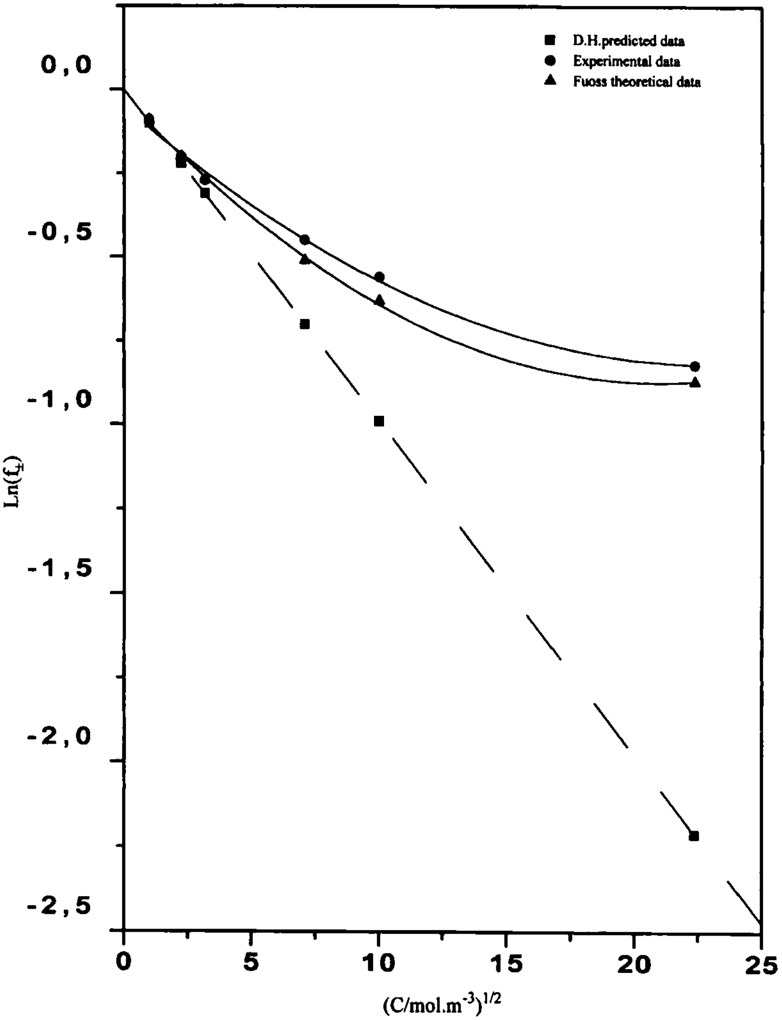

FIGURE 6 Mean ionic activity coefficient of LiCl–EG *versus* square root of concentration; $R_G = 0.259\,\text{nm}$, $\alpha = 0.550$.

where

$$\beta = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r KT} \tag{7}$$

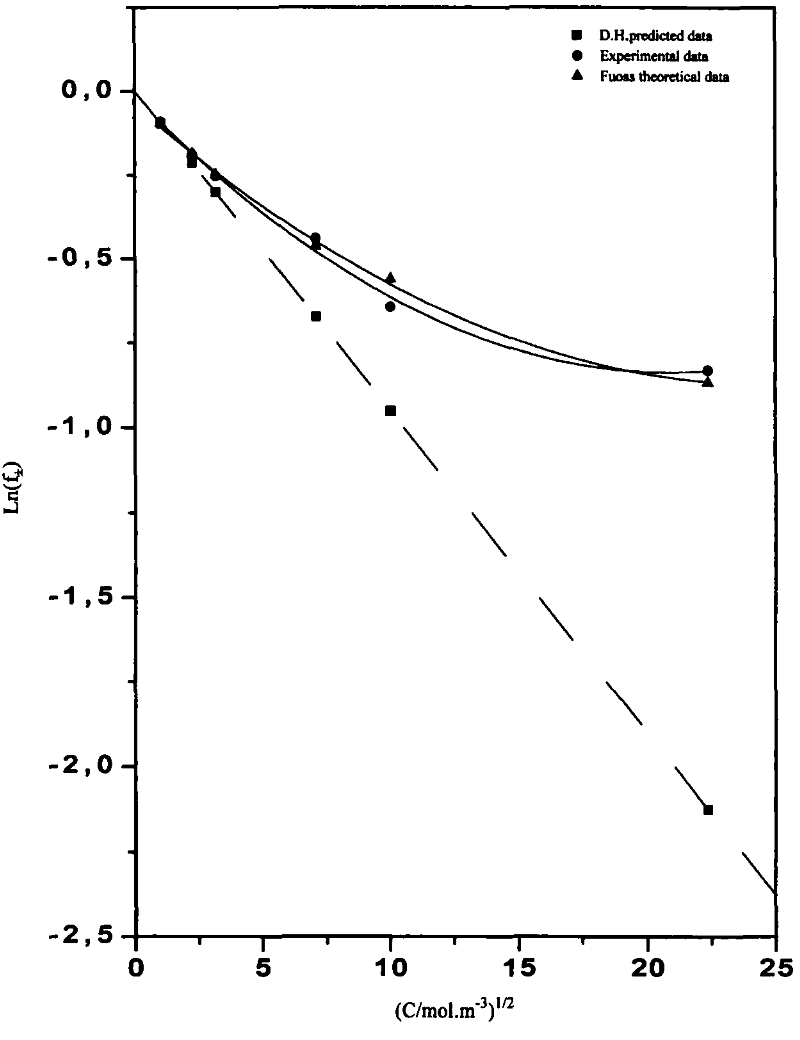

FIGURE 7 Mean ionic activity coefficient of KCl–Glycerol *versus* square root of concentration; $R_G = 0.314\,\text{nm}$, $\alpha = 0.600$.

but, according to Fuoss's model, we have the modified expression of the inverse radius of the ionic atmosphere, *i.e.*,

$$\kappa = \left(\frac{2N_0 C \gamma e^2}{\varepsilon_0 \varepsilon_r KT} \right)^{1/2} \tag{8}$$

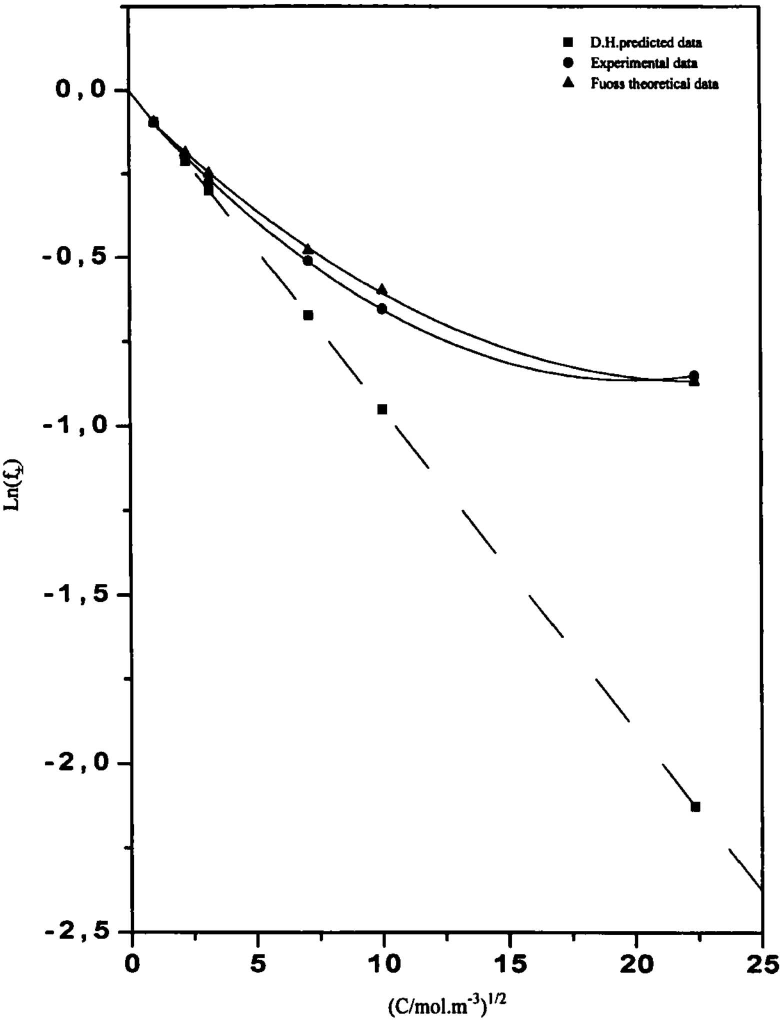

FIGURE 8 Mean ionic activity coefficient of NaCl–Glycerol *versus* square root of concentration; $R_G = 0.276\,\text{nm}$, $\alpha = 0.600$.

γ being the fraction of the unpaired ions, and its expression may be obtained by combining the equations of Fuoss 1.13, 1.9, 4.12–4.14 [4] *i.e.*,

$$\gamma = 1 - \frac{\gamma^2 4\pi N_0 R_G^3 C}{3(1-\alpha)} \exp\left(\frac{\beta}{R_G\left(1 + R_G\sqrt{8\pi\beta N_0 \gamma C}\right)}\right) \tag{9}$$

It should be pointed out that for dilute solutions, Eq. (6) can be approximated to yield the D.H. limiting law given by Eq. (3).

We have started the fitting by fixing the value of R_G equal to the sum of the crystallographic radii of the interacting ions. The value of α is set equal to 0.5 as a first approximation as it is recommended by Fuoss [4], in high dielectric constant solvents. Then, we have carried out a series of successive changes, until the best curve fitting is obtained (see Figs. 1–8). However, at concentrations 100 and $500\,\mathrm{mol \cdot m^{-3}}$, discrepancies are found in the case of LiCl because the experimental data are, perhaps, surestimated. Other values of R_G greater than the sum of the Pauling crystallographic radii have been used but they did never allow a fitting up to $500\,\mathrm{mol \cdot m^{-3}}$.

The resolution of Eq. (9) has been done by a numerical analysis method. In fact, for given values of R_G, C and α, we have set, initially, the value of γ equal to 1 and, after, we have carried out a series of iterations until the value of γ converged towards a constant value close to 1. Then, the value of κ has been calculated. Therefore, the value of $f_\pm$ has been deduced. This method has been followed for all the concentrations. In Table IX, we summarize the values of R_G and α that correspond to the best fitting.

From this table, we may make the following comments:

- The value of R_G is exactly equal to the sum of the Pauling crystallographic radii of the interacting ions being in contact (CP).
- When the size of the electrolyte increases, the value of α decreases in Water, increases in EG, and remains constant in Glycerol. Moreover, its variation in water is more important than in EG, probably because of the increase in the viscosity. In addition, for a given electrolyte, α varies in the following order *i.e.*,

$$\alpha_{\mathrm{Water}} > \alpha_{\mathrm{Glycerol}} > \alpha_{\mathrm{EG}}$$

This order is well correlated to that of their dielectric constants *i.e.*,

$$\varepsilon_r^{\mathrm{Water}} > \varepsilon_r^{\mathrm{Glycerol}} > \varepsilon_r^{\mathrm{EG}}$$

Consequently, the fitting of activity parameter makes in evidence only the ion–ion interaction, regardless the medium. Both in concentrated solutions (the short repulsive forces) and dilute solutions (long range Coulombic interactions), the interacting distance (R_G) does not change and it is not influenced by the surrounding solvent molecules. This result seems entirely different to that found in the conductivity fitting [4, 5].

3.2. Ionic Association

In order to understand the ionic association, it is worthwhile to mention the dependence of both γ and p upon concentration; p being the fraction of conducting ions. These two parameters decrease with increasing concentration. For each concentration, the value of p is found to be greater than that of γ, as has already been noticed by Champeney [4]. This is illustrated in Figure 9

$$p = 1 - \alpha(1 - \gamma) \tag{10}$$

Moreover, the values of p and γ vary in the following sequence:

$$p(\mathrm{KCl}) > p(\mathrm{NaCl}) > p(\mathrm{LiCl})$$
$$\gamma(\mathrm{KCl}) > \gamma(\mathrm{NaCl}) > \gamma(\mathrm{LiCl})$$

These sequences are well shown in Figures 10–15.

3.3. Conductimetric Pairing Constant

As a result of the thermal motion and inter-ionic forces, an equilibrium can be established and may be represented by the following reaction:

$$\mathrm{A^+ + B^-} \leftrightharpoons (\mathrm{A^+ \ldots\ldots B^-}) \leftrightharpoons \mathrm{A^+B^-} \leftrightharpoons \mathrm{AB} \tag{11}$$

where $\mathrm{A^+}$, $\mathrm{B^-}$, $(\mathrm{A^+ \ldots\ldots B^-})$, $\mathrm{A^+B^-}$ and AB represent respectively, free ions, Solvent Separated Pairs (SSP), Contact Pairs (CP$^{\cdot\cdot}$) and neutral molecules. The association constant K_a of this pairing process may be given by the following formula [6]:

$$K_a = \frac{10^3 \rho(1 - \gamma)}{MC\gamma^2 f_\pm^2} \tag{12}$$

M is the molecular weight of the solvent and ρ is its density. $K_\Lambda = ((1 - \gamma)/C\gamma^2 f_\pm^2)$ being the conductimetric pairing constant. It may be

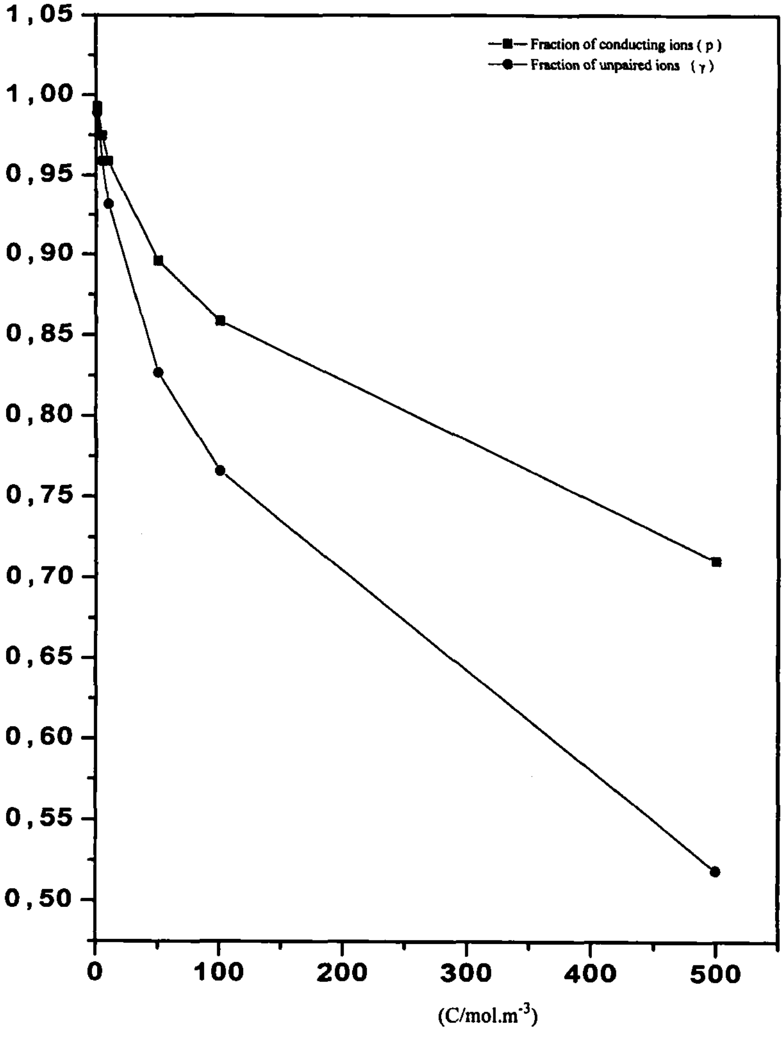

FIGURE 9 Fractions of conducting ions and unpaired ions of KCl–Glycerol *versus* concentration.

calculated explicitly by the following formula,

$$K_\Lambda = K_R(K_s + 1) \tag{13}$$

K_R is the pairing constant which corresponds to the formation of (SSP) from free ions; K_s is the pairing constant which corresponds to

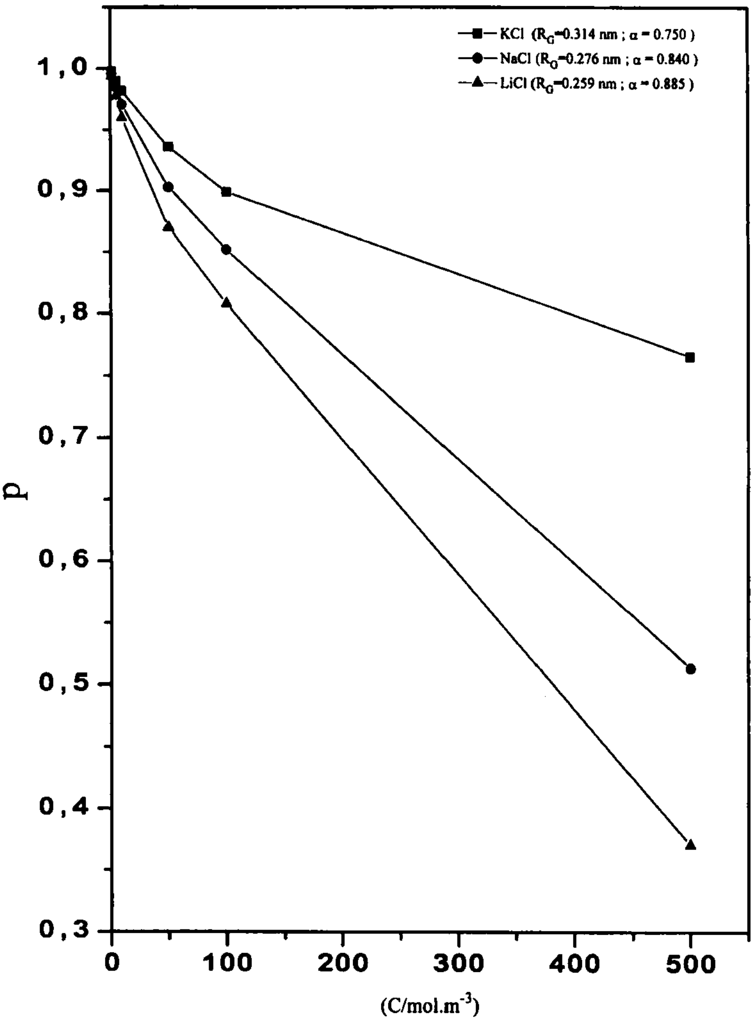

FIGURE 10 Fraction of conducting ions in Water *versus* concentration.

the formation of (CP) from (SSP).

$$K_R = \frac{(1-\alpha)(1-\gamma)}{Cf_{\pm}^2\,\gamma^2} \tag{14}$$

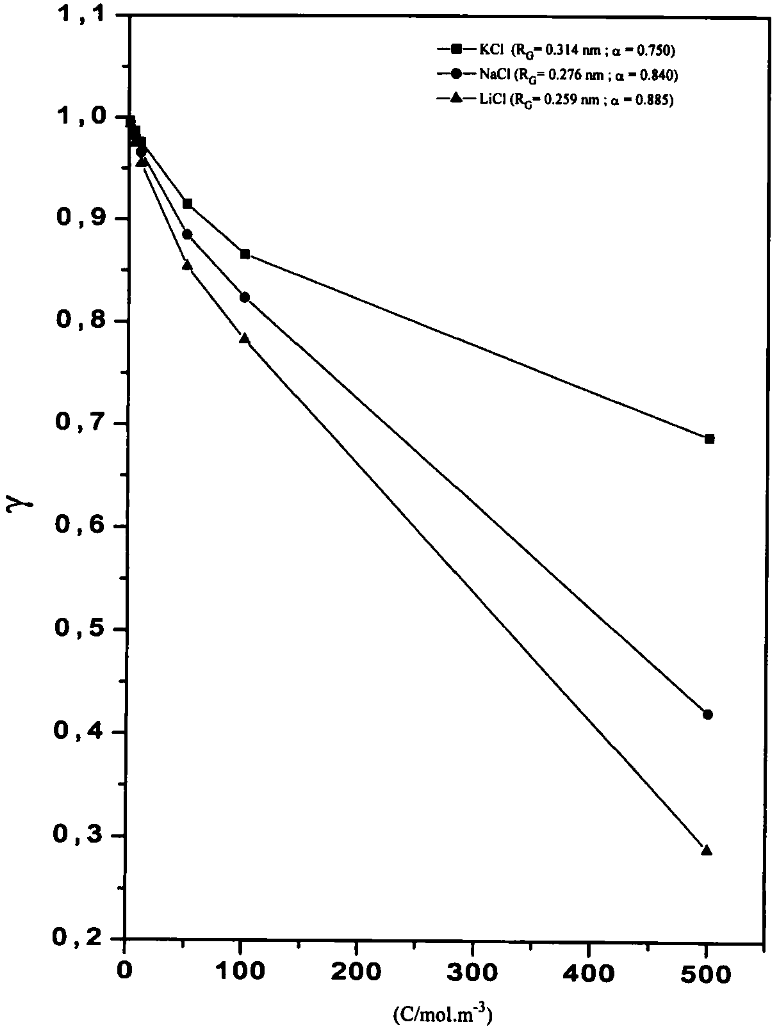

FIGURE 11 Fraction of unpaired ions in Water *versus* concentration.

$$K_s = \frac{\alpha}{1-\alpha} \tag{15}$$

Except the anomalous behaviour of KCl in Glycerol, the values of K_Λ remain almost constant up to a concentration of about 100 mol · m^{-3},

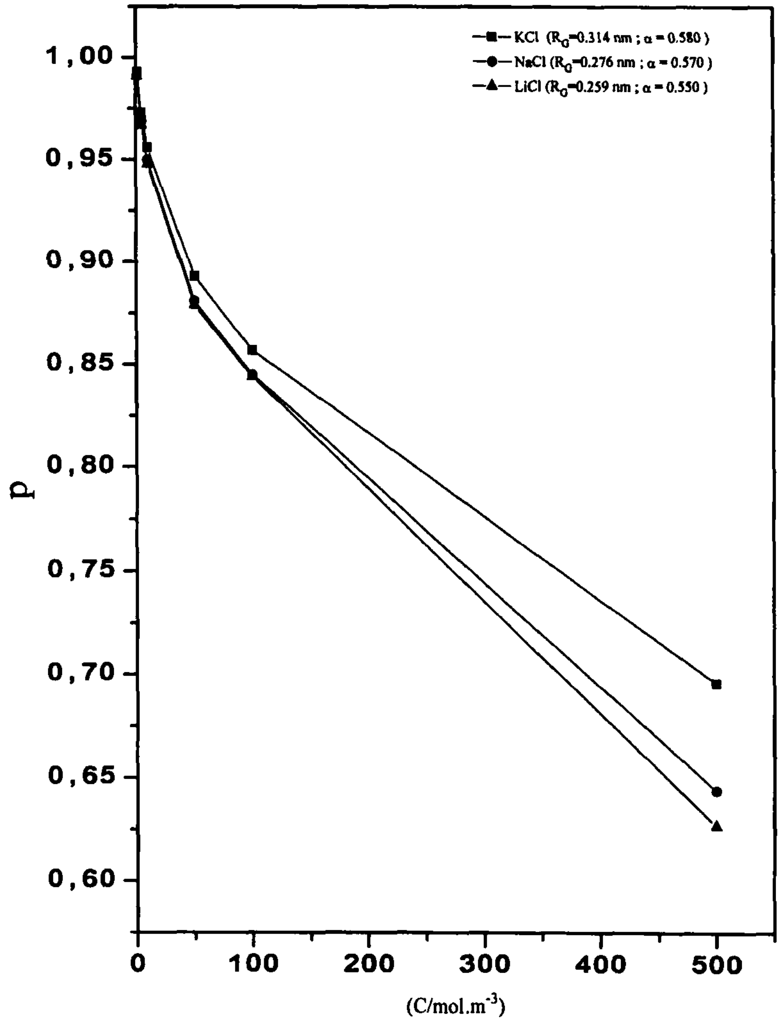

FIGURE 12 Fraction of conducting ions in EG *versus* concentration.

and increase sharply at 500 mol · m^{-3} (see Figs. 16–18). In addition, it can be noticed that the curves lie one above another with the following order,

$$K_\Lambda(\mathrm{LiCl}) > K_\Lambda(\mathrm{NaCl}) > K_\Lambda(\mathrm{KCl})$$

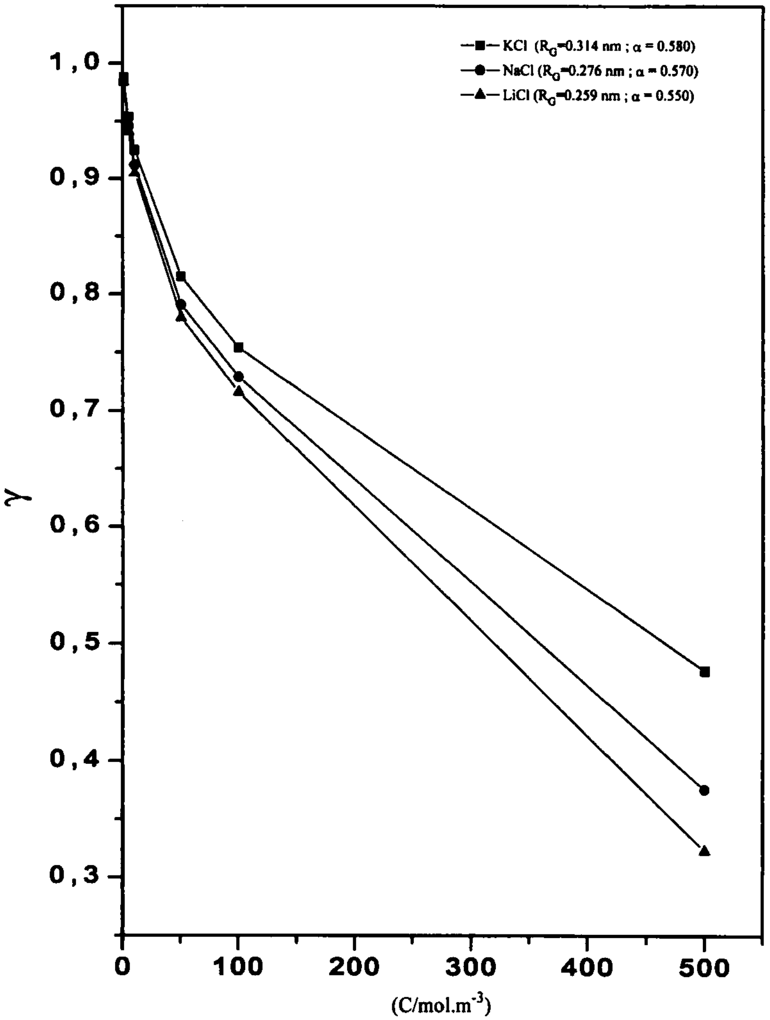

FIGURE 13 Fraction of unpaired ions in EG *versus* concentration.

Therefore, the increase of K_A associated with reduction in ion radius is usually attributed to the increase of the Coulombic force while the ions are in interaction.

Besides, for a given electrolyte, the sharp increases beyond $100\,\text{mol} \cdot \text{m}^{-3}$, in EG and Glycerol are higher than in Water. This is probably due to the smallness values of their dielectric constants.

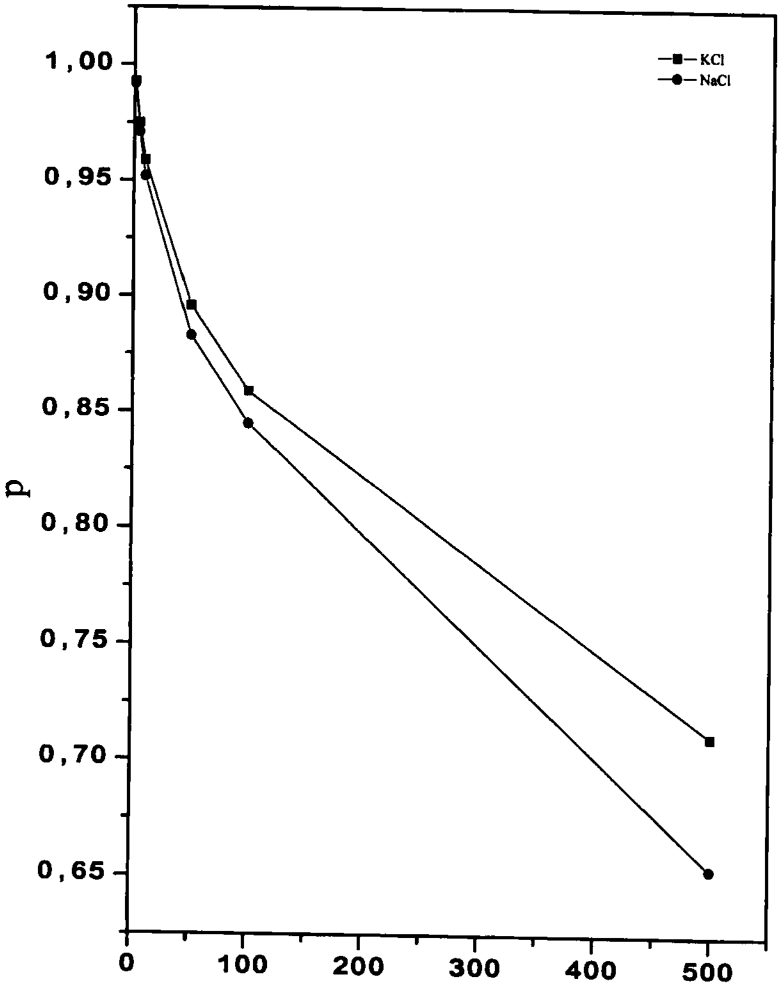

FIGURE 14 Fraction of conducting ions in Glycerol *versus* concentration.

3.4. Gibbs Free Energy of the Pairing Equilibrium

Gibbs free energy ΔG of the pairing equilibrium may defined by the following formula:

$$\Delta G = -RT \, \mathrm{Ln}(K_a) \tag{16}$$

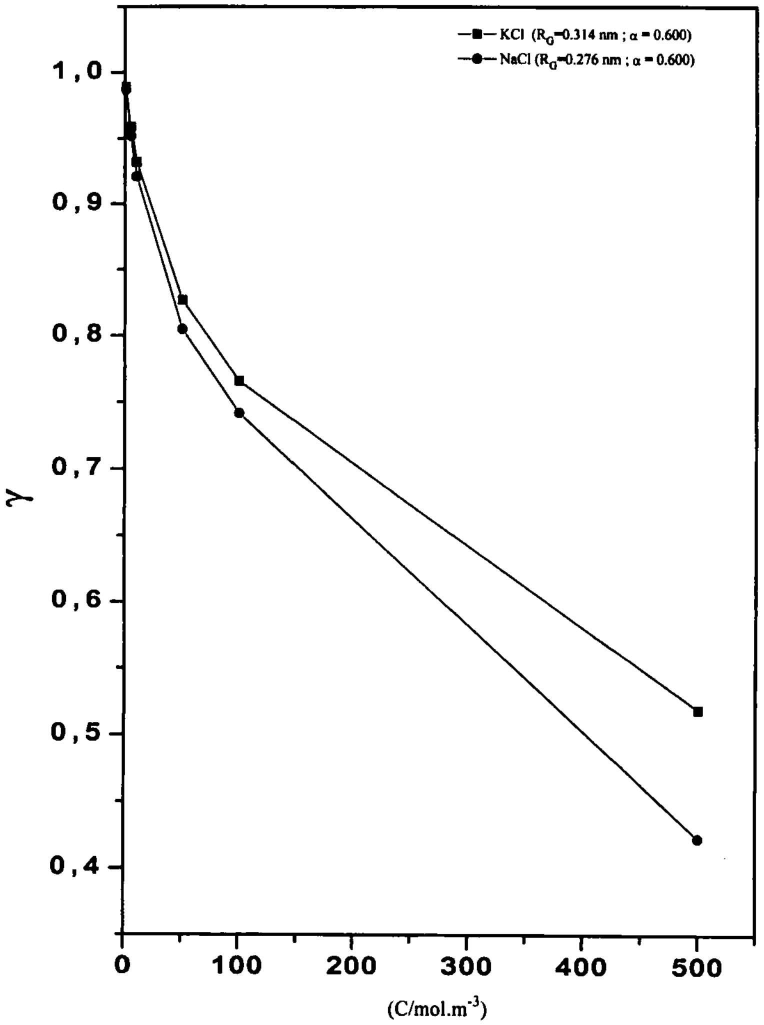

FIGURE 15 Fraction of unpaired ions in Glycerol *versus* concentration.

As it is well known, the Gibbs free energy is the sum of the Enthalpy (ΔH) and Entropy ($-T\Delta S$). The enthalpy contains two energies. A negative energy that contains the necessary work in separating a Contact Pair to infinity, and a positive energy that corresponds to

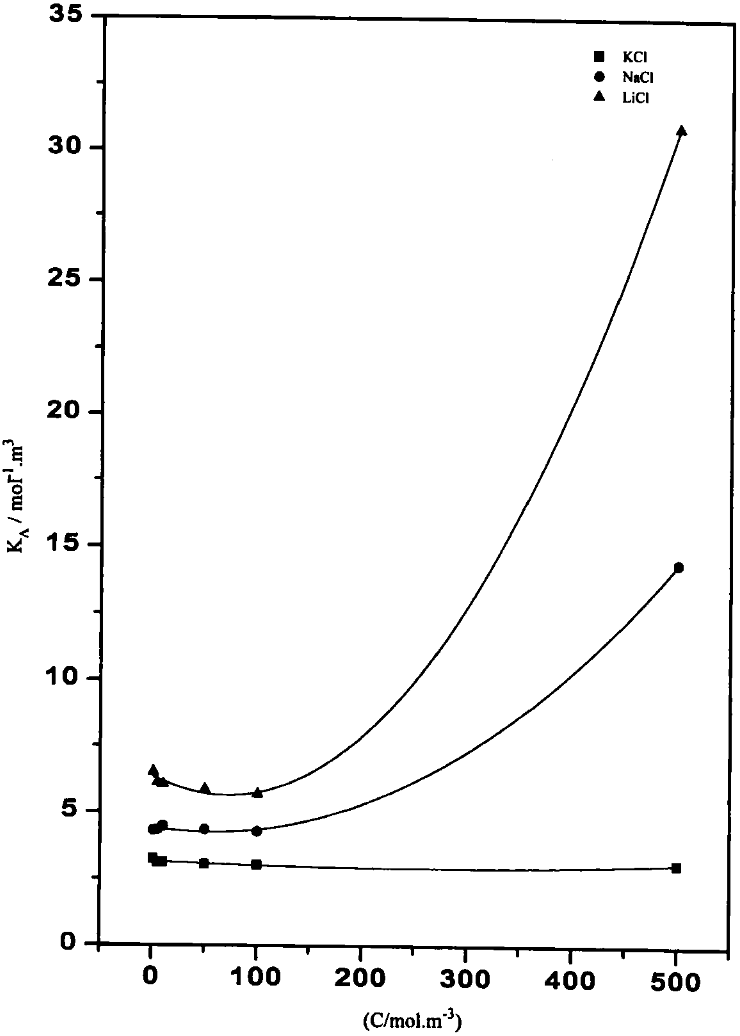

FIGURE 16 Conductimetric pairing constant in aqueous solutions *versus* concentration.

the last step of formation of a Contact Pair from a Solvent Separated Pair.

As it is illustrated in Tables I–VIII, the values of the Gibbs free energy are close to each other. For that reason, we have calculated the

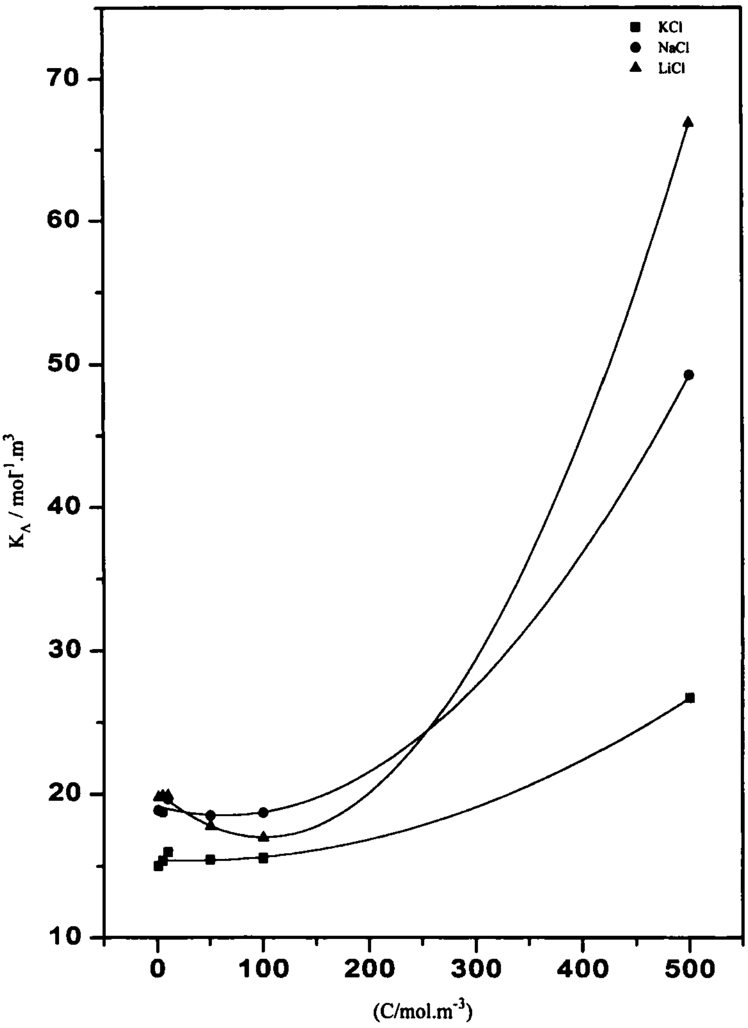

FIGURE 17 Conductimetric pairing constant in EG.

average values of three electrolytes which yielded the following sequence,

$$\Delta G(\mathrm{LiCl}) > \Delta G(\mathrm{NaCl}) > \Delta G(\mathrm{KCl})$$

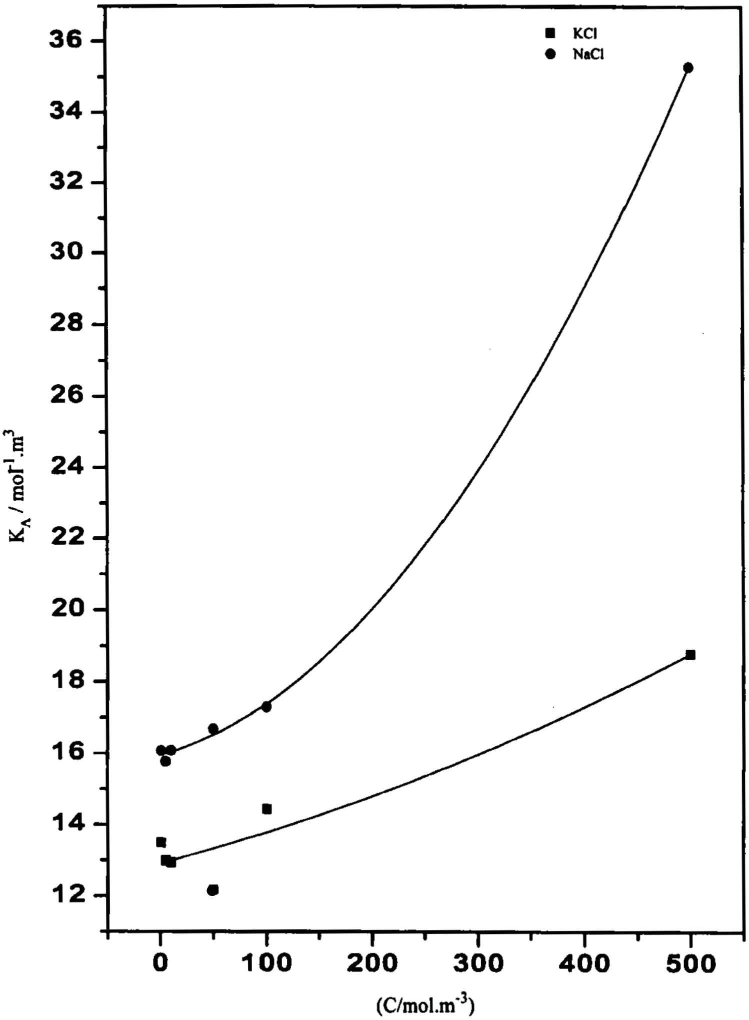

FIGURE 18 Conductimetric pairing constant in Glycerol *versus* concentration.

The obtained values of ΔG are, therefore, well correlated with those of conductimetric pairing constants, since we need more energy to separate two ions very close to each other to infinity (see Tab. X). The sign $(-)$ means that the energy is given to the system.

TABLE I Mean ionic activity coefficient data of aqueous solutions of KCl at 25°C: Comparison between experimental data and Fuoss theoretical data; $R_G = 0.314\,\mathrm{nm}$, $\alpha = 0.750$ (experimental data were taken from Ref. [7])

$\sqrt{C}\ (mol \cdot m^{-3})^{1/2}$	$-Ln(f_\pm)$ D.H.L.L.	$-Ln(f_\pm)$ Exp.	$-Ln(f_\pm)$ Fuoss	p	γ	$K_\Lambda\,(10^{-3}\,mol^{-1}\,m^3)$	$-\frac{\Delta G}{RT}$
1.000	0.037	0.035	0.041	0.998	0.997	3.237	5.192
2.236	0.083	0.075	0.083	0.990	0.987	3.101	5.149
3.162	0.117	0.104	0.105	0.982	0.976	3.102	5.149
7.071	0.261	0.203	0.211	0.936	0.915	3.047	5.131
10.000	0.370	0.264	0.261	0.899	0.866	3.029	5.125
22.360	0.827	0.432	0.431	0.766	0.689	3.108	5.151

TABLE II Mean ionic activity coefficient data of aqueous solutions of NaCl at 25°C: Comparison between experimental data and Fuoss theoretical data; $R_G = 0.276\,\mathrm{nm}$, $\alpha = 0.840$ (experimental data were taken from Ref. [7])

$\sqrt{C}\ (mol \cdot m^{-3})^{1/2}$	$-Ln(f_\pm)$ D.H.L.L.	$-Ln(f_\pm)$ Exp.	$-Ln(f_\pm)$ Fuoss	p	γ	$K_\Lambda\,(10^{-3}\,mol^{-1}\,m^3)$	$-\frac{\Delta G}{RT}$
1.000	0.037	0.034	0.041	0.996	0.996	4.316	5.480
2.236	0.083	0.075	0.083	0.985	0.982	4.337	5.484
3.162	0.117	0.102	0.105	0.971	0.966	4.468	5.514
7.071	0.261	0.197	0.211	0.903	0.885	4.354	5.488
10.000	0.370	0.251	0.274	0.852	0.824	4.282	5.472
22.360	0.827	0.399	0.385	0.514	0.422	14.418	6.686

TABLE III Mean ionic activity coefficient data of aqueous solutions of LiCl at 25°C: Comparison between experimental data and Fuoss theoretical data; $R_G = 0.259$ nm, $\alpha = 0.885$ (experimental data were taken from Ref. [7])

$\sqrt{C}\ (mol \cdot m^{-3})^{1/2}$	$-Ln(f_\pm)$ D.H.L.L.	$-Ln(f_\pm)$ Exp.	$-Ln(f_\pm)$ Fuoss	p	γ	$K_\Lambda\ (10^{-3}\ mol^{-1}\ m^3)$	$-\frac{\Delta G}{RT}$
1.000	0.037	0.035	0.036	0.994	0.994	6.513	5.891
2.236	0.083	0.075	0.077	0.978	0.975	6.111	5.827
3.162	0.117	0.101	0.106	0.960	0.955	6.038	5.815
7.071	0.261	0.190	0.207	0.870	0.854	5.854	5.784
10.000	0.370	0.237	0.266	0.808	0.783	5.686	5.755
22.360	0.827	0.302	0.338	0.371	0.290	30.889	7.448

TABLE IV Mean ionic activity coefficient data of KCl–EG solutions at 25°C: Comparison between experimental data and Fuoss theoretical data; $R_G = 0.314$ nm, $\alpha = 0.580$

$\sqrt{C}\ (mol \cdot m^{-3})^{1/2}$	$-Ln(f_\pm)$ D.H.L.L.	$-Ln(f_\pm)$ Exp.	$-Ln(f_\pm)$ Fuoss	p	γ	$K_\Lambda\ (10^{-3}\ mol^{-1}\ m^3)$	$-\frac{\Delta G}{RT}$
1.000	0.10	0.10	0.09	0.993	0.988	15.015	5.595
2.236	0.22	0.21	0.20	0.973	0.954	15.385	5.620
3.162	0.31	0.30	0.26	0.956	0.925	15.972	5.657
7.071	0.70	0.51	0.49	0.893	0.815	15.448	5.624
10.000	0.99	0.64	0.61	0.857	0.754	15.563	5.631
22.360	2.21	0.88	0.91	0.696	0.477	26.721	6.172

TABLE V Mean ionic activity coefficient data of NaCl–EG solutions at 25°C: Comparison between experimental data and Fuoss theoretical data; $R_G = 0.276\,\mathrm{nm}$, $\alpha = 0.570$

$\sqrt{C}\ (mol \cdot m^{-3})^{1/2}$	$-Ln(f_\pm)$ *D.H.L.L.*	$-Ln(f_\pm)$ *Exp.*	$-Ln(f_\pm)$ *Fuoss*	p	γ	$K_\Lambda (10^{-3}\,mol^{-1}\,m^3)$	$-\frac{\Delta G}{RT}$
1.000	0.10	0.10	0.09	0.991	0.985	18.883	5.825
2.236	0.22	0.22	0.20	0.969	0.946	18.738	5.817
3.162	0.31	0.31	0.27	0.950	0.912	19.668	5.865
7.071	0.70	0.51	0.49	0.881	0.791	18.527	5.806
10.000	0.99	0.65	0.63	0.845	0.729	18.711	5.815
22.360	2.21	0.86	0.89	0.644	0.376	49.297	6.784

TABLE VI Mean ionic activity coefficient data of LiCl–EG solutions at 25°C: Comparison between experimental data and Fuoss theoretical data; $R_G = 0.259\,\mathrm{nm}$, $\alpha = 0.550$

$\sqrt{C}\ (mol \cdot m^{-3})^{1/2}$	$-Ln(f_\pm)$ *D.H.L.L.*	$-Ln(f_\pm)$ *Exp.*	$-Ln(f_\pm)$ *Fuoss*	p	γ	$K_\Lambda (10^{-3}\,mol^{-1}\,m^3)$	$-\frac{\Delta G}{RT}$
1.000	0.10	0.09	0.09	0.991	0.984	19.783	5.871
2.236	0.22	0.20	0.20	0.967	0.941	19.880	5.876
3.162	0.31	0.27	0.27	0.948	0.905	19.904	5.877
7.071	0.70	0.45	0.51	0.879	0.780	17.788	5.765
10.000	0.99	0.56	0.63	0.844	0.716	16.978	5.718
22.360	2.21	0.82	0.87	0.627	0.323	66.904	7.090

TABLE VII Mean ionic activity coefficient data of KCl–Glycerol solutions at 25°C: Comparison between experimental data and Fuoss theoretical data; $R_G = 0.314\,\text{nm}$, $\alpha = 0.600$

$\sqrt{C}\ (mol \cdot m^{-3})^{1/2}$	$-Ln(f_\pm)$ *D.H.L.L.*	$-Ln(f_\pm)$ *Exp.*	$-Ln(f_\pm)$ *Fuoss*	p	γ	$K_A\,(10^{-3}\,mol^{-1}\,m^3)$	$-\frac{\Delta G}{RT}$
1.000	0.095	0.091	0.094	0.993	0.989	13.491	5.218
2.236	0.212	0.188	0.186	0.975	0.959	12.986	5.180
3.162	0.300	0.251	0.248	0.959	0.932	12.933	5.176
7.071	0.672	0.439	0.462	0.896	0.827	12.172	5.111
10.000	0.950	0.643	0.560	0.859	0.766	14.430	5.285
22.360	2.124	0.830	0.867	0.711	0.519	18.783	5.549

TABLE VIII Mean ionic activity coefficient data of NaCl–Glycerol solutions at 25°C: Comparison between experimental data and Fuoss theoretical data; $R_G = 0.276\,\text{nm}$, $\alpha = 0.600$

$\sqrt{C}\ (mol \cdot m^{-3})^{1/2}$	$-Ln(f_\pm)$ *D.H.L.L.*	$-Ln(f_\pm)$ *Exp.*	$-Ln(f_\pm)$ *Fuoss*	p	γ	$K_A\,(10^{-3}\,mol^{-1}\,m^3)$	$-\frac{\Delta G}{RT}$
1.000	0.095	0.093	0.094	0.992	0.987	16.072	5.393
2.236	0.212	0.199	0.186	0.971	0.952	15.770	5.374
3.162	0.300	0.273	0.248	0.952	0.921	16.078	5.393
7.071	0.672	0.510	0.478	0.883	0.805	16.690	5.431
10.000	0.950	0.653	0.598	0.845	0.742	17.298	5.466
22.360	2.124	0.850	0.867	0.654	0.423	35.304	6.180

D.H.L.L.: values calculated using Debye Huckel Limiting Law.
Exp.: experimental data.
Fuoss: Fuoss theoretical data.

TABLE IX Values of R_G and α that correspond to the best fitting

Salt	*LiCl*	*NaCl*	*KCl*	*LiCl*	*NaCl*	*KCl*	*LiCl*	*NaCl*	*KCl*
R_G (nm)	0.259	0.276	0.314	0.259	0.276	0.314	0.259	0.276	0.314
α	0.885	0.840	0.750	*	0.600	0.600	0.550	0.570	0.580

Water: $\varepsilon_r = 78.35$; $\eta = 0.00089$ Pa s.
Glycerol: $\varepsilon_r = 42.7$; $\eta = 0.91$ Pa s.
EG: $\varepsilon_r = 40.7$; $\eta = 0.0168$ Pa s.

TABLE X Values of Gibbs free energies

Salt	*LiCl*	*NaCl*	*KCl*	*LiCl*	*NaCl*	*KCl*	*LiCl*	*NaCl*	*KCl*
R_G (nm)	0.259	0.276	0.314	0.259	0.276	0.314	0.259	0.276	0.314
$-\frac{\Delta G}{RT}$	6.086	5.687	5.149	*	5.539	5.254	6.033	5.985	5.716

Water: $\varepsilon_r = 78.35$; $\eta = 0.00089$ Pa s.
Glycerol: $\varepsilon_r = 42.7$; $\eta = 0.91$ Pa s.
EG: $\varepsilon_r = 40.7$; $\eta = 0.0168$ Pa s.

4. CONCLUSION

We have shown that Debye-Huckel law can be used successfully to reproduce experimental mean ionic activity coefficient of some alkali metals, up a concentration less than $10\,\text{mol}\cdot\text{m}^{-3}$. However, it fails for concentrations greater than $10\,\text{mol}\cdot\text{m}^{-3}$ and extending to $500\,\text{mol}\cdot\text{m}^{-3}$. As a matter of fact, the Fuoss paired ion model has been used instead to reproduce all the experimental data. By using this model, fits to the data could be obtained with a value of the Gurney radius (R_G) equal to the sum of the Pauling crystallographic radii of the ions being in interaction, provided the value of the fraction of contact pairs (α) is chosen properly. The three solvents used behave similarly in this context despite the differences in viscosity and molecular size. The similarity is presumably caused by the solvents being hydrogen bonded and having high relative permitivities. The parameter (α) has been found to increase with increasing of the dielectric constant of the solvent. Fuoss's parameters (p) and (γ) have been also deduced and show that the fraction of the ions contributing to the conductivity process is always higher than that of unpaired ions. The results of the conductimetric pairing constant and Gibbs free energy make in evidence the fact that the smaller the size of the electrolyte, the stronger the coupling between its interacting ions.

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