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ISTITUTO DI CHIMICA-FISICA
UNIVERSITA' DEGLI STUDI DI PALERMO

CONDUCTANCE OF SOME ALKALI HALIDES IN WATER-GLYCEROL
MIXTURE AT 25°C

by
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Contract number: DA - 91 - 591 - EUC - 2086

FINAL TECHNICAL REPORT

Period covered: 1 january 1962 - 31 december 1962

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CONTENTS

I	- Abstract	Page	1
II	- Main body of the report		
	Introduction	"	3
	Conductance and viscosity	"	6
	Experimental part	"	7
	Results	"	11
	Discussion	"	22
III	- Implications of the results for possible future works	"	26
IV	- Summary of personnel utilized during the reporting period together with a summary of other administrative actions.	"	28
V	- Unofficial summary of the number of manhours expended on the contract and expenses for material expended in carrying out the contract.	"	29

I. A B S T R A C T

The electrical conductance of sodium chloride in glycerol-water mixture has been measured at 25°C, in order to test the validity of the Fuoss-Onsager theory in the case of a mixture with viscosity varying in a very large range. With the mixture used as solvent, it is possible to vary the viscosity of a factor of a thousand. For all the mixtures the concentration method has been used. For the solution in pure glycerol the dilution method has been used since the experimental difficulties due to the high viscosity.

The results show that the sodium chloride is not associated up to the lowest dielectric constant corresponding to the pure glycerol. This evidence results from the plots of the quantity Λ^t versus c which are linear for all the mixtures. The results have also permitted the analysis of the coefficient of the conductance equation in function of the viscosity of the medium. These coefficients, in the limit of the validity of the Walden rule, should depend only on the dielectric constant and not on the viscosity. In effect the results have confirmed this dependence. The Walden product increases going from pure water to pure glycerol. Because the same behaviour has been found with some other electrolytes in solution of the same mixture, the tentative hypothesis of a relaxation effect between the

ions and the dipoles of the solvent, present when both the components of the mixture are polar, has been confirmed. Such effect seems to be dependent on the number of hydrogen bonds which is related to the number of hydroxyl present in the molecules.

II

Main body of the report

II. 1. The decreasing equivalent conductance of electrolytic solutions with increasing concentration has been a problem which has been interesting the physical chemistry for a long time. A limit solution of this problem has been done by Onsager (1) who was able to predict the form of the limiting equation. A test of the Onsager equation against a large body of precise data showed that the equation was the limiting tangent to the experimental conductance curve. This limitation is a consequence of the model used by Onsager where the ions were represented as point charges and of the boundary conditions used in evaluating the constants for the integration of the differential equations valid for point charges. Moreover Onsager did not evaluate terms of order higher than $c^{\frac{1}{2}}$.

Quite recently Fuoss and Onsager (2) have obtained a solution of the problem, using a model in which the ions were represented by charged spheres in a continuum. The equation they obtained for an un-associated electrolyte is:

$$\Lambda = \Lambda_0 - S c^{\frac{1}{2}} + J c + E c \log c. \quad (1)$$

This equation confirms: a) the Onsager equation; for low

concentration the terms Jc and $Ec \log c$ became negligible; b) the experimental results of a very large number of investigated systems. The coefficients of the equation \underline{S} , \underline{J} , \underline{E} , involve the absolute temperature, the dielectric constant and the viscosity of the solvent medium and, in addition, the limiting conductance Λ_0 ; the coefficient J involves the parameter \underline{a} , the distance of the closest approach of the centers of the two ions in contact.

The validity of the equation derives from the limit due to the used model and from the mathematical approximations. Such a limit is given by the concentration corresponding to $\kappa a = 0,2$ (κ = Debye parameter). Accascina, Kay and Kraus (3) tested the applicability of the equation, measuring the conductance of the tetrametilammonium picrate in a dioxan-water mixture (55% of dioxan). They showed a very sharp deviation of the experimental curve from the theoretical in the correspondence of $\kappa a = 0,2$.

In a solvent with high dielectric constant the decrease in conductance is due primarily to the long range electrostatic forces between ions, reducing the mobility as the concentration increases; with decreasing dielectric constant the conductance decreases still more rapidly because part of the solute is associated with ion pairs. The revised conductance equation (4) for associated electrolytes

is:

$$\Lambda = \Lambda_0 - S c^{\frac{1}{2}} \gamma^{\frac{1}{2}} + E c \gamma \log c \gamma + J c \gamma - K_A c \gamma f^2 \Lambda - F \Lambda_0 c \quad (2)$$

where the symbols have the following meaning: Λ = observed equivalent conductance, Λ_0 = limiting equivalent conductance, S = the Onsager coefficient, c = concentration in equivalents per liter, γ = fraction of electrolyte present as free ions, E = the Fuoss-Onsager coefficient, J = an explicit function of \underline{a} (ion size), K_A = association constant, f = activity coefficient and F = the Einstein coefficient = $(5\varphi/2) c$, where φ is the volume fraction of the solute.

In the solvent of dielectric constant below $20 \div 25$, the association to ion pairs is so great that the modified Ostwald dilution (5) law can be used to analyze the experimental data, because the Onsager square root term is a satisfactory approximation⁽⁶⁾ to the effect of long range electrostatic forces on conductance; the higher terms in the Fuoss-equation became nearly negligible compared to the effects of pairwise association.

With the new theory a complete exploration of the behaviour of an electrolyte in a solution of a solvent of dielectric constant varying from high to very low values is possible. The transition from the case of negligible association to that of high association has been studied by

different authors (7) and the validity of the equation has been proved in all the cases within the experimental errors. Since the theory uses the value of the macroscopic dielectric constant, and since the equation has been verified for variation of dielectric constant 80 - 2 we can conclude that the model on which the theory is based is correct.

Conductance and viscosity

In order to test hydrodynamically the continuum model and investigate the validity of the conductance equation in a large range of viscosity values, in some previous works we have studied the conductance of some solutions of uni-univalent electrolytes in highly viscous mixtures⁽⁸⁾. The solutions in water-glycerol have a viscosity vaying from 0,008949 to 9,4 poises and a dielectric constant from 78 to 42 going from pure water to pure glycerol. Consequently it is possible to obtain a series of solvents with viscosity varying by a factor of thousand and with dielectric constant varying by a factor of two. Due to the tremendous difference between the two factors, it has been possible to study the dependence of the conductance on the viscosity alone. The results obtained with the system potassium chloride-water-glycerol, potassium chloride-water-ethylene glycol and tetraethylammonium picrate-water-glycerol and tetraethylam-

monium picrate-water ethilen-glycol have suggested the extension of the investigation to similar systems such as sodium chloride-water-glycerol and lithium chloride-water-glycerol. In this report we shall relate the result obtained measuring the conductance of a solution of sodium chloride in water-glycerol mixtures.

Experimental part

Reagents - The conductance water has been prepared by passing bidistillated water over an anionic-cationic exchange resin and then distillating it in a quartzum distillator in an inert atmosphere of nitrogen. The water so obtained has a specific conductance of $0.5 - 0.9 \Omega^{-1} \text{ cm.}^{-1}$.

Glycerol - (Commercial Montecatini product). The glycerol has been purified by distillation at a pressure of 1 - 2 mm.Hg. After two or three distillations the central fraction has been collected and stored in a dried vessel. The glycerol so obtained has a specific conductance of $6 - 8 \cdot 10^{-9} \Omega^{-1} \text{ cm.}^{-1}$ and a percentage of water inferior to 0.03. The water has been determined by the Fisher method.

Sodium Chloride - (Merck Product). The sodium chloride has been purified by means of five crystallisations from conductance water and then dried in high vacuum at a tempera-

ture of 180°C. The purity of sodium chloride has been checked spectroscopically.

Potassium Chloride - (Merck Product). The potassium chloride has been purified by six crystallizations from conductance water and then dried in high vacuum at a temperature of 250°C. The purity of purified potassium chloride has been checked spectroscopically.

Apparatus

Conductance cell - The conductance cell was of the type suggested by Dagget, Bair and Kraus (9) except for the leads. In place of the mercury contacts, platinum wires were connected directly to the electrodes and extended to the tops of the cell arms. The electrodes were lightly platinized.

Conductance bridge - A Leeds and Nortrupp Jones bridge has been used for the conductance measurements. For the determination of the ballast point a Du Mont oscilloscope has been used (10). All the measurements have been made at the temperature of 25°C. The thermostat was an oil bath and the temperature regulator was a Leeds and Nortrupp photoelectric device. The temperature was controlled by a platinum resistance thermometer connected with a Mueller bridge. The temperature was constant at 25°C \pm 0.003°C.

Determination of the cell constant

The constant of the conductance cells used has been determined following the method proposed by Fuoss(11). The conductance of the potassium chloride aqueous solutions has been calculated from the equation:

$$\Lambda = 149.93 - 94.65 c^{\frac{1}{2}} + 58.74 c \log c + 198.4 c$$

For the two cells used, the cell constants were:

$$k_1 = 0.24721 \quad k_2 = 0.07159$$

Method

The water-glycerol mixtures have been prepared by weight directly in the conductance cell. First, water was pumped into the empty cell, previously weighed, by means of nitrogen pressure; then the weight of the water was determined and the amount of glycerol to obtain the desired composition of the mixture was calculated and added in a similar way. The final weight of the cell gave the exact composition of the solvent. The cell with the solvent was placed in the thermostat bath and the conductance of the solvent determined. Then successive samples of sodium chloride were added. The sample weight was determined by a mi-

crobalance; it was never inferior to 50 mg. This method was used for all the mixtures except for the solution in pure glycerol. Due to the high viscosity of this solution, the accuracy of the conductance obtained with the previous method was very poor; the velocity of the solution process of the added samples was very low as was the diffusion in the electrodes chamber. If the stirring of the solution was increased, some gas bubbles appeared in it and by placing themselves between the two electrodes, falsified the measurements. In addition, because of the opening of the cell during each addition of the samples, the probability of hydration of the solvent increased. For all these reasons we preferred a different method for the solution in pure glycerol. By dilution of a homogeneous concentrated solution we prepared outside the conductance cell the solutions of different concentrations. In this way it was possible to stir the solutions and then to wait for the complete elimination of the bubbles. When the solutions were homogeneous and the bubbles completely eliminated, they were stored in a dried atmosphere and then pumped one at a time directly into the conductance cell.

A magnetic stirrer assured the uniform temperature in the conductance cell in all the cases, except for pure glycerol solutions; in that case the stirring was done

by hand before each reading of the resistance, maintaining the cell into the thermostat bath before taking each measurement one hour was allowed to reach the temperature equilibrium; the readings of the cell resistance were made at intervals of 10 min. until successive readings checked to 0.01%. The room temperature was maintained at 25°C. in order to avoid the condensation of the solvent in the cap of the cell.

Results

The results concern six different compositions of the mixture from pure water to pure glycerol. The properties at 25°C of the mixtures are summarized in table 1°. The dielectric constant (D) has been interpolated from the data of Albright (12), the viscosities from the data of Sheely (13) and the densities from the data of Bosart (14). The concentrations of the sodium chloride have been chosen in the of validity of the Fuoss-Onsager equation ($\chi_a < 0.2$).

The conductance data are given in the tables from 2 to 7: the tables show: the concentration c in equivalents/liter in the 1st column; the experimental equivalent conductance Λ_{exp} in the second column; the quantity Λ' , the significance of which will be explained later, in the 3rd column); the theoretical equivalent conductance (Λ_{theor} in the 4th column; the difference between the theoretical

and experimental equivalent conductance, that is the deviation of the experimental values from those calculated by means of conductance equation (5th column) and the percentage deviation of the experimental values (6th column).

TABLE N.1Properties of water-glycerol mixtures at 25°C

Number	Glycerol %	D	$\eta \cdot 10^3$	d
1	0	78.54	8.944	0.99707
2	21.59	75.64	12.08	1.023
3	38.84	69.15	30.45	1.096
4	61.45	62.27	90.00	1.153
5	80.12	54.00	462	1.207
6	100.00	42.48	9450	1.2580

Discussion - The six systems investigated cover the range $80 > D > 42$; the analysis of the experimental data has been done, on the supposition that the electrolyte is not associated. In this case the conductance equation is:

$$\Lambda = \Lambda_0 - S c^{\frac{1}{2}} + E c \log c + J c$$

which can be arranged as follows:

$$\Lambda' \equiv \Lambda + S c^{\frac{1}{2}} - E c \log c = \Lambda_0 + J c$$

The quantity Λ' can be calculated from the experimental data since the constants S and E are calculable from the constants of the solvent (dielectric constant and viscosity) and from an approximate value of the limiting conductance Λ_0 , extrapolated from a $\Lambda / c^{\frac{1}{2}}$ plot. (15) If the equation is valid, that means that the ions are not associated to form ion-pairs and consequently the quantity Λ' is a linear function of the concentration:

$$\Lambda' = \Lambda_0 + J c$$

The plot of (fig.2) shows, within the experimental errors, the linearity of Λ' and we can conclude that the sodium chloride is not associated in the six systems we have examined.

In effect, if some appreciable association were to

be present, the experimental line should show a curvature at high concentration due to the influence of an additional term of the equation which can be neglected only in the case of very low association.

Applying the least mean squares method to the set of Λ'/c data, we calculated the value of Λ_0 and \underline{J} , which is shown at the bottom of each table. With these two constants it is possible to write the full equation with the numerical coefficients for each system; the equations are also in the tables. The deviation increases going from pure water to pure glycerol: in water it is 0,02% and in pure glycerol it is in average 0,4%. The reason for this increase is due to the greater experimental difficulties present in the glycerol rich mixtures which have a very high viscosity. From the \underline{J} value we have calculated the \underline{a} value which represents the distance of closest approach of two counter ions. The values we obtained do not seem to be constant and show a tendency to increase with the lowering of the dielectric constant.

TABLE N.2Sodium chloride in water-glycerol mixtures at 25°C

Mixture n.1

% of glycerol = 0

% of water = 100.00

Constants:

$$D = 78.54; \quad \eta = 0.008949; \quad \alpha = 0.2289; \quad \beta = 60.24$$

$c \cdot 10^4$	$\Lambda_{\text{exp.}}$	Λ'	$\Lambda_{\text{theor.}}$	$\Lambda_{\text{theor.}} - \Lambda_{\text{exp.}}$	$\frac{\Delta\Lambda}{\Lambda} \%$
46.4084	120.283	126.857	120.304	+ 0.021	+ 0.018
93.1657	118.072	127.552	118.059	- 0.013	- 0.011
142.356	116.402	128.255	116.382	- 0.020	- 0.017
192.091	115.039	128.920	115.057	- 0.018	+ 0.015
242.853	113.943	129.650	112.949	+ 0.006	+ 0.005

$$\Lambda_0 = 126.22_1$$

$$J = 141.3$$

$$a = 2.57 \text{ \AA}$$

Equation:

$$\Lambda = 126.22 - 89.13 c^{\frac{1}{2}} + 46.26 c \log c + 141.3 c$$

TABLE N.3Sodium chloride in water-glycerol mixtures at 25°C

Mixture n.2

% of glycerol = 11.59

% of water = 88.41

Constants:

D = 75.65;

 $\eta = 0.01208$; $d = 0.2422$ $\beta = 45.4605$

$c \cdot 10^4$	$\Lambda_{\text{exp.}}$	Λ'	$\Lambda_{\text{theor.}}$	$\Lambda_{\text{theor.}} - \Lambda_{\text{exp.}}$	$\frac{\Delta \Lambda}{\Lambda} \%$
52.2554	94.525	100.079	94.544	+ 0.019	- 0.02
101.024	92.868	100.715	92.865	- 0.003	+ 0.003
145.871	91.765	101.302	91.738	- 0.027	+ 0.03
198.132	90.724	101.947	90.710	- 0.014	+ 0.02
250.170	89.857	102.559	89.884	+ 0.027	- 0.03

$$\Lambda_0 = 99.42_2$$

$$J = 125.7$$

$$a = 2.74 \overset{\circ}{\text{A}}$$

Equation:

$$\Lambda = 99.42 - 69.55 c^{\frac{1}{2}} + 42.46 c \log c + 125.7 c$$

TABLE N.4Sodium chloride in water-glycerol mixtures at 25°C

Mixture n.3

% of glycerol = 38.84

% of water = 61.16

Constants:

$$D = 69.15; \quad \eta = 0.03045; \quad \alpha = 0.2771 \quad \beta = 16.6535$$

$c \cdot 10^4$	$\Lambda_{\text{exp.}}$	Λ'	$\Lambda_{\text{theor.}}$	$\Lambda_{\text{theor.}} - \Lambda_{\text{exp.}}$	$\frac{\Delta \Lambda}{\Lambda} \%$
40.5561	44.819	47.123	44.840	+ 0.021	+ 0.05
87.1173	44.029	47.513	44.010	- 0.019	- 0.04
131.754	43.474	47.835	43.467	- 0.007	- 0.02
170.523	43.107	48.125	43.100	- 0.007	- 0.01
212.926	42.762	48.423	42.775	+ 0.013	+ 0.03

$$\Lambda_0 = 46.84_1$$

$$J = 74.9$$

$$a = 2.98 \text{ \AA}$$

Equation:

$$\Lambda = 46.84 - 31.84 c^{\frac{1}{2}} + 28.49 c \log c + 74.9 c$$

TABLE N.5Sodium chloride in water-glycerol mixtures at 25°C

Mixture n.4

% of glycerol = 60.45 % of water = 39.55

Constants:

$$D = 62.27 \quad \eta = 0.0900; \quad \alpha = 0.3243; \quad \beta = 6.727$$

$c \cdot 10^4$	$\Lambda_{\text{exp.}}$	Λ'	$\Lambda_{\text{theor.}}$	$\Lambda_{\text{theor.}} - \Lambda_{\text{exp.}}$	$\frac{\Delta \Lambda}{\Lambda} \%$
57.0813	17.653	18.828	17.662	+ 0.009	+ 0.05
113.739	17.330	19.055	17.318	- 0.012	- 0.07
170.223	17.103	19.264	17.088	- 0.065	- 0.09
221.893	16.938	19.445	16.931	- 0.007	- 0.04
276.880	16.788	19.623	16.803	+ 0.015	+ 0.09

$$\Lambda_0 = 18.62_g$$

$$J = 36.4$$

$$a = 3.18 \text{ \AA}$$

Equation:

$$\Lambda = 18.63 - 12.76 c^{\frac{1}{2}} + 16.48 c \log c + 36.4 c$$

TABLE N.6Sodium chloride in water-glycerol mixtures at 25°C

Mixture n.5

% of glycerol = 80.12

% of water = 19.88

Constants:

$$D = 54 ; \quad \eta = 0.462 \quad \alpha = 0.4016 \quad \beta = 1.407$$

$c \cdot 10^4$	$\Lambda_{\text{exp.}}$	Λ'	$\Lambda_{\text{theor.}}$	$\Lambda_{\text{theor.}} - \Lambda_{\text{exp.}}$	$\frac{\Delta \Lambda}{\Lambda} \%$
41.2629	4.323	4.594	4.321	- 0.002	- 0.05
85.5601	4.256	4.670	4.252	- 0.004	- 0.09
127.006	4.202	4.722	4.215	+ 0.013	+ 0.3
172.643	4.200	4.821	4.189	- 0.011	- 0.3
206.154	4.173	4.862	4.176	+ 0.003	+ 0.07

$$\Lambda_0 = 4.52$$

$$J = 16.6$$

$$a = 3.92 \text{ } ^\circ \text{A}$$

Equation:

$$\Lambda = 4.52 - 3.342 c^{\frac{1}{2}} + 6.453 c \log c + 16.6 c$$

TABLE N.7Sodium chloride in water-glycerol mixtures at 25°C

Mixture n.6

% of glycerol = 100

% of water = 0

Constants:

D = 42.48;

 $\eta = 9.45$ $\alpha = 0.5755$; $\beta = 0.076$

$c \cdot 10^4$	$\Lambda_{\text{exp.}}$	Λ'	$\Lambda_{\text{theor.}}$	$\Lambda_{\text{theor.}} - \Lambda_{\text{exp.}}$	$\frac{\Delta \Lambda}{\Lambda} \%$
31.1676	0.292	0.315	0.294	+ 0.002	+ 0.17
38.2994	0.290	0.315	0.292	+ 0.002	+ 0.62
105.509	0.282	0.328	0.281	- 0.001	- 0.28
127.402	0.277	0.330	0.279	+ 0.002	+ 0.43
153.251	0.277	0.336	0.276	- 0.001	- 0.22

$$\Lambda_0 = 0.31_0$$

$$J = 1.6$$

$$a = 2.99^\circ$$

Equation:

$$\Lambda = 0.31 - 0.256 c^{\frac{1}{2}} + 0.971 c \log c + 1.6 c$$

The results obtained allow the dependence of the coefficients of conductance equation from the viscosity of the medium to be studied. In effect the coefficients $\underline{S}, \underline{E}$ and J are functions of the dielectric constant and of the viscosity of the solvent: each coefficient derives from the sum of two different quantities, one due to the electrostatic relaxation field and the other due to the hydrodynamic velocity field. To show this dependence the conductance equation may be written in the form:

$$\Lambda = \Lambda_0 - (\alpha c^{\frac{1}{2}} - E_1 c \log c - \sigma_1 c) \Lambda_0 - (\beta c^{\frac{1}{2}} + E_2 c \log c - \sigma_2 c) \Lambda_0 \quad (3)$$

and then

$$\Lambda = \Lambda_0 - \Lambda_0 \Delta_R - \Delta_H \quad (4)$$

where the quantity $\Lambda_0 \Delta_R$ represents the decrease of the conductance due to the relaxation field and Δ_H the decrease due to the hydrodynamic field. The term Δ_R depends only on the dielectric constant and not on the viscosity; the term Δ_H depends on both dielectric constant and viscosity. Dividing the equation (4) by Λ_0 and calling Δ_H' the part of Δ_H independent from η , we obtain

$$\Lambda / \Lambda_0 = 1 - \Delta_R - \frac{\Delta_H'}{\eta \Lambda_0}$$

and then

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \Delta_R + A \Delta_H'$$

From the last equation it is shown that the relative conductance is a function of the concentration of the electrolyte and, in the limit of validity of the Walden rule ($\Lambda_0 \eta = \text{const.} = 1/A$) depends only on the dielectric constant being independent of the viscosity of the solvent. To show the validity of this conclusion we can write equation (1) in the form:

$$\Lambda/\Lambda_0 = 1 - \frac{S}{\Lambda_0} c^{\frac{1}{2}} + \frac{E}{\Lambda_0} c \log c + \frac{J}{\Lambda_0} c$$

where, for the above mentioned reasons the quantities $\frac{S}{\Lambda_0}$, $\frac{E}{\Lambda_0}$ and $\frac{J}{\Lambda_0}$ depend only on the dielectric constant. Because in our system the dielectric constant varies only by a factor of two, and the viscosity by a factor of 1000, it is clear that the above quantities should remain practically constant with composition of the solvent. In the plot of (Fig. 3) these quantities are reported.

The larger deviation of E/Λ_0 and J/Λ_0 compared to that of S/Λ_0 is due to the fact that the first two quantities are proportional to D^{-3} and the last one to $D^{-3/2}$.

Considering the term Δ_R and Δ_H we have reconfirmed the results we obtained with potassium chloride in the same mixture.

The Walden product (Fig. 3) of sodium chloride in water-glycerol mixture increases with decreasing dielectric con-

stant as does that of potassium chloride and of $\text{Et}_4\text{N}^+\text{Pi}^-$ in the same solvent; instead, for most electrolytic solutions in mixed solvent an opposite behaviour of the Walden product has been observed: it decreases with decreasing dielectric constant. A tentative explanation of the inconstancy of the Walden product⁽¹⁶⁾, is based on the hypothesis of an interaction between the electrostatic field of the moving ion and that of the dipoles of the solvent. According to this hypothesis, at low dielectric constant the electrostatic interaction ion-solvent dipoles which is opposing the movement of the ions, increases. This interaction is of the same kind as the relaxation effect between ions of opposite charge in the Debye theory; when the steady state is reached, the orientation distribution of solvent molecules around the ion is asymmetrical because of the finite time occurring to the dipoles to renew the new distribution. Such effect acts as an increase in viscosity and consequently the conductance is lowered and the Walden product decreases as the dielectric constant decreases. The mathematical treatment of this hypothesis of an ion-dipoles relaxation effect, leads to the possibility of calculating the ion-size from conductance data. The final relation between the hydrodynamic radius R , the dielectric constant D and the hydrodynamic radius of the ion R_0 in a hypothetical solvent of infinite dielectric constant becomes:

$$R = R_{\infty} + \frac{B}{D} + O(D^{-2})$$

Plotting the quantity R , determinable from conductance data, against $1/D$, it is possible to calculate R_{∞} . This equation has been verified in a mixture solvent with a polar component, but it has been found that it is not valid when both components are polar. In such cases the lack of validity has been explained by a selective solvation effect of two different molecules, depending on the composition of the mixture; it seems that when the two polar components are both hydroxilic an additional effect should be considered, deriving from the interactions between the molecules of the two components. These interactions lead to the formation of mixed associates depending on the composition of the mixture. One type of interaction is the hydrogen bond between the solvent molecules; in such conditions in a mixture of two components (A and B), both polar and hydroxilic, at least three different sorts of associates are possible: AA, BB, and AB. The distribution of the associates depends on the composition of the mixture as other experimental evidence has shown, like the variation of the partial molar volume, of the vapor pressure and of the adiabatic compressibility. The different associated have a different volume and, more important, a different polar moment. Consequently, varying the dielectric constant, the

composition of the dipoles-atmosphere around the ion also varies. If such a hypothesis is correct such effect should be emphasized when we use as solvent a mixture of water and polyhydric alcohol, like glycerol or glycol, which have more than one hydroxile in the molecule. In effect the results we obtained in water-glycerol mixture confirm, at least from a qualitative point of view, this hypothesis: the Walden product of NaCl in water-glycerol increases at low dielectric constant and that can be interpreted with minor number of dipoles, having a larger volume, coordinate around the moving ion; because of the smaller number of dipoles, the retarding effect due to dipole relaxation effect be weaker and the conductance higher. We are at present working with the system-lithium chloride water-glycerol and then we plan to study the same alkalyne chlorides in water-ethilen glycol mixture in order to confirm our hypothesis with more experimental data.



Fig. 1 - Conductance Cell

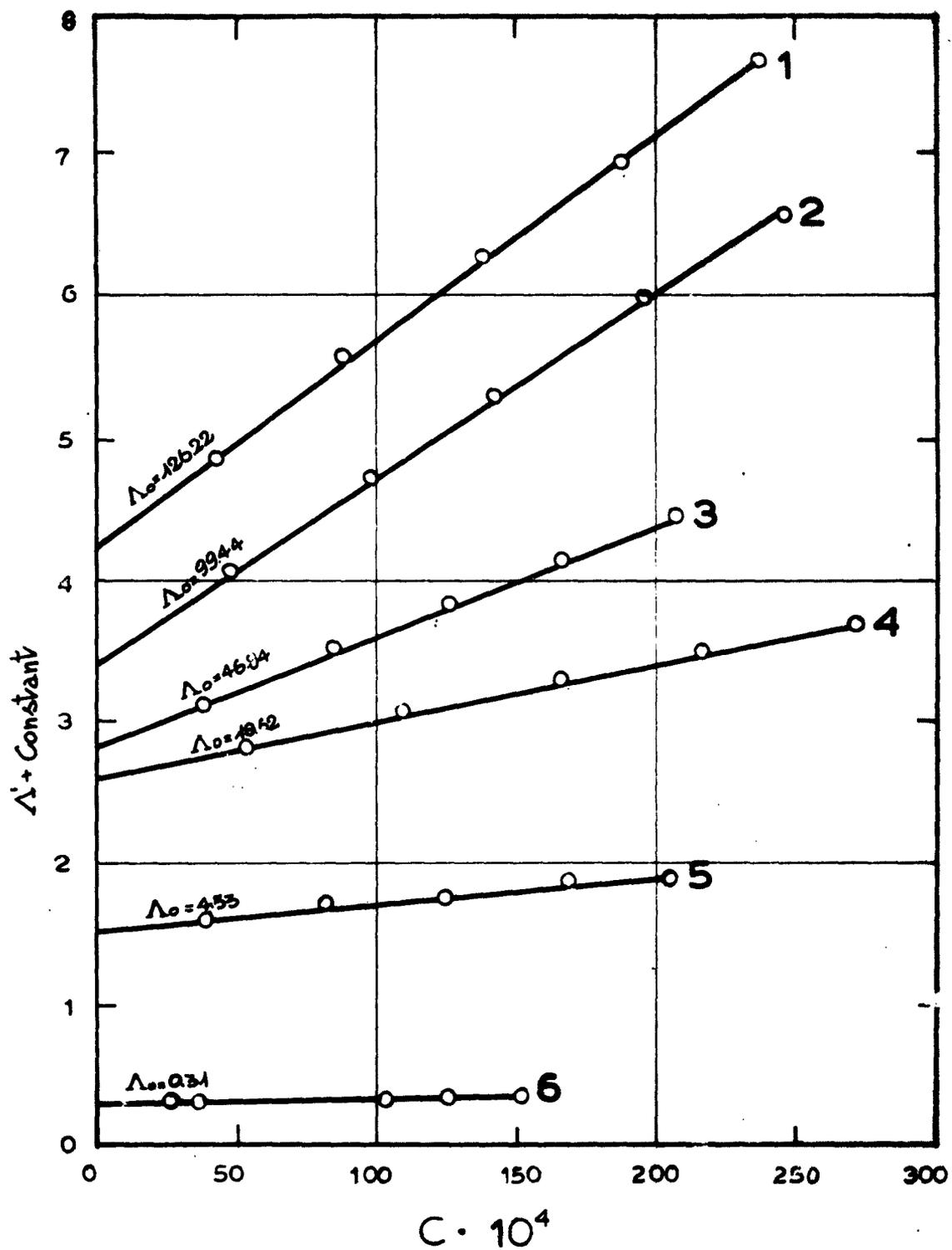


Fig.2 - Conductance of sodium chloride in water-glycerol mixtures.

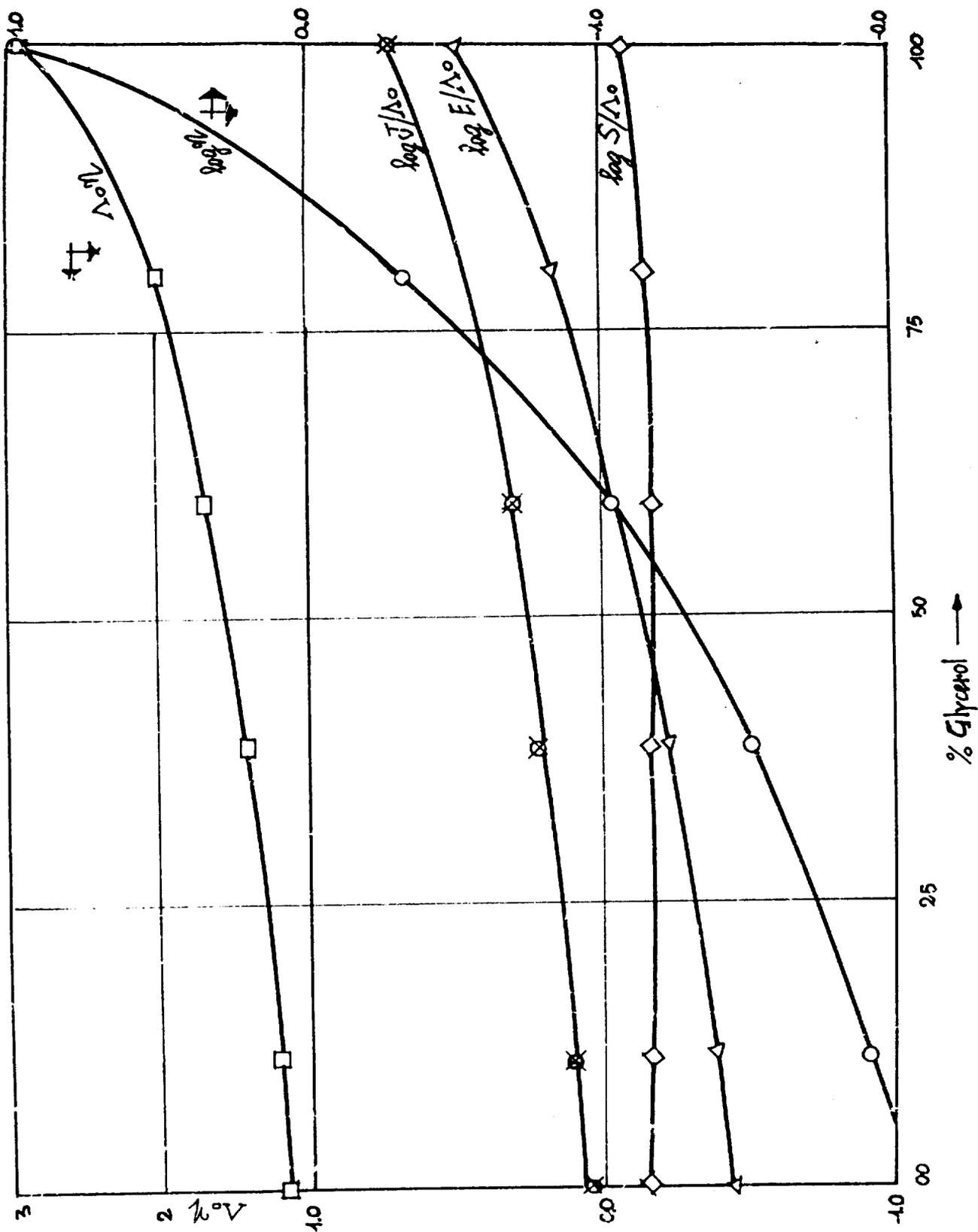


Fig. 3- Dependence of $\log \eta$, $\log S/\Delta_0$, $\log J/\Delta_0$, $\log E/\Delta_0$ and of Walden product of sodium chloride on the composition of mixtures water-glycerol.

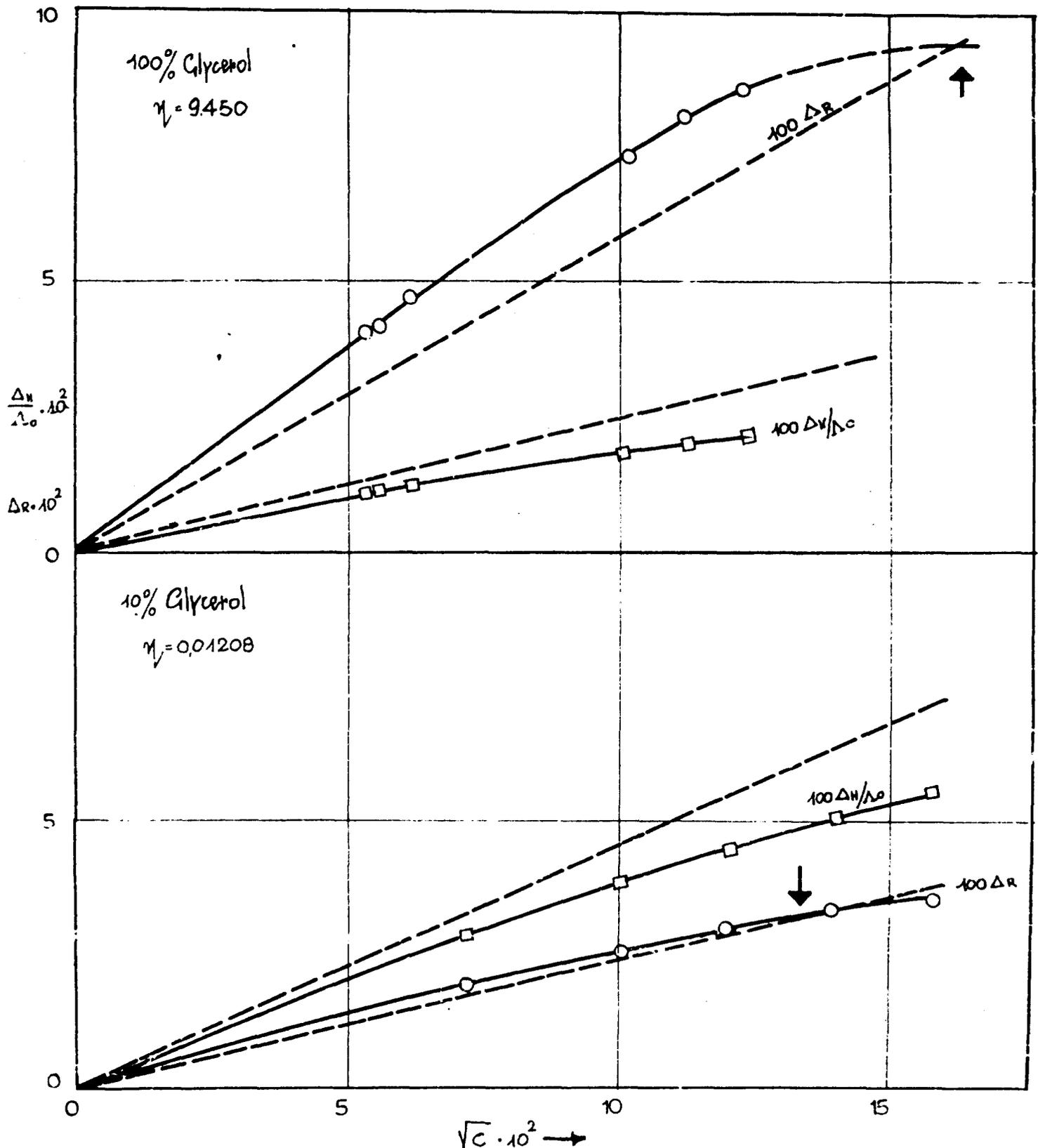


Fig. 4 - ΔR and $\Delta H / \Delta_0 \cdot C^{1/2}$ in pure glycerol and in water-glycerol mixture (10% glycerol)

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IV. - SUMMARY OF PERSONNEL UTILIZED DURING THE REPORTING PERIOD TOGETHER WITH A SUMMARY OF OTHER ADMINISTRATIVE ACTIONS.

Personnel

1. Principal Investigator: Prof. Filippo Accascina
2. Post-doctoral research Assistant: Dr. Mario Goffredi

V. - UNOFFICIAL SUMMARY OF THE NUMBER OF MANHOURS EXPENDED ON
THE CONTRACT AND EXPENSES FOR MATERIAL EXPENDED IN CAR-
RYING OUT THE CONTRACT.

Manhours

Principal Investigator: Prof. Filippo Accascina (1/3 time)		
2 hours, 288 days	576	manhours
Research Assistant: Dr. Mario Goffredi (full time)		
6 hours, 288 days	1728	"
	<hr/>	
	2304	"

Sums already paid or engaged for materials, chemical, ap-
paratus and general expenses:

Chemical reagents and consumable material . . .	Lira 600.000
Overhead expenses, including secretary work, typing and printing of the reports	" 600.000
Contribution of 30% to the price paid for the acquirement of a L.N. Muller bridge with accessories	" <u>500.000</u>
	Lira 1.700.000