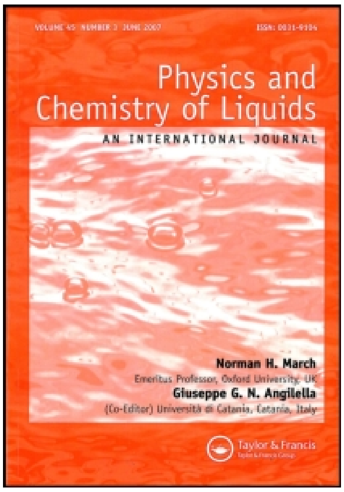

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Electro-Motive Forces Generated in Concentration Cells of LiCl-Glycerol Solutions

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

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ELECTRO-MOTIVE FORCES GENERATED IN CONCENTRATION CELLS OF LiCl-GLYCEROL SOLUTIONS

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,*
M'Nouar 1505, Algéie; [b]*School of Physics, University of East Anglia,*
NR4 7TJ, Norwich; [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

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Mean ionic activity coefficients of LiCl in Glycerol have been calculated in the concentration range $0.5-500\,\mathrm{mol \cdot m^{-3}}$, using the concentration cell technique. Up to the limit of the Debye-Huckel theory ($C \leq 1\,\mathrm{mol \cdot m^{-3}}$), the experimental values lie below the limiting line, showing that the measured Electro-Motive-Force might have been false by using our previous cell design. An alternative method based on Fuoss Paired Ion Model has been used to deduce the theoretical data, and consequently, the values of the EMF's. By comparing these data to those obtained experimentally with KCl and NaCl, we find that they are consistent with the results in aqueous solutions.

Keywords: Concentration cells; Activity; Conductivity; Electrolytes; Glycerol; Fuoss model

1. INTRODUCTION

The reliability of concentration cell technique for determining mean ionic activity coefficients of strong univalent electrolytes, has been

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[*] Corresponding author. Tel.: (9)81-591078, Fax: (9)81-595012.

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applied successfully in viscous hydrogen bonded solvents [1, 2], as well as in water [3–5].

Interest in the present contribution is focused in studying the activity of lithium chloride salt dissolved in Glycerol, because we are not aware of any previous data.

The lithium is the lightest alkaly metal, and its ion is the least mobile in this solvent compared to potassium and sodium ions. In addition, it has the smallest Walden product [6]. Moreover, it is interesting to investigate, in that it has a mobility which is much higher than that of the nickel ion [7]; Li^+ and Ni^{2+} have the same crystallographic radii.

Glycerol was chosen as a solvent, because it is similar to water in that it displays intermolecular hydrogen bonding, and because it has a high dielectric constant ($\varepsilon_r = 42.7$). It is also a good solvent for common salts.

One difficulty has been encountered in measuring the most dilute Electro-Motive Force (EMF) which is generated in the a concentration cell with transference. The situation is even worse when measuring the EMF of the concentration cell without transference. Its value was erratic because the lithium amalgam was not easy to control.

The values of the transference numbers and mean ionic activity coefficients deduced from this experiment are not in good agreement with Debye-Huckel theory (D.H.), showing the failure of the method used in such viscous system.

Fortunately, a set of data obtained from the fitting of the conductivity using Fuoss's theory, is available, has enabled us to compute theoretically values of the activity and, therefore those of the EMF's.

2. EXPERIMENTAL

Materials, preparation of Ag/AgCl electrodes, apparatus and experimental procedure are described in details in Ref. [1].

In spite of that, we outline the whole experiment briefly.

LiCl salt and Glycerol used throughout this experiment are Aldrich gold label (more than 99% pure).

Ag/AgCl electrodes were prepared by electrolysis in $100\,\mathrm{mol \cdot m^{-3}}$ solution of HCl, with a current density of about $0.6\,\mathrm{mA \cdot cm^{-2}}$. 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 mol · m^{-3}.

The EMF's were measured using a Solartron 7065 digital voltmeter which has an input resistance greater than 100 GΩ.

The concentration cell with transference called also cell with liquid junction, is illustrated by the schematic diagram in Figure 1, whilst that without transference (with the amalgam bridge) is well described in Ref. [3].

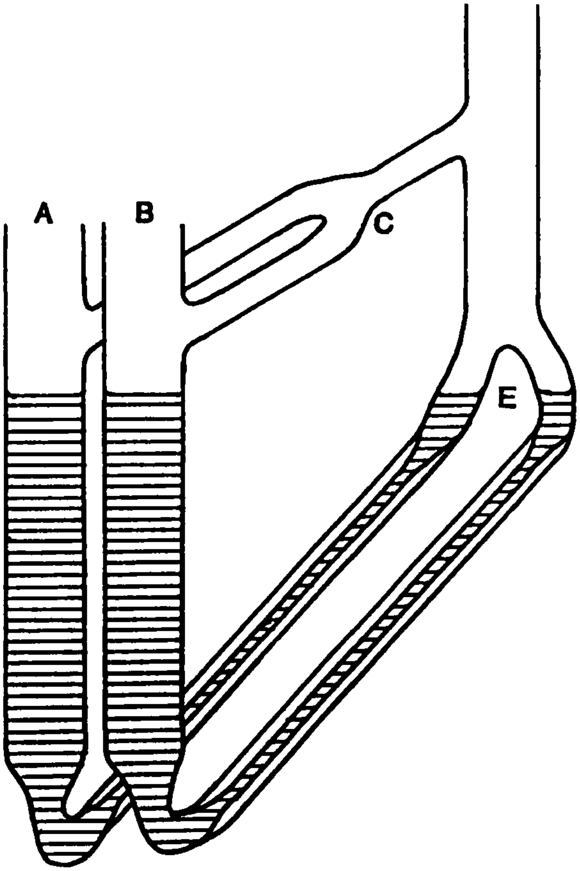

FIGURE 1 Schematic diagram of the concentration cell with transference (with a liquid junction).

On account of the high hygroscopic nature of both LiCl and Glycerol, solutions were prepared inside a glove box filled with purified Argon gas.

3. METHOD

The computational method for deducing mean ionic activity coefficients is described in details in Ref. [1], and that based on Fuoss paired ion model is reviewed elsewhere [8]. We present, therefore, a general outline of these two methods, so that the present paper becomes self contained.

3.1. Transference Number

The experiment consists of measuring the EMF's with transference (using a liquid junction) and without transference (using a lithium amalgam bridge to link the two half cells). The cell with transference E_{LJ} may be represented by

E_{LJ} : Ag/AgCl || LiCl-Glycerol (C_1) ::: (C_2)LiCl-Glycerol || AgCl/Ag

The cell without transference may be represented by

E_{AMALG} : Ag/AgCl || LiCl-Glycerol(C_1) |**Li-Hg**|(C_2) LiCl-Glycerol ||AgCl/Ag

C_1 and C_2 are the concentrations of the two half-cells ($C_2 \approx 10C_1$). AgCl/Ag electrodes are reversible to chlorine ion. |**Li-Hg**| being the lithium amalgam bridge to join the two half-cells. By taking the ratio between these two EMF's, we may find the transference number t_{Li^+} of the lithium ion, if one assumes that it is constant within the concentration range ($C_1 - C_2$), *i.e.*,

$$t_{Li^+} \approx \frac{|E_{LJ}|}{|E_{AMALG}|} \tag{1}$$

where

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

and

$$|E_{AMALG}| = \frac{2RT}{F} Ln\frac{a_{\pm 2}}{a_{\pm 1}} \tag{3}$$

called Nernst equations.

($a_{\pm} = f_{\pm}C$) is the mean ionic activity, R is the molar ideal gas constant, F is the Faraday constant and T is the absolute temperature.

Equation (1) has been used to deduce the transference number from the most concentrated E_{LJ} and E_{AMALG} cells ($50\,\mathrm{mol \cdot m^{-3}}$: $500\,\mathrm{mol \cdot m^{-3}}$), whereas those of the remaining cells, may be calculated from the following Debye-Huckel formula.

In S.I.units,

$$t_{Li^+} = t^0_{Li^+} + \frac{(t^0_{Li^+} - 0.5)}{\eta\Lambda^0_{LiCl}}\left(\frac{2e^6N_0C}{9\pi^2\varepsilon_0\varepsilon_r KT}\right)^{1/2} \tag{4}$$

$t^0_{Li^+}$ being the transference number at infinite dilution ($C \approx 0\,\mathrm{mol \cdot m^{-3}}$). It can be obtained from the formula given below, by assuming the Kohlrausch independent migration of ions, *i.e.*,

$$t_{Li^+} = \frac{\Lambda^0_{Li^+}}{\Lambda^0_{Li^+} + \Lambda^0_{Cl^-}} \tag{5}$$

$\Lambda^0_{Li^+}$ and $\Lambda^0_{Cl^-}$ are respectively the ionic molar conductivities of Li^+ and Cl^- ions at infinite dilution ($C \approx 0\,\mathrm{mol \cdot m^{-3}}$); η is the viscosity of the solvent assumed equal to that of the solution in the concentration range used; Λ^0_{LiCl} is the molar conductivity of LiCl at infinite dilution; 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 and K is the Boltzman constant.

Equation (4) is expected to be strictly valid up to a concentration of about $100\,\mathrm{mol \cdot m^{-3}}$. This means that the transference number of the most concentration cell ($50\,\mathrm{mol \cdot m^{-3}}$: $500\,\mathrm{mol \cdot m^{-3}}$), can easily be evaluated by this formula.

3.2. Activity Coefficient

Values of the mean ionic activities $f_{\pm}$ at concentrations less than $1\,\mathrm{mol \cdot m^{-3}}$, can solely be calculated from the Debye-Huckel limiting law (D.H.L.L.), *i.e.*,

$$Lnf_{\pm} = \frac{-e^3(2N_0C)^{1/2}}{8\pi(\varepsilon_0\varepsilon_r KT)^{3/2}} \tag{6}$$

In view of the fact that electrical conductivity is well represented by the Debye-Huckel-Onsager (D.H.O.) limiting law [9], we have used the following extended Debye-Huckel limiting law to calculate the mean ionic activity coefficient at $C = 5\,\mathrm{mol \cdot m^{-3}}$,

$$Lnf_{\pm} = \frac{-e^3(2N_0C)^{1/2}}{8\pi(\varepsilon_0\varepsilon_r KT)^{3/2}} + AC \tag{7}$$

where A is an empirical constant, found equal to -11.21×10^{-3} in our case.

3.3. Conductimetric Pairing Constant

Fuoss's theory consists of fitting in the appropriate value of the Gurney radius R_G and that of α the fraction of Contact Pairs that contribute nothing to the conductance process, to reproduce theoretically almost the experimental data. The values of the fractions of unpaired ions γ can, therefore, be deduced. Hence, the conductimetric pairing constant K_R of the Solvent Separated (SSP) Pairs [9], can easily be deduced from the following equation,

$$K_R = \frac{4}{3}\pi N_0 R_G^3 \exp\left(\frac{e^2}{4\pi\varepsilon_0\varepsilon_r KTR_G}\right) \tag{8}$$

According to Fuoss's paired ion model, an equilibrium may be established through the following reaction,

$$Li^+ + Cl^- \leftrightarrows (Li^+ \ldots Cl^-) \leftrightarrows (Li^+Cl^-) \leftrightarrows (LiCl)$$

Li^+ and Cl^- are free ions; $(Li^+ \ldots Cl^-)$ are Solvent Separated Pairs; (Li^+Cl^-) are Contact Pairs and (LiCl) are neutral molecules.

On the basis of this equilibrium, K_R that corresponds to the formation of SSP, can be expressed by the following expression, *i.e.*,

$$K_R = \frac{(1-\alpha)(1-\gamma)}{Cf_{\pm}^2\gamma^2} \tag{9}$$

So, by combining Eqs. (7) and (8), we may derive the expression of the activity function $f_{\pm}(C)$, *i.e.*,

$$f_{\pm}^2(C) = \frac{3(1-\alpha)(1-\gamma)}{4N_0R_G^3Cf_{\pm}^2\gamma^2}\exp\left(\frac{e^2}{4\pi\varepsilon_0\varepsilon_r KTR_G}\right) \tag{10}$$

From Fuoss's conductivity fitting, we compute values of R_G, α and γ. Thence, from Eq. (9), the values of $f_{\pm}$ can be deduced at each concentration.

4. RESULTS AND DISCUSSION

4.1. Experimental Mean Ionic Activity Coefficients

The method used to calculate the mean ionic activities of LiCl-Glycerol is the same as that already described in Ref. [1].

The values at concentrations $0.5\,\mathrm{mol\cdot m^{-3}}$ and $1\,\mathrm{mol\cdot m^{-3}}$, can readily be calculated from the Debye-Huckel limiting law (D.H.L.L.). However, those at higher concentrations are deduced iteratively from the liquid junction EMF's, provided the values of the transference numbers are well known.

From the EMF of the most dilute liquid junction cell ($0.5\,\mathrm{mol\cdot m^{-3}}$: $1\,\mathrm{mol\cdot m^{-3}}$), we have found a value of t_{Li^+} equal to 0.3812. By comparing this value to that obtained from ionic molar conductivities at infinite dilution of Li^+ and Cl^- ($t^0_{Li^+} = 0.3262$) [6], we can regard it as being wrong, because the EMF ($|E_{LJ}| = 13.05\,\mathrm{mV}$) must have been false, as it was the case for the concentration cell using solution of LiCl-Ethylene Glycol [1].

As a matter of fact, we have used ($t^0_{Li^+} = 0.3262$) and combined it to the value obtained from the ratio of the most concentrated cells E_{LJ} and E_{AMALG} ($t_{Li\pm} = 0.3090$). Thus, by assuming a linear interpolation between these two numbers, we have deduced values of t_{Li^+} at intermediate concentrations. Unfortunately, these results have yielded values of Lnf$_\pm$ which lie below the D.H.L.L. The same situation exists in the other way, when we use values of t_{Li^+} calculated from Eq. (4).

The results are given in Table I and are represented in Figure 2. We can, consequently, conclude that our measured EMF's are erroneous, probably, because of the high reactivity of the Lithium metal inside the solution of Glycerol, at the interface solution/electrode, causing an enormous error in measuring the potential difference. We, therefore, believe that the measurements of EMF's generated in concentration cells of LiCl-Glycerol solutions by using our cell design, are not reliable.

4.2. Fuoss Conductivity Fitting

In order to overcome this problem, we have thought to a theoretical approach to compute these data. As a matter of fact, Fuoss's theory seems reasonable to apply in this context.

Fuoss paired ion model has been applied successfully to fit experimental conductance data of alkaly metal halides dissolved both in water and hydro-organic media [10]. It has, also, been tested satisfactorily with KCl in pure Glycerol [11]. In the latter, almost the experimental data were reproduced up to a concentration of about 400 mol·m^{-3}, with a fixed value of R_G equal to 0.3 nm and a fixed value of α equal to 0.16. Other good fittings were also obtained but they did not extend to higher concentrations.

TABLE I Experimental mean ionic activity coefficients of LiCl in Glycerol at 25°C

C (*mol·m*$^{-3}$)	$-Lnf_\pm$	$-Lnf_\pm$*	$-Lnf_\pm$** *D.H.L.L.*
0.5	0.067	0.067	0.067
1	0.105	0.106	0.094
5	0.267	0.269	0.212
10	0.409	0.415	0.299
50	0.696	0.708	0.670
100	0.885	0.905	0.949
500	1.150	1.193	2.136

* Using Debye-Huckel formula with $t^0_{Li^+} = 0.3262$, to calculate intermediate transference numbers.

** Values predicted by Debye-Huckel Limiting Law. N.B. The concentrations listed in all tables are nominal and correspond to those used in the measurements.

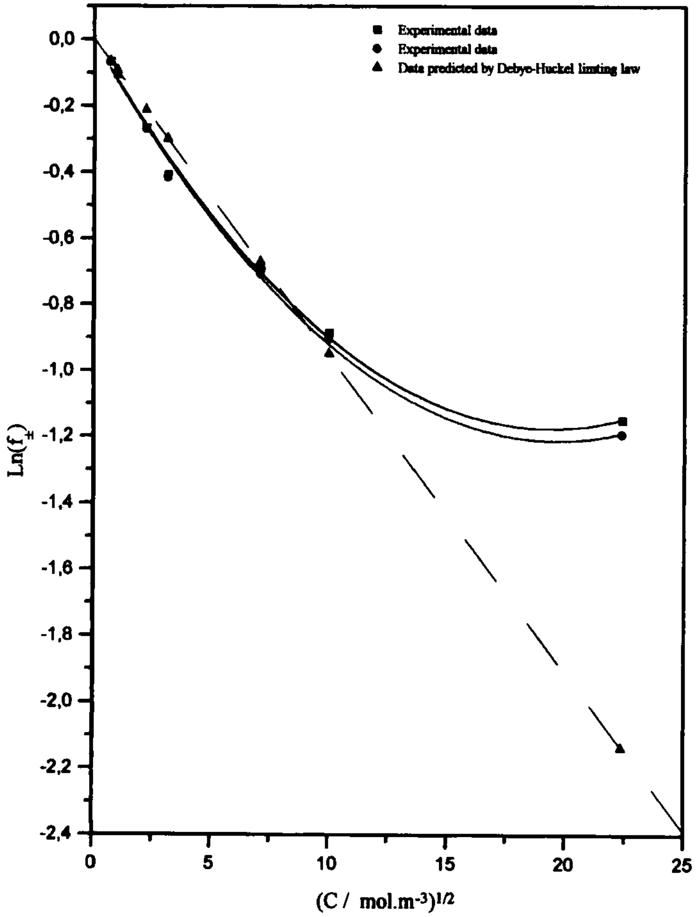

FIGURE 2 The dependence of Ln($f_{\pm}$) on $C^{1/2}$ for LiCl dissolved in Glycerol at 25°C; see text for details of experimental data.

Thence, following Fuoss's theory, we have also fitted our experimental conductance data of LiCl-Glycerol [6] with a manner which is quite different from that followed by Champeney [11].

That is to say, that R_G decreases and α increases with increasing concentration. These variations seem reasonable since the interacting distance R_G ought to decrease (free ions approach to each other) when the concentration increases. However, α should increase because the conductivity decreases.

Up to the limit set by Debye-Huckel-Onsager limiting law ($C \approx 10\,mol \cdot m^{-3}$) [6], R_G has been found constant ($R_G = 1.059\,nm$), and falls down to 0.359 nm at $C \approx 500\,mol \cdot m^{-3}$. However, the values of α vary right since the beginning from 0.400 to 0.694 (see Tab. II). The values of γ, are therefore deduced, and they, of course, decrease with increasing concentration. The comparison between experimental and Fuoss theoretical data of the conductivity are given in Table IIa and are illustrated on Figure 3.

The details of computing values of conductivity using D.H.O. limiting law, are reported in Ref. [6]. Only for comparison, we have listed them in Table IIb.

4.3. Theoretical Values of Mean Ionic Activity Coefficients

The values of $f_\pm$ can, easily be deduced from Eq. (10), and they are shown in Table III. In Figure 4, $\operatorname{Ln} f_\pm$ is plotted against $C^{1/2}$. The broken line represents the predictions of D.H. theory, whilst the

TABLE IIa Comparison between experimental and Fuoss theoretical molar conductivities in Glycerol at 25°C

C $(mol \cdot m^{-3})$	Λ_{exp} $(\mu Sm^2 mol^{-1})$	Λ_{Fuoss} $(\mu Sm^2 mol^{-1})$	α	R_G (nm)	γ
0.5	25.27	23.23	0.400	1.059	0.992
1	25.00	25.00	0.480	1.059	0.983
5	24.12	24.15	0.500	1.059	0.933
10	23.45	23.47	0.510	1.059	0.887
50	21.69	21.68	0.511	0.859	0.769
100	20.14	20.17	0.610	0.659	0.712
500	15.85	15.85	0.694	0.359	0.432

TABLE IIb Conductivity experimental data of LiCl in Glycerol compared to Fuoss theoretical data and those predicted by D.H.O. hinting law

C $(mol \cdot m^{-3})$	Λ_{exp} $(\mu Sm^2 mol^{-1})$	Λ_{Fuoss} $(\mu Sm^2 mol^{-1})$	Λ_{DHO} $(\mu Sm^2 mol^{-1})$
0.5	25.27	25.23	25.25
1	25.00	25.00	25.04
5	24.12	24.15	24.16
10	23.45	23.47	23.49
50	21.69	21.68	20.69
100	20.14	20.17	18.59
500	15.85	15.85	9.73

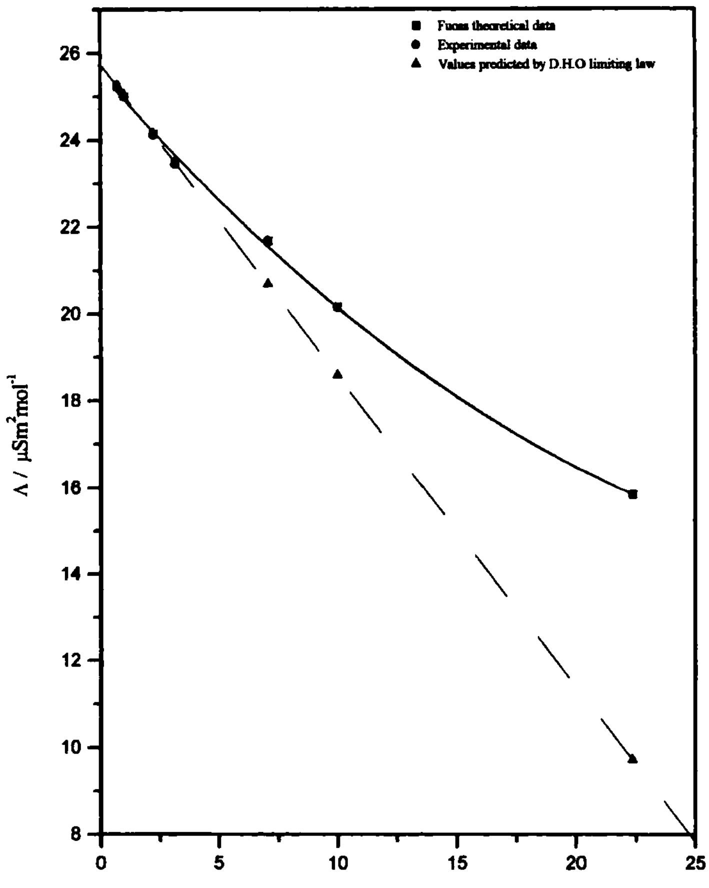

FIGURE 3 Molar conductivity of LiCl in glycerol *versus* the square root of concentration at 25°C; fuoss theoretical data compared to experimental data.

TABLE III Comparison between experimental and Fuoss theoretical mean ionic activity coefficients of LiCl in Glycerol at 25°C

C $(mol \cdot m^{-3})$	$-Lnf_{\pm\,exp}$	$-Lnf_{\pm\,th}$	$-Lnf_{\pm}$* (D.H.L.L.)
0.5	0.067	0.027	0.067
1	0.105	0.059	0.094
5	0.267	0.145	0.212
10	0.409	0.190	0.299
50	0.696	0.324	0.670
100	0.885	0.426	0.949
500	1.150	0.441	2.136

* Values predicted by Debye-Huckel Limiting Law.

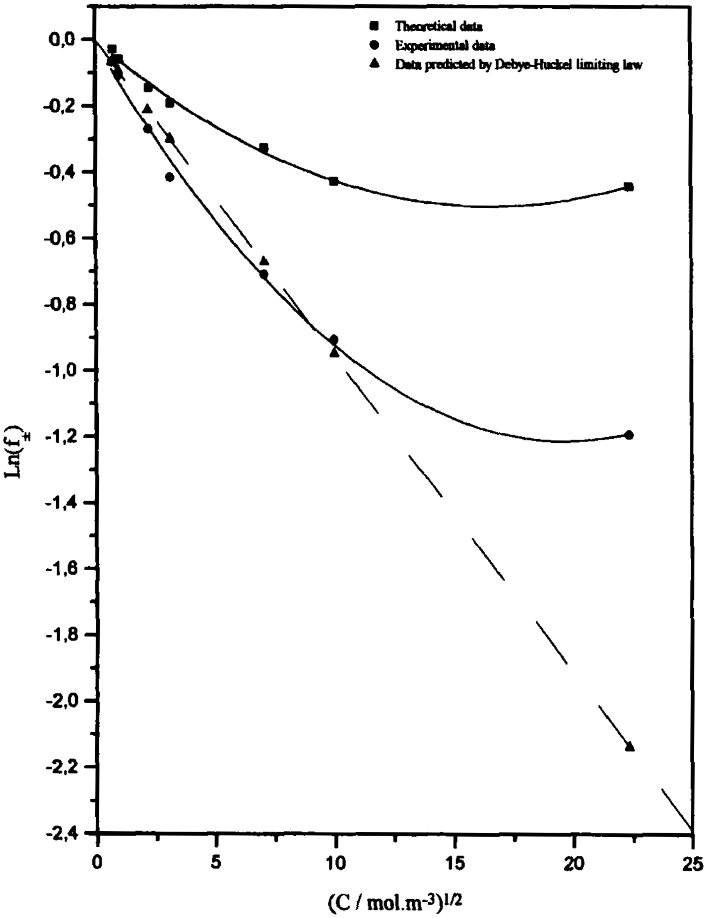

FIGURE 4 Comparison between experimental and theoretical data of mean ionic activity coefficients of LiCl in glycerol.

continuous curves illustrate the experimental and theoretical values of $\mathrm{Ln}\, f_{\pm}$. As it is shown on this figure, the theoretical values agree quite well with the D.H.L.L. up to $C \approx 1\,\mathrm{mol} \cdot \mathrm{m}^{-3}$, and at higher concentrations, they are found greater than those predicted by D.H. theory, as it is the case for KCl and NaCl in Glycerol [2]. Moreover, our theoretical data of LiCl are higher than the experimental values of NaCl and KCl (see Tab. IV), and are in concordance with data in aqueous solutions [3–5]. The difference between these values as is

TABLE IV Fuoss theoretical mean ionic activity coefficients of LiCl in Glycerol compared to the experimental data of NaCl-Glycerol and KCl-Glycerol solutions

C ($mol \cdot m^{-3}$)	$-Lnf_{\pm\,exp}$ (KCl)	$-Lnf_{\pm\,exp}$ ($NaCl$)	$-Lnf_{\pm\,th}$ ($LiCl$)
0.5			0.027
1	0.091	0.093	0.059
5	0.188	0.199	0.145
10	0.251	0.273	0.190
50	0.439	0.510	0.324
100	0.643	0.653	0.426
500	0.830	0.850	0.441

illustrated by Figure 5, arises, probably, from the fact that the properties of lithium metal differ greatly from those of potassium and sodium metals.

The experimental activity data of KCl and NaCl have been successfully, verified by Fuoss theory, in a recent paper in progress for publication [12].

Moreover, Lnf$_\pm$ curves of KCl and NaCl are close to each other, forming one family, whilst the curve of LiCl lies on its own and forms itself another family. This behaviour is similar in water (see Fig. 6).

Besides, when we compare data in Glycerol and Water, we may make the following comment; the gap between the two family curves is more important in Glycerol than in Water.

This comes, probably, from the fact that the number of Hydrogen Bonds formed per a Glycerol molecule is greater than that formed per a Water molecule. A useful check should be made with a monoalcohol.

As a result, we may conclude that the method followed to compute theoretically the mean ionic activity coefficient data from experimental conductivity data using Fuoss theory, seems reasonable, when it is so difficult to obtain reliable EMF measurements.

4.4. Theoretical Electromotive Forces

Finally, by combining the theoretical values of f$_\pm$ to those of the transference numbers, we obtain the values of E_{LJ} and E_{AMALG} using Nernst equations (see Tab. V).

As it can be seen on this table, the discrepancies between experimental and theoretical data, magnify with increasing concentration.

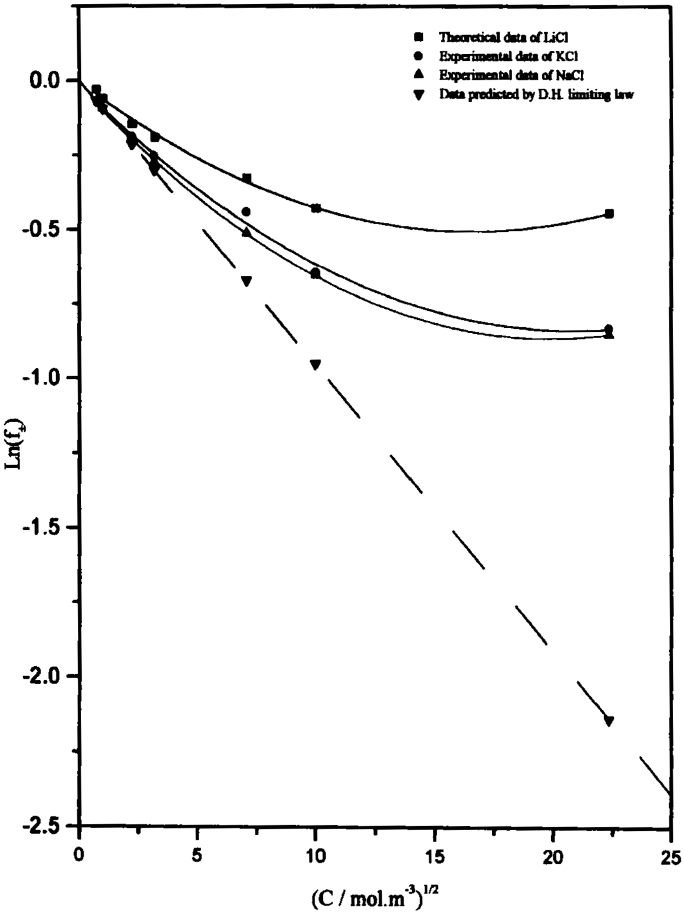

FIGURE 5 Theoretical mean ionic activity coefficient data of LiCl compared to experimental mean ionic activity coefficient data of both KCl and NaCl, in glycerol.

They are even bigger in the case of the amalgam cell. This confirms the fact that the concentration cells as they have been designed by us [1], are not suitable for measuring the EMF's generated in LiCl-Glycerol solutions.

Nevertheless, the magnitudes of our calculated E_{LJ} are less than those measured using NaCl and KCl solutions, as it was also the case in aqueous solutions [3 – 5]. For comparison, see Table VI. As a result, the use of a cationic exchange membrane using Hittorf unsymmetrical

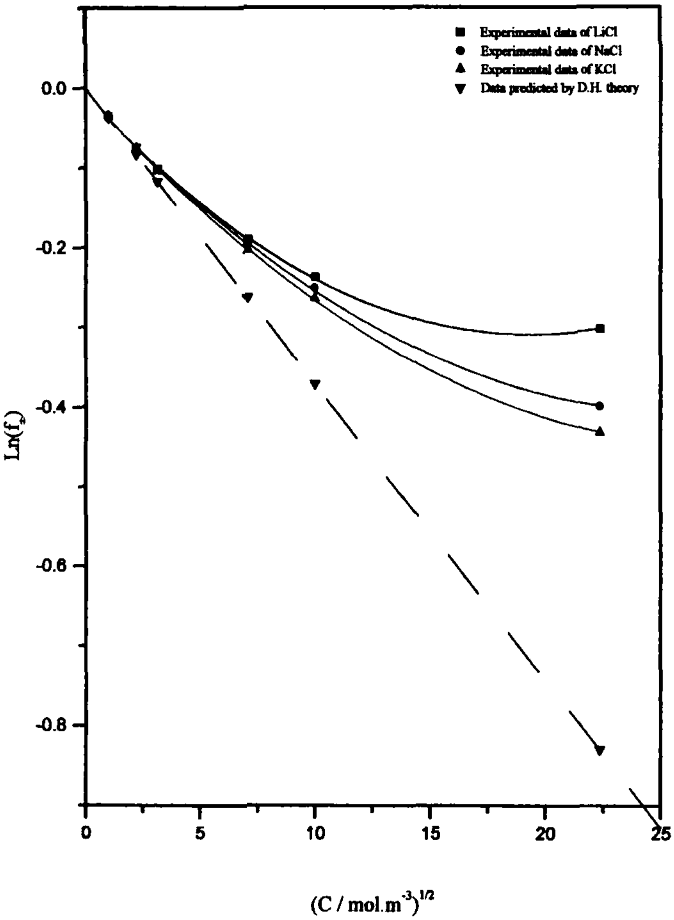

FIGURE 6 The dependence of Ln(f ±) on $C^{1/2}$ for LiCl, NaCl and KCl dissolved in water at 25°C.

TABLE V Comparison between experimental and theoretical electromotive forces generated in concentration cells of LiCl-glycerol solutions at 25°C

Cell ($mol \cdot m^{-3}$)	E_{LJ}^{exp} (*V*)	E_{LJ}^{th} (*V*)	E_{AMALG}^{exp} (*V*)	E_{AMALG}^{th} (*V*)
0.5:1	−0.01305	−0.01104	*	−0.03397
1:10	−0.03327	−0.03623	*	−0.11165
5:50	−0.03091	−0.03522	*	−0.10924
10:100	−0.02994	−0.03412	*	−0.10636
50:500	−0.02959	−0.03555	−0.09574	−0.11314

* Not measured experimentally.

TABLE VI Theoretical E_{LJ} EMF's of LiCl-glycerol solutions compared to those measured in NaCl-glycerol and KCl-glycerol solutions

Cell $(mol \cdot m^{-3})$	E_{LJ}^{exp} *(KCl)* *(V)*	E_{LJ}^{exp} *(NaCl)* *(V)*	E_{LJ}^{th} *(LiCl)* *(V)*
0.5:1	*	*	−0.01104
1:10	−0.05278	−0.04549	−0.03623
5:50	−0.05055	−0.04268	−0.03522
10:100	−0.04709	−0.04119	−0.03412
50:500	−0.04711	−0.04206	−0.03555

* Not measured experimentally.

electro-chemical cell design [13], would be, perhaps, the next experimental set up to be carried out to determine the transference number of the lithium ion. Such an experiment will avoid us, specially the use of lithium amalgam bridge. The latter was difficult to control because of the high reactivity of lithium with the inevitable penetration of oxygen during the course of the experiment.

5. CONCLUSION

We have shown that the concentration cell designs used in Refs. [1,3] are not reliable for measuring EMF's generated in solutions of LiCl-Glycerol. An alternative method based on Fuoss's theory has been used to compute the theoretical values of the mean ionic activities coefficients. By comparing them to those of NaCl and KCl, we notice that they are consistent with the values in aqueous solutions. The data of the different EMF's can, readily, be obtained from Nernst (Eqs. (2), (3)) by using transference numbers calculated with the Debye-Huckel formula Eq. (4).

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