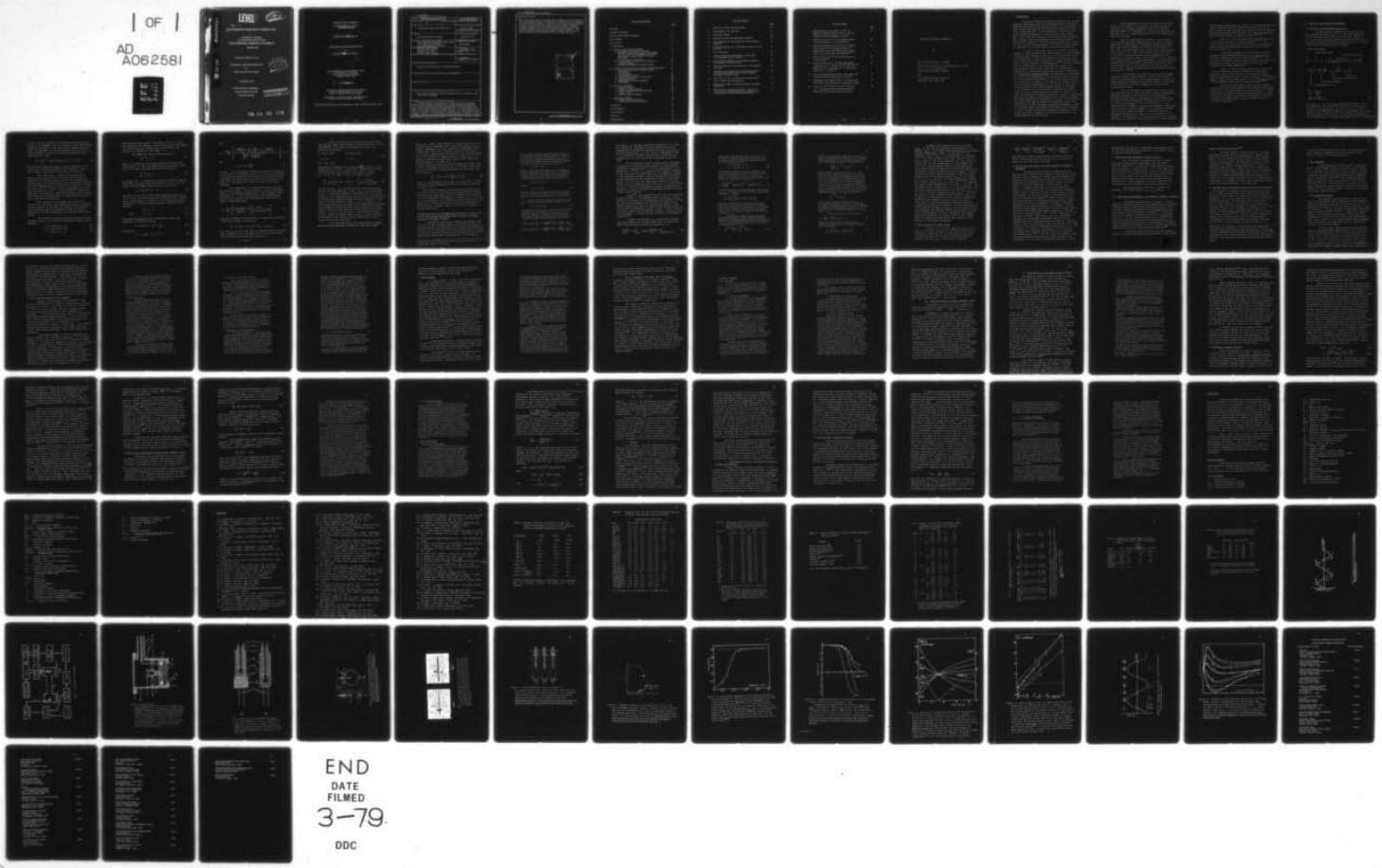
AD-A062 581 CASE WESTERN RESERVE UNIV CLEVELAND OHIO ULTRASONICS --ETC F/G 20/1
ULTRASONIC VIBRATION POTENTIALS.(U)
NOV 78 R ZANA, E YEAGER N00014-75-C-0557
UNCLASSIFIED TR-45 NL

| OF |
AD A062581



END
DATE FILMED
3-79
DDC

AD A062581

DDC FILE COPY

LEVEL II

(12) B.S.

Use 2

ULTRASONICS RESEARCH LABORATORY

DEPARTMENT OF CHEMISTRY

JOHN SCHOFF MILLIS SCIENCE CENTER

CASE WESTERN RESERVE UNIVERSITY

Cleveland, Ohio

TECHNICAL REPORT NO. 45

ULTRASONIC VIBRATION POTENTIALS

by

Raoul Zana and Ernest Yeager

DDC
DEC 29 1978
F

15 November 1978

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0557

Project NR 384-305

This document has been approved for public release and sale; its distribution is unlimited.

78 12 26 118

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0557
Project NR 384-305

TECHNICAL REPORT NO. 45

ULTRASONIC VIBRATION POTENTIALS

by

Raoul Zana* and Ernest Yeager

Case Laboratories for Electrochemical Studies
Case Institute of Technology
Case Western Reserve University
Cleveland, Ohio 44106

15 November 1978

Manuscript prepared for publication in Modern Aspects of Electrochemistry, J. Bockris and B. E. Conway, eds., Plenum Press.

Reproduction in whole or in part is permitted for any purpose of the United States Government

*Centre de Recherches Sur Les Macromolecules, CNRS, Strasbourg-Cedex, France

403881

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: 45	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): ULTRASONIC VIBRATION POTENTIALS		5. TYPE OF REPORT & PERIOD COVERED: Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): Raoul Zana and Ernest Yeager		8. CONTRACT OR GRANT NUMBER(s): N00014-75-C-0557 (IN FILE) NOT IN SOURCE
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Case Laboratories for Electrochemical Studies, Case Institute of Technology, Case Western Reserve University, Cleveland, Ohio 44106		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 384-305
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Arlington, VA 22217, Physics Section, Code 421		12. REPORT DATE: 15 November 1978
		13. NUMBER OF PAGES: 73
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report): Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

ionic vibration potentials, colloidal vibration potentials, ultrasound, ionic double layer, electrolytes

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Vibration potentials are generated when sound waves are propagated through an ionic solution, polyelectrolyte or colloidal suspension in an electrolyte. Accurate measurements of vibration potential can be now performed on a routine basis, using pulse modulated ultrasonic waves for the generation of the effect, in a variety of solvents and solvent mixtures. The results obtained thus far have been used to check the theoretical treatments of the ultrasonic vibration potentials. Moreover the combination of vibration potential and density data has provided us with the partial molal volumes of ions in a series of solvents. These

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

S/N 0102-LF-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Continued (Block #20)

data should prove useful in checking theories dealing with electrostriction once they can accurately be split into a geometric contribution, and a contribution due to ion-solvent interactions. There have been relatively few investigations of polyelectrolyte solutions and colloidal systems by means of vibration potentials, although the study of these systems should prove interesting. Vibration potentials may be useful for the monitoring of changes of potential of colloidal suspensions upon addition of various agents, in some industrial processes of major importance such as paper processing.

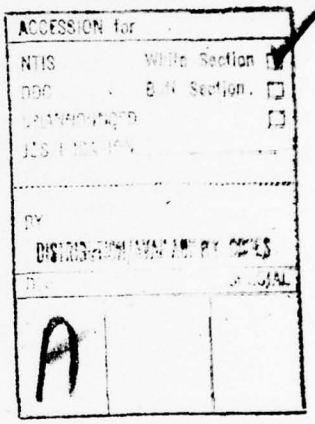


TABLE OF CONTENTS

	Page
Title Page	i
Document Control Data	ii
Document Control Data (Continued)	iii
List of Figures	v
List of Tables	vi
I. Introduction	1
II. Theory of Ionic Vibration Potentials	4
1. Derivation of the express for the IVP	4
2. Physical meansing of the apparent molar masses W_+ and W_- and their relationship to the partial molal volumes at infinite dilution of the ions, V_+° and V_-°.	9
3. IVP of mixtures of electrolytes	14
4. Case of solutions where occur fast physical or chemical processes	15
5. Solutions of electrolytes in organic solvents	16
III. Quantitative Measurements of Ultrasonic Vibration Potentials	16
1. Generation of the electrical impulse driving the transducer	17
2. The transducer	18
3. The propagation system	18
4. Double electrode probe and cell assembly	19
5. Detection electronics	20
6. Determination of velocity amplitudes	21
7. False effects	23
IV. Review of IVP Studies	26
1. Aqueous solutions	26
2. Solutions in organic solvents	31
3. Factors which determine the partial molal volumes of ions	34
4. IVP's and solvation numbers	37
V. Miscellaneous Studies	37
1. Colloidal vibration potentials	37
2. Polyelectrolyte vibration potentials	41
Conclusions	45
Acknowledgments	45
List of Symbols	45
References	49
Distribution List	74

LIST OF FIGURES

		Page
1.	Mechanism for ionic vibration potentials.	60
2.	Block diagram of the apparatus .	61
3.	Transducer housing .	62
4.	Design of the tip of the double probe assembly.	63
5.	Cell arrangement for the measurement of ionic vibration potentials.	64
6.	Oscilloscope displays for 10^{-2} M aqueous solutions of CsCl and NaCl.	65
7.	Cell arrangements.	66
8.	Terminal responses in KCl solutions at 220 kc with cell arrangements shown in Figure 7.	67
9.	Concentration dependence of the vibration potential of CsCl solutions at 220 kHz in water.	68
10.	Vibration potential of binary mixtures of 1-1 electrolytes at 110 kHz.	69
11.	Illustration of the method used for the determination of the partial molal volumes of ions and their standard deviations in organic solvents.	70
12.	Plots of $\bar{V}_i^{\circ} \cdot r_i$ vs r_i^4 for alkali metal and halide ions in water, methanol and ethylene glycol.	71
13.	Mechanism for colloidal vibration potentials: oscillating dipole model.	72
14.	Variation of the vibration potential of a 3×10^{-2} mono-mole/l solution of polyacrylic acid (M_n =130,000), upon neutralization by various alkali metal hydroxydes.	73

LIST OF TABLES

		Page
1.	Estimated errors in $(t_+/z_+)\bar{V}^{\circ}_{+} - (t_-/z_-)\bar{V}^{\circ}_{-}$ for alkali metal bromides in water at 25°C, caused by assuming isothermal propagation of sound.	52
2.	Values of Φ/a (in μV s cm^{-1}) for aqueous solutions of typical electrolytes at 22°C and 220 kHz.	53
3.	Partial molal volumes of monovalent ions calculated from the values of the vibration potentials Φ/a, partial molal volume of salts $\bar{V}^{\circ}_2$ and cation transport number of t_+ in these salts, from reference 6[(a)].	54
4.	Values of $\bar{V}^{\circ}(H^+)$ in cm^3/mole obtained by means of various methods[(a)].	55
5.	Values of Φ/a in μV s cm^{-1} for alkali metal iodides in Methanol (I) [12], Ethanol (II) [13], DMF (III) [13], DMSO (IV) [14], Acetonitrile (V) [15] and Ethylene Glycol (VI) [16] at 22°C [(a)].	56
6.	Values of the partial molal volumes of monovalent ions obtained from IVP and $\bar{V}^{\circ}_2$ data, in cm^3/mole [(a)].	57
7.	Comparison of the values of $\bar{V}^{\circ}(Cl^-)$ in cm^3/mole from IVP's and by three different non-experimental methods.	58
8.	Values of A (cm^3 $\mathring{A}^{-3}$ $mole^{-1}$) and B (cm^3 $\mathring{A}$ $mole^{-1}$) at 25°, obtained from the partial molal volumes of alkali metal and halide ions in various solvents.	59

78 12 26 118

ULTRASONIC VIBRATION POTENTIALS

by

Raoul ZANA and Ernest B. YEAGER

Centre de Recherches sur les Macromolécules, CNRS
U.L.P., 6, rue Boussingault
67083 Strasbourg-Cedex, France

and

Case Western Reserve University
Cleveland, Ohio, 44106 USA

I. INTRODUCTION

Ultrasonic vibration potentials are one of the various phenomena which result from the interaction between ultrasonic waves and electrolytic solutions in the bulk or at interfaces[1]. These effects have thus far received little attention in spite of the information that can be obtained from their study and their possible applications in various fields. This review deals mainly with the ultrasonic vibration potentials generated when ultrasonic waves are propagated in solutions of simple electrolytes (referred to as ionic vibration potentials or IVP) and their use for the determination of the partial molal volumes of individual ions and the study of ion-solvent interactions.

In 1933, in the first issue of the Journal of Chemical Physics, P. Debye predicted that the propagation of longitudinal ultrasonic waves through an electrolytic solution should result in the generation of alternating potential differences between points within the solution, separated by a phase distance other than an integral multiple of the wavelength[2]. The effect arises because of differences in the amplitudes and phases of the displacements of the cations and anions as a consequence of differences in the effective masses and frictional coefficients of the solvated cations and anions. The mechanism is represented in Figure 1 with displacements at a particular instant represented on the ordinate and distance in the direction of propagation on the abscissa. The length of the arrows are intended to indicate the relative displacements of the cations (+) and anions (-) at any instant with the former assumed smaller (for purposes of illustration). For the conditions represented in Figure 1, region A will be charged positively relative to region B. If inert metal probes are placed at positions A and B, an alternating potential difference will be observed since the curve representing displacement may be considered as traveling in the positive direction at the speed of sound in a progressive sound field. The frequency of the alternating potentials corresponds to that of the sound field. Ionic vibration potentials can be measured in terms of either the potential difference between two points or the potential variations at any one point relative to the average potential of the solution.

Debye suggested the use of this effect for the measurements of the masses of the solvated ions and the study of ion-solvent interactions. Subsequent theoretical work has shown the effect to be dependent on the effective masses of the solvated ions, i.e., their mass minus that of the free solvent which they displace.

The first experimental evidence for the existence of IVP was reported some sixteen years after Debye's original prediction by Yeager et al.[3] at Western Reserve University. This delay mostly reflects the difficulties encountered at that time in the measurement of an acoustically produced signal of the order of 10 μV when many watts of electrical energy of the same frequency are used in close proximity for the generation of the sound waves. These workers[3] used a standing wave technique where the spatial dependence of the node-antinode structure of the standing wave field permitted the IVP to be distinguished from the electromagnetically induced signals. Similar work, based on the same method, was reported by Derouet and Denizot in 1951[4].

It was, however, only with the use of pulse modulated ultrasonic waves in 1953 by Yeager, Dietrick and Hovorka[5] that a clear differentiation was obtained between acoustically produced and electromagnetically induced effects, on the basis of the difference in time of propagation of acoustic and electromagnetic waves.

The first systematic and quantitative studies of IVP were performed only in 1966. The use of a double probe assembly partially immersed in the solution under investigation[6] provided the experimental verification of several predictions of the most thorough theoretical treatment of the IVP, given in 1947 by Bugosh et al.[7]. On the other hand, a closer examination of the physical meaning of the apparent molar masses of the solvated ions which appear in this treatment indicated that the IVP is closely related to a weighted difference between the partial molal volumes of the ions present in the system[6] (see Section II). It thus became possible by combining the value of the IVP for a given electrolyte in a given solvent,

and the partial molal volume at infinite dilution for the same electrolyte in the same solvent to obtain the values of the partial molal volumes of the individual ions constituting this electrolyte This was done between 1966 and 1968 for a series of electrolytes of widely differing nature in aqueous solutions[6,8-10].

Since 1971, IVP measurements have been performed also in electrolyte solutions in organic solvents[11-17]. The primary purpose of these studies was to find out the parameters which determine the magnitude of the partial molal volume of ions (see Section IV).

It should be pointed out that ultrasonic vibration potentials have been predicted also to arise when ultrasonic waves are propagated through colloidal systems[18-20]. The existence of colloidal vibration potentials has been established somewhat more easily than that of IVP's because they are usually of much larger magnitude[21].

Finally, it has also been experimentally shown that ultrasonic vibration potentials constitute a very general phenomena, which arises in every instance where ultrasonic waves are propagated through a solution containing ionic species, however complex these species may be, as for instance proteins[23] or polyions in solutions of polyelectrolytes[24-27].

After this Introduction we shall briefly examine in the two next sections the theory of IVP's and the experimental setup used in the measurements. The results relative to simple electrolytes in aqueous solutions and to solutions in organic solvents are reviewed in Section IV while Section V describes the results for more complex systems (polyelectrolytes and colloidal suspensions).

II. THEORY OF IONIC VIBRATION POTENTIALS

1. Derivation of the expression for the IVP

The most thorough theoretical treatment of IVP is that reported by Bugosh et al.[7] in 1947. The expression of the IVP is obtained by solving the following system of 2j + 1 equations which describes the propagation along the x-direction of plane longitudinal ultrasonic waves in a solution of electrolytes containing j ionic species:

electrical force; frictional force; relaxational force

$$e_{\underline{i}}X - \rho_{\underline{i}}(v_{\underline{i}} - v_o) - e_{\underline{i}}\left[\frac{|e_1\ e_2|\ q\kappa X}{(3DkT)\left[1 + q^{1/2}(1 + i\omega\theta)^{1/2}\right]}\right]$$

$$- \frac{e_{\underline{i}}\ X\kappa\ \rho_{\underline{i}}}{6\ \pi\eta_o} - \frac{kT}{n_{\underline{i}}}\frac{\partial n_{\underline{i}}}{\partial x} - \underline{v}_{\underline{i},s}\ d_o\frac{dv_o}{dt} = m_{\underline{i},s}\frac{dv_{\underline{i}}}{dt}$$

electrophoretic force; diffusion gradient; pressure gradient force; reaction

$$\frac{\partial n_{\underline{i}}}{\partial t} + \frac{\partial (n_{\underline{i}} v_{\underline{i}})}{\partial x} = 0 \qquad (2)$$

$$\frac{\partial X}{\partial x} = \frac{4\pi}{D}\sum n_{\underline{i}}\ e_{\underline{i}} \qquad (3)$$

where $m_{\underline{i},s}$, $n_{\underline{i}}$, $e_{\underline{i}}$, $v_{\underline{i}}$ and $\underline{v}_{\underline{i},s}$ are respectively the mass, the number per unit volume, the charge, the velocity and the volume of the solvated $\underline{i}$-th ion. D, v_o, η_o and d_o are the dielectric constant at zero frequency, the velocity, the viscosity and the density of the solvent. ω is the angular frequency of the ultrasonic wave, k the Boltzmann constant and T the temperature

$1/\kappa$ and θ are the thickness in centimeters and relaxation time of the ionic atmosphere. X is the electrical field which arises because of the motion of the ions in the ultrasonic velocity field. The parameter q in the relaxational force term for the ionic atmosphere is given for a solution consisting of two types of ions 1, 2 by :

$$q = (e_1\rho_1^{-1} + e_2\rho_2^{-1}) \left[(e_1-e_2)(\rho_1^{-1} - \rho_2^{-1})\right]^{-1} \qquad (4)$$

For solutions containing j types of ions, equations 1 to 3 involve 2j+1 unknowns consisting of the electrical field X, the j values of n_i and the j velocities v_i of the ions.

The j equations (1) express that the sum of the forces acting on the i-th ion in solution must be equal to the product of its mass and acceleration. The meaning of the various terms in the left hand side of eq.1 have been indicated. Note that Debye's original treatment[2] included only the first two terms. Oka[28] introduced the electrophoretic and relaxation terms already in 1933. In 1938, Hermans[19] showed that these two terms amounted to less than one percent and suggested the inclusion of terms accounting for the pressure gradient as well as the effect of diffusion.

The j equations (2) represent the equations of continuity of the system. They express that the gain in number of ions contained in an element of volume can only be due to ions entering or leaving the element through its surfaces. Equation (3) is Poisson's equation for the system under investigation.

The solution of these differential equations proceeds as follows. First, v_o, v_i and X are expressed as simple harmonic functions.

$$v_o = a_o \exp i(\omega t - \sigma x) \qquad (5)$$

$$v_i = a_i \exp i(\omega t - \sigma x) \qquad (6)$$

$$X = A \exp i(\omega t - \sigma x) \qquad (7)$$

where the amplitudes $a_{\underline{i}}$ and A are complex and $\sigma=\omega/c$, c being the velocity of the ultrasonic waves in the solution. For moderately dilute solutions c differs very little from c_o, the velocity of ultrasound in the solvent.

The numbers of ions $n_{\underline{i}}$ may be written as :

$$n_{\underline{i}} = \bar{n}_{\underline{i}} + \gamma_{\underline{i}} \tag{8}$$

with $\gamma_{\underline{i}} << n_{\underline{i}}$, where $\bar{n}_{\underline{i}}$ is a constant equal to the equilibrium value, that is, to the time independent average number of ions $\underline{i}$ per unit volume, and obeys the neutrality equation :

$$\sum_{\underline{i}=1}^{j} \bar{n}_{\underline{i}} \, e_{\underline{i}} = 0 \tag{9}$$

In equation (8), $\gamma_{\underline{i}}$ represents the periodic variation from the equilibrium value $\bar{n}_{\underline{i}}$, owing to the motion of ions $\underline{i}$ under the action of the ultrasonic waves so that one can write :

$$\gamma_{\underline{i}} = \gamma_{\underline{i}}^{\,o} \exp i(\omega t - \sigma x) \tag{10}$$

Equations (8) and (10) are also substituted into equations (1) to (3) and the resulting equations are rearranged and combined into a single equation. To obtain a first order approximation expression of A the following substitution is made into this equation :

$$a_{\underline{i}} = a_o + \beta_{\underline{i}} \tag{11}$$

with $$\beta_{\underline{i}} << a_o \tag{12}$$

The resulting expression of A is then used to obtain the expression of the IVP by writing

$$X = A \exp i(\omega t - \sigma x) = - \frac{\partial \Phi}{\partial x} \tag{13}$$

One obtains

$$\Phi = \Phi_o \exp \; i(\omega t - \sigma x - \Delta) \tag{14}$$

with

$$\Phi_o = \frac{4\pi c a_o}{\omega D} \left[\frac{\sum_i \frac{\bar{n}_i e_i m_{i,s}}{\rho_i} - \frac{kT}{c^2} \sum_i \frac{\bar{n}_i e_i}{\rho_i} - d_o \sum_i \frac{\bar{n}_i e_i v_{i,s}}{\rho_i}}{\left[\left(\frac{D_\omega}{D} \right)^2 + \left(\frac{4\pi L_\omega}{\omega D} \right)^2 \right]^{1/2}} \right] \quad (15)$$

and

$$\Delta = \arctan \frac{\omega D_\omega}{4\pi L_\omega} \quad (16)$$

D_ω and L_ω are the dielectric constant and specific conductance of the solution at frequency ω and D the value at zero frequency. Δ represents the phase angle by which the alternating potential lags behind the ultrasonic waves. Numerical calculations yield values of a few degrees for moderately dilute electrolytic solutions.

For frequencies of a few hundred kilohertz or less the terms D_ω/D and L_ω are very close to 1 and L_o, respectively, where L_o is the specific conductance at zero frequency. These approximations may be introduced into equation (15) and are equivalent of neglecting the electrophoretic and relaxation terms in equation (1). Thus,

$$\Phi_o = \frac{c a_o}{N_A} \left[\frac{\sum_i \bar{n}_i e_i (W_i - r)/\rho_i}{\sum_i \bar{n}_i e_i^2/\rho_i} \right] \left[\frac{4\pi L_o/\omega D}{(1+(4\pi L_o/\omega D)^2)^{1/2}} \right] \quad (17)$$

where N_A is Avogadro's number and W_i is the apparent molar mass of the i-th solvated ion, given by :

$$W_i = N_A (m_{i,s} - v_{i,s} d_o) = M_{i,s} - V_{i,s} d_o \quad (18)$$

$M_{i,s}$ and $V_{i,s}$ are the molar mass and volume of the i-th solvated ion. In equation (18) r represents the correction associated with the diffusion gradient and is given by :

$$r = RT/c^2 \quad (19)$$

In most instances one is dealing with salts of the type $C_{m_+}^{z_+} A_{m_-}^{z_-}$ where C and A stand for cation and anion. If the concentration of the electrolyte solution is $\underline{C}$ and e the elementary charge then :

$$\bar{n}_+ = N_A m_+ \underline{C}/10^3 \quad ; \quad \bar{n}_- = N_A m_- \underline{C}/10^3$$

$$e_+ = z_+ e \quad ; \quad e_- = -z_- e \qquad (20)$$

and $m_+ z_+ = m_- z_-$

Substituting in equation (17), and noting that $\lambda z_+/\rho_+$ and z_-/ρ_- are proportional to λ_+° and λ_-° (the limiting conductivities of the cation and anion) and introducing the transport numbers $t_+ = \lambda_+^\circ/(\lambda_+^\circ + \lambda_-^\circ)$ and $t_- = 1-t_+$, one finally obtains

$$\frac{\phi_o}{a_o} = \frac{c}{N_A e}\left[\frac{t_+}{z_+}(W_+ - r) - \frac{t_-}{z_-}(W_- - r)\right] \frac{4\pi L_o/\omega D}{\left[1+(4\pi L_o/\omega D)^2\right]^{1/2}} \qquad (21)$$

In this equation, Φ_o/a_o is the ultrasonic vibration potential per unit velocity amplitude (1 cm/s), i.e., Φ_o is the amplitude of the a.c. potential measured at anyone point in the solution relative to the average potential of the solution. The amplitude of the potential difference measured between two points of the solution one half wavelength apart, $\Phi_{o,\lambda/2}$, is twice Φ_o. In calculations using $\Phi_{o,\lambda/2}$ a factor 2 must therefore be introduced in the numerator of the left hand side of equation (21). This equation shows that the correction introduced by the diffusion term is $r\left[(t_+/z_+)-(t_-/z_-)\right]$. Even in the extreme case where t_+ and t_- differ strongly, this correction is small, generally of the order or even smaller than the experimental error in Φ_o/a_o and may thus be neglected.

On the other hand, equation (21) indicates that Φ_o/a_o depends on the electrolyte concentration $\underline{C}$ through the L_o term which is propor-

tional to $\underline{C}$. When $\underline{C}$ tends towards 0, $L_o \to 0$ and $\Phi_o/a_o \to 0$. As $\underline{C}$ is increased, the $\underline{C}$ - dependent term tends towards unity and Φ_o/a_o becomes independent of $\underline{C}$. This concentration dependence can be interpreted in terms of the internal loading of the effect by the intrinsic capacitance of the solution. Thus, the translation of the ions involves an impedance which is proportional to the specific conductance L_o while the intrinsic shunt capacitance is proportional to ωD. When $4\pi L_o >> \omega D$, the shunt capacitance does not have any appreciable effect. For a simple electrolyte such as KCl and $\omega = 10^6$ rad./s, this condition is fulfilled * at concentrations above 10^{-3}M. Equation (21) then reduces to

$$\frac{\Phi_o}{a_o} = 1.037 \times 10^{-6} c \left[\frac{t_+}{z_+} W_+ - \frac{t_-}{z_-} W_-\right] \qquad (22)$$

where Φ_o is expressed in μV, a_o and c in cm/s, and W in g/mole. The concentration dependence of the IVP is further discussed in Section III 6.

This treatment leads to the prediction that IVP's should not be sensitive to ion association as long as neutral species are formed since such species do not contribute to the generation of the potential. The formation of triple ions in solutions of 1-1 electrolytes, or of charged micelles in solutions of ionic amphiphiles or cation association in solutions of tetraalkylammonium halides, however, should and do result in changes of IVP (see Section IV).

2. Physical meaning of the apparent molar masses W_+ and W_- and their relationship to the partial molal volumes at infinite dilution of the ions, $\overline{V}^\circ_+$ and $\overline{V}^\circ_-$

The apparent molar masses include contributions from only those solvent molecules whose volume differ from that in the bulk owing to the electrostriction (compression) effects and difference in the packing of these solvent molecules with respect to bulk water. Solvent molecules which are part of the solvation shell without appreciable electrostriction or difference in

---

* Note that $L_o \sim 9.10^8 \underline{C}\ (\lambda^\circ_+ + \lambda^\circ_-)$ where L_o is in cgs units, $\underline{C}$ in mole/L and λ°_+ and λ°_- in $\Omega^{-1}\,cm^2$

packing contribute equally to the two terms $M_{\underline{i},s}$ and $\underline{V}_{\underline{i},s}d_o$ in equation (18) and their contribution will cancel out. Therefore the definition of the extent of the solvation shell of the ion is not critical in the present consideration, provided all solvent molecules affected by the ion are included. In equation (18), the molar mass of the solvated ion is given by :

$$M_{\underline{i},s} = M_{\underline{i}} + (M_{\underline{i}})_s \tag{23}$$

where $M_{\underline{i}}$ is the intrinsic molar mass of the ion, and $(M_{\underline{i}})_s$ is the mass of "bound solvent" per mole of ion. As just indicated, the precise definition of what constitutes "bound solvent" is unnecessary since $(M_{\underline{i}})_s$ will cancel out in the calculations. In dilute solutions, the ionic partial molal volume $\overline{V}_{\underline{i}}$ is :

$$\overline{V}_{\underline{i}} = V_{\underline{i},s} - M_{\underline{i},s}/d_o \tag{24}$$

so that :

$$W_{\underline{i}} = M_{\underline{i}} - d_o \ \overline{V}_{\underline{i}} \tag{25}$$

where $\overline{V}^\circ_{\underline{i}}$ is expressed in cm^3/mole. For moderately dilute solutions, i.e., when $\underline{C}$ is in the range 10^{-3} - 10^{-2} M, $\overline{V}_{\underline{i}}$ differs very little from the partial molal volume at infinite dilution, $\overline{V}^\circ_{\underline{i}}$.

While the values of $\overline{V}^\circ_+$ and $\overline{V}^\circ_-$ are unknown the partial molal volume $\overline{V}^\circ_2$ of the electrolyte under investigation, given by

$$\overline{V}^\circ_2 = m_+ \overline{V}^\circ_+ + m_-\overline{V}^\circ_- \tag{26}$$

can be obtained from density data. Therefore, from the knowledge of $\overline{V}^\circ_2$ and $\Phi_{o,\lambda/2}$, with equations (22), (25) and (26) it is possible to determine the individual values for the partial molal volumes of ions at infinite dilution, as well as apparent molar masses. Combining these three equations one obtains :

$$\overline{V}^\circ_+\left(m_-\frac{t_+}{z_+} + m_+\frac{t_-}{z_-}\right) = \overline{V}^\circ_2\frac{t_-}{z_-} - m_-\frac{4.824\times10^5}{d_o c}\frac{\Phi_{o,\lambda/2}}{a_o} + \frac{m_-}{d_o}\left[\frac{t_+}{z_+}M_+ - \frac{t_-}{z_-}M_-\right]$$

$$\overline{V}^\circ_-\left(m_-\frac{t_+}{z_+} + m_+\frac{t_-}{z_-}\right) = \overline{V}^\circ_2\frac{t_+}{z_+} + m_+\frac{4.824\times10^5}{d_o c}\frac{\Phi_{o,\lambda/2}}{a_o} - \frac{m_+}{d_o}\left[\frac{t_+}{z_+}M_+ - \frac{t_-}{z_-}M_-\right] \tag{27}$$

Note that $\Phi_{o,\lambda/2}$ has been introduced in equations (27), rather than keeping ϕ_o. The reason for this substitution is that although IVP's are generally expressed as Φ_o/a_o, the quantity usually measured is $\Phi_{o,\lambda/2} = 2\Phi_o$, and it is the quantity used in the calculations of ionic partial molal volumes by means of equations (27), with the procedure presented in Section IV 2.[12].

The evaluation of values of partial molal thermodynamic properties of individual ions requires non-thermodynamic assumptions or measurements[29]. With the IVP approach to the evaluation of $\bar{V}°(ion)$, a *critical non-thermodynamic* assumption is that the probe electrodes sense the a.c. potential changes in the electrolyte solution without thermodynamic equilibrium at the electrodes. At the frequencies involved in these measurements (10^5 to 10^6 Hz) the double layer capacity of the electrodes very well couples the detection probes to the electrolyte for the a.c. potential measurements and this non-thermodynamic assumption is easily accepted for electrodes for which there is no fast faradaic process.

Conway[29] has suggested that the IVP's are determined by the difference in the hydrodynamically significant volumes while $\bar{V}_2^o$ is the sum of the thermodynamically significant volumes $\bar{V}_i^o$. The latter correspond to the pressure derivative of the chemical potential of the ions. Equation (22), however, can be derived from thermodynamics considering just an electrolyte with a periodic pressure and acceleration gradient, assuming isothermal conditions, in a manner similar to that for centrifugation potentials[30].

Consider the transfer of t_i ions of type i between two planes parallel to the wave front within the electrolyte under thermodynamically reversible conditions, i.e.,

$$\frac{t_i}{z_i}\left[Y_i^{z_i} + h_i S\right]_{p,\ddot{u}} \rightleftharpoons \frac{t_i}{z_i}\left[Y_i^{z_i} + h_i S\right]_{p+\delta p,\ddot{u}+\delta\ddot{u}} \qquad (28)$$

where z_i carries the sign of the charge of the ion i, S and Y_i refer to a solvent molecule and ion i and δp and $\delta\ddot{u}$ are the periodic pressure and acceleration differences between the two planes and are given by :

$$\delta p = dca_o \exp i(\omega t - \sigma x) \tag{29}$$

$$\delta\ddot{u} = i\omega a_o \exp i (\omega t - \sigma x) \tag{30}$$

for a separation distance of $\lambda/4$, with d the density of the solution. The quantities h_i represent the numbers of solvent molecules transferred with each ion. The free energy of transfer of one equivalent of charge(one Faraday) between these planes under isothermal conditions is then :

$$\Delta G = \sum \frac{t_i}{z_i} \left[\int_p^{p+\delta p} (\bar{V}_i + h_i \bar{V}_S) dp + \int_x^{x+\lambda/4} (M_i + h_i M_S)\ddot{u}\, dx \right] \tag{31}$$

The corresponding potential difference* between the two planes is then : $\phi = -\Delta G/N_A e$. Thus, with $\bar{V}_i$ and $\bar{V}_S$ assumed constant with respect to pressure :

$$\frac{\phi_o}{a_o} = \frac{c}{N_A e} \sum \frac{t_i}{z_i} \left[(M_i + h_i M_S) - (\bar{V}_i + h_i \bar{V}_S) d \right] \tag{32}$$

Note that z_i in equation (32) is positive for cations and negative for anions. With $M_S = \bar{V}_S d$, equation (32) reduces to equation(22). The potential ϕ_o generated between planes separated by $\lambda/4$ is equivalent of that at any point in the sound field, relative to the spatial average of the electrolyte and is equal to $\phi_{o,\lambda/2}/2$.

This treatment has assumed isothermal propagation. The temperature modulation is small in aqueous electrolytes

*Equation (31) involves the assumption that the pressure modulation of the chemical potential of the electrons in the probes contributes negligibly to ΔG, i.e.,

$$\int_p^{p+\delta p} \frac{d\mu_e}{dp} dp = \int_p^{p+\delta p} \bar{V}_e\, dp \approx 0 \tag{31a}$$

because the thermal expansion coefficient $\alpha_E=(\partial V/\partial T)_p/V$ is small. In non aqueous electrolytes, however, α_E will generally be considerably larger and the non-isothermal contribution larger. For non-isothermal conditions the additional term

$$-\sum \frac{t_i}{z_i} \int_T^{T+\delta T} (\bar{S}_t)_i \, dT \qquad (33)$$

should be added to the right side of equation (31). The quantity δT is the temperature modulation of a particular point in the electrolyte, produced by the sound waves. The term $(\bar{S}_t)_i$ corresponds to the transported entropy involved in the various treatments of non-isothermal electrochemical cells (e.g. ref.31). For the i-th ion, $(\bar{S}_t)_i=\bar{S}_i+S_i^*$ where $\bar{S}_i$ is the ionic partial molal entropy and S_i^* is the entropy of transfer, given by $S_i^* = Q_i^*/T$, where Q_i^* is the heat transferred by ion i. The expression (33) does not take into account the temperature modulation of the probes. An additional correction terms appears necessary to ΔG in equation (31), i.e.,

$$-\int_{T'}^{T'+\delta T'} (\bar{S}_t)_{e^-} \, dT'$$

where T' refers to the probe temperature and $(\bar{S}_t)_{e^-}$ is the transported entropy of the electron in the probe metal. For purpose of simplification we shall consider the temperature at the surface of the metal probes to follow that of the bulk solution even at ultrasonic frequencies, i.e., T=T' and $\delta T=\delta T'$.

The temperature modulation is then given by :

$$\delta T = \frac{\alpha_E T}{dC_p} \delta p = \frac{\alpha_E T}{C_p} ca_o \, \exp i(\omega t-\sigma x) \qquad (35)$$

where C_p is the specific heat at constant pressure. Assuming $(\bar{S}_t)_i$ to be constant, the additional term needed in equation (32) becomes :

$$-\frac{c}{N_A e} \frac{\alpha_E T}{C_p} \left[(\bar{S}_t)_{e^-} + \Sigma \frac{t_i}{z_i} (\bar{S}_t)_i \right] \qquad (36)$$

It appears that the absolute values for both $(\bar{S}_t)_{e^-}$ and $(\bar{S}_t)_{\underline{i}}$ are all measurable independently[31]. The quantity $(\bar{S}_t)_{e^-}$ is available from thermoelectric measurements (Thomson coefficients). Temkin and Khoroshin[32] have reported a value of $(\bar{S}_t)_{e^-}$ = 0.104cal/deg.mole for platinum at 25°. This value is sufficiently small that the electron term in equation (36) can be neglected. The $(\bar{S}_t)_i$ values for various ions have been determined by various workers from the initial (without thermal diffusion) and steady-state (with thermal diffusion) potentials of thermocells (see ref.31). On the basis of data obtained by Goodrich *et al.*[33] with a thermocell involving Ag-AgBr electrodes in various bromide electrolytes, the estimated values of $(\bar{S}_t)_i$ for Li^+, Na^+ and K^+ are 11.4, 5.9 and 16.8 e.u.. Using these values together with handbook values for t_+, t_-, C_p and α_E[34,35], we estimate the error in the difference term $(t_+/z_+)\bar{V}^\circ_+ + (t_-/z_-)\bar{V}^\circ_-$ for LiBr, NaBr and KBr in water to be -1.1, -0.7 and -0.2cm^3/mole, respectively, and the corresponding errors in $\bar{V}^\circ(Br^-)$ to be 1.1, 0.7 and 0.2 cm^3/*mole, respectively* (see Table I). The errors are relatively small compared to the estimated accuracy of $\pm$ 2cm^3/mole for the absolute values of $\bar{V}^\circ_i$ from combined IVP and $\bar{V}^\circ_2$ data but perhaps a correction should be made in future work for the non-isothermal contribution when the necessary entropy data are available. IVP measurements should also be made at 4°C where α_E goes to zero for water and the non-isothermal term vanishes. The $\bar{V}^\circ_i$ values should vary relatively little between 4°C and for example 20°C for simple electrolytes and hence the comparison of the $\bar{V}^\circ_i$ values at these two temperatures can provide some insight as to the validity of this entropy correction.

3. IVP of mixtures of electrolytes

Equation (17) is valid both for solutions of one electrolyte and for solutions of mixtures of electrolytes. For binary mixtures of two 1-1 electrolytes AB and CD, at concentration such that for each electrolyte separately $4\pi L_o >> \omega D$, the IVP $\Phi_{o,M}$ of the mixture is given by

$$\frac{\Phi_{o,M}}{a_o} = \frac{\Phi_{o,AB}}{a_o}\left[1 + \frac{\Lambda^\circ_{CD}\,\underline{C}_{CD}}{\Lambda^\circ_{AB}\,\underline{C}_{AB}}\right]^{-1} + \frac{\Phi_{o,CD}}{a_o}\left[1 + \frac{\Lambda^\circ_{AB}\underline{C}_{AB}}{\Lambda^\circ_{CD}\underline{C}_{CD}}\right]^{-1} \qquad (37)$$

where the $\underline{C}$'s refer to concentration, the Λ°'s to the equivalent limiting conductivities and the Φ_o's to the IVP for solution of AB alone and of CD alone.

4. Case of solutions where occur fast physical or chemical processes

The theory of IVP for such systems has not yet been developed. Of particuliar interest is the situation where the mean time for exchange of solvent molecules between the hydration sheaths of the ions and the bulk of the solvent are comparable to the period of the ultrasonic waves. One might expect the frequency dependence of the vibration potential to deviate significantly from that predicted by equation (17) and moreover that this dependence on frequency might be used to study the kinetics of such exchange process. Unfortunately, the following reasoning indicates that IVP's cannot be used for this purpose[6]. When a solvent molecule associated with an ion exchanges with a bulk solvent molecule, the velocity of the ion momentarily increases or decreases, depending on its velocity relative to the solvent, because the newly bound solvent molecule must acquire the same velocity as the ion. The steady state velocity relative to the bulk solvent is reached in about 10^{-12} - 10^{-13}s., depending on the mass and frictional coefficient of the ion. A significant deviation in the frequency dependence of the IVP will be observed only if the exchange rates for either the cations or anions or both are sufficient so that the velocity of the ions relative to the solvent is perturbed substantially (10^{11} - 10^{12} exchanges/s). In addition, the frequency of the ultrasonic wave would need to approach within one order of magnitude the exchange rates (10^{10} - 10^{11} Hz). While the exchange rates for water molecules associated with simple univalent ions such as Na^+, K^+, Cl^- or Br^- are probably sufficient to affect

significantly the velocity of these ions, measurements of IVP at such high frequencies are impossible in the present state of the art (see next section).

5. Solutions of electrolytes in organic solvents

For non-aqueous electrolytes the non-isothermal contribution may be quite significant since the thermal expansion coefficient is usually much larger than for water (e.g. for ethanol, $\alpha_E \sim 8 \times 10^{-4}$/deg. at 25°C, as compared with 2×10^{-4}/deg for water). The omission of this term could lead to errors of 1 to 5 cm^3/mole in the individual ionic partial molal volumes. Data for the transported entropies $(\bar{S}_t)_i$ is probably not available for most organic solvent-electrolyte systems and it may be necessary to initiate thermocell emf measurements in such systems to obtain the entropy data.

In the following, for the sake of clarity, the subscript o has been omitted on Φ_o, $\Phi_{o,\lambda/2}$ and a_o.

III. QUANTITATIVE MEASUREMENTS OF ULTRASONIC VIBRATION POTENTIALS

Quantitative measurements of ultrasonic vibration potentials are best carried out with progressive pulse modulated ultrasonic waves since the pulse modulation permits a clear distinction between acoustically and electromagnetically produced signals. The double probe arrangement[6] is preferred since the differential amplifier used with this arrangement cancels out most of the electromagnetically induced signal and thus avoids the severe amplifier overload recovery time problem associated with the single probe assembly. The double probe arrangement also avoids certain ill defined false effects associated with the cell containing the electrolyte[6].

A brief description will be given of the apparatus used by the authors for aqueous electrolytes[6] and, more recently,

organic solvent electrolytes[12] *.

The block diagram is shown on Figure 2. The pulse modulated ultrasonic waves are produced by a ceramic transducer (Figure 3) driven by a pulse modulated radio frequency electric carrier of about 100W peak power with the carrier frequency corresponding to the fundamental frequency of the transducer. The acoustic waves propagate over a length of deionized water acting as a delay line before reaching the cell containing the solution under study. The IVP is detected by means of a double probe assembly whose output is fed to a differential cathode follower, amplified and displayed on the screen of an oscilloscope. The absolute value of the potential is obtained by a comparison method using a calibrated voltage source of the same frequency as the sound wave.

1. Generation of the electrical impulse driving the transducer

The oscillator is usually a signal generator delivering an a.c. signal of good stability in frequency and amplitude in the 0.1 - 1MHz range. This signal and a pulse of appropriate length (0.3 - 1.2 ms) and repetition period (25 - 400 ms) are fed to the modulator. The resulting electrical pulses are fed to a power amplifier. The matching of the impedances of the power amplifier and transducer is necessary to insure high acoustical output of the transducer and to prevent the ringing of the transducer when the pulse is over. In studies with organic solvents[11-16], pulses of shorter duration and longer repetition period were used to reduce problems associated with acoustically produced cavitation. The onset of cavitation occurs at lower ultrasonic intensities in

---

* The reader is referred to the literature for details of the experimental measurements with the apparatus. For the most part the equipment used vacuum tube electronics and did not take advantage of modern signal processing techniques. The modern version of this apparatus should present much improved performance.

in organic solvents than in water. The occurrence of cavitation results in instabilities of the acoustical signal as well as limits the acoustic amplitude.

2. The transducer

In the authors' more recent work[12] the transducer is a 6-cm diameter plate of the ceramic lead zirconate (e.g., ceramic P7/62 , Quartz and Silice, France) vibrating at 207 kHz. This type of ceramic transducer provides better conversion efficiency than the barium titanate transducers used in the earlier work[6,8-10]. The transducer diameter should be about ten times the wavelength in water to keep the acoustic energy in the diffraction side lobes low and to insure a reasonably uniform acoustic field in the IVP measurement cell. The transducer housing is made out of stainless steel and is shown on Figure 3.

3. The propagation system

Over the past two decades the authors have used both single and double tank arrangements for containing the acoustic propagation system and IVP measurement cell. The preferred arrangement is a two tank setup connected by a steel or plastic pipe, as shown in Figure 2. The single tank arrangement requires acoustic baffles to prevent the acoustic energy in the diffraction side lobes of the source from reaching the IVP detection cell and causing envelope distortion. This problem is far less with the two tank arrangement since the energy in the side lobes does not directly enter the pipe from the sound source.

The path length between acoustic source and the detection electrode probes must provide a delay time longer than the pulse modulation duration to prevent any electromagnetically induced signal from interfering with the IVP signal. Longer path length is usually undesirable because of the reduction in the acoustic amplitude. The minimum pulse modulation length in turn is set up by the bandwidth of the tuned radio frequency amplifier used in the detection of

the effect. The probe electrodes-electrolyte system is intrinsically noisy particularly with dilute solutions and hence a narrow bandpass detector system is necessary for quantitative studies. For the system used in the authors' earlier work in Cleveland[6] the band pass was about 2kHz at 200 kHz and the pulse duration was about 1-2 ms with a distance of about 300 cm between the acoustic source and detection probes, corresponding to a delay times of about 2 ms. In more recent work in Strasbourg the band-pass of the detection amplifier system has been about 5kHz, permitting the use of pulse duration of about 0.5 ms without causing distortion of the pulse envelope and hence a shorter propagation system (about 150 cm).

4. Double electrode probe and cell assembly

Figure 4 indicates glass[6] and Teflon[12] type mounts for the double wire probes. The Teflon mount has the advantage that it facilitates precise spacing and alignment of the parallel thin wire probes. The wire diameter and the deviation from parallelism must be small compared to the wavelength λ in the electrolyte (less than $\lambda/20$). Quantitative measurements presently appear practical only in the range 100 - 500 kHz. Measurements in the low megahertz range would involve platinum wires of 0.01 mm diameter with very rigid requirements with respect to parallelism, for instance anchoring the wires in some type of frame under mechanical tension. Quantitative measurements above 20 MHz appear quite impossible.

The distance between the parallel wires should be equal or greater than $\lambda/2$. When greater than $\lambda/2$, the probe assembly can be rotated about its axis[6] to adjust the phase distance to $\lambda/2$. The wire probes are typically 1 to 2 cm long for work at 200 kHz. Shorter lengths increase the effective internal impedance of the IVP's and hence cause loading problems with respect to the input impedance of the measuring electronics, particularly in dilute electrolytes. Greater lengths increase alignment problems with respect to parallelism and also require more uniform ultrasonic fields. The probe should be of a noble metal that does not support any faradaic process or corrode in the electrolyte (e.g. Pt, Au).

The probe assembly and electrolyte are contained in a cell[6] of the type shown in Figure 5 consisting of a plastic tube with an internal diameter of 15 cm, a length of 4 cm, and a wall thickness of 0.5 cm. The sound waves are transmitted into and out of this cell through Mylar film windows stretched over the ends of the cylinder. Immediately behing the cell are placed several sheets of a butyl rubber (supplied by the B.G. Goodrich Co.) which has substantially the same acoustical impedance as water and which serve as an absorber for the sound waves transmitted through the cell.

5. Detection electronics

The signal from the dual probes is fed into a differential cathode follower (as in Figure 2) consisting of two symmetrical channels of unity gain. It is essential that the input impedance loading the probes be as high as possible for work in dilute electrolytes. Therefore the shields surrounding the lead wires and the input capacities coupling the probes to the cathode follower are driven, thus lowering the effective input capacitance to less than 5 pF shunted by a resistance of about 1 MΩ , minimum value at 200 kHz. To avoid introduction of further capacitances into the input circuit, the switch gear for introducing the calibration r.f. voltage is located after cathode follower A, with a second cathode follower B (Figure 2) used to ensure proper impedance matching. In the apparatus constructed in the 1960's the authors used a r.f. shielded transformer (General Radio type 578C) to match the double ended output of differential cathode follower B to the single ended input of the r.f. amplifier[6]. Operational amplifier integrated circuits of adequate frequency response are now available for this function and avoid the small but not negligible asymmetry in the transformer and the compensation circuitry in cathode follower B needed to correct for it.

The switch unit between cathode followers A and B provides for checking that the two channels after cathode follower A are symmetrical (balanced) and for measuring the a.c. signal from either probe relative to ground, as well as the differential signal. The symmetry should be better than

1% of the input signal on either channel.

The r.f. tuned amplifier in Figure 2 is a conventional narrow band high gain amplifier with a gain of about 80 dB and an intrinsic equivalent input noise of less than 1μV . The r.f. input amplifier plus heterodyne amplifier of a commercial high performance communication (long wave) radio receiver are quite suitable for this purpose.

The sound level typically used in IVP measurements corresponds to a velocity amplitude of at least 6 cm/s within the acoustical cell. With a noise level of about 2μV with the double probe assembly, the corresponding sensitivity for Φ/a is about 0.15 μVs cm^{-1}. This corresponds to a difference in $\Sigma(t_i/z_i)(M_i - d_o\bar{V}_i^\circ)$ in equation (22) of about 0.1g/mole or for aqueous electrolyte with $(t_+/z_+)=(t_-/z_-)$, a precision of 0.1 cm^3/mole. The signal to noise ratio can be greatly improved through the use of a fast data acquisition signal averaging system but in most instances the accuracy is limited by the factors discussed below.

Figure 6 shows two oscilloscope displays, one for an unsymmetrical electrolyte where the molecular weights of the cation and anion are very different, yielding a large IVP, the other for a fairly symmetrical electrolyte characterized by a small IVP. The difference in the signal/noise ratio in the two displays corresponds essentially to the difference between the IVP's for these two electrolytes.

6. Determination of velocity amplitudes

The velocity amplitudes can be determined through radiation pressure measurements with a pressure gauge similar to that of Herrey[36], which employs a highly absorbing acoustically matched rubber disk of, for example, 6 cm - diameter, mounted perpendicular to the direction of propagation of the sound waves. The force on the disk is related to the velocity amplitude by the equation $F = (1/2)\, da^2/A$ where A is the area of the disk. The inhomogeneity of the sound field over the area subtended by the radiation disk must be taken into account. The profile of the acoustic amplitude over the dimensions of the disk can be determined with a small hydrophone

employing a ferroelectric ceramic cylindrical element as the sensor (see for example ref. 37). At 200 kHz with a 6-cm diameter source transducer and a propagation distance of 300 cm, the acoustic amplitude is uniform to within 10% in the central propagation lobe over a circular area of 2.5 cm diameter[6]. Since the probe wires used to obtain the final data are usually 1.5 to 2 cm long and positioned centrally within the cell, the velocity amplitude is practically uniform between and over the length of the dual probes. Once calibrated against the radiation pressure gauge, the hydrophones can be used as secondary standards. The calibration carried out in water will hold reasonably well within the aqueous solutions in the acoustic cell, as long as the acoustical impedance of the solution is essentially the same as that of pure water. With the organic solvent solutions, this condition is not met. The situation is further complicated by the fact that part of the sound waves will be reflected at both the front and rear cell windows because of the difference in acoustic impedance between the organic solvent and water. A substantial standing wave ratio will occur within the cell with the arrangement in Figure 2. To avoid this complication with organic solvents an additional propagation system filled with the same solvent can be fitted to the rear of the cell and prevents reflections from the rear window[12]. Under such circumstances the velocity amplitude within the cell for normal incidence is related to that in the water in front of the cell by the equation :

$$a_x = a_w \, 2(dc)_w / \left[(dc)_w + (dc)_x\right] \qquad (38)$$

where $(dc)_x$ and $(dc)_w$ are the acoustic impedances of water and organic solvent. The a_x values calculated with this equation are only approximate since this equation holds only for plane waves at normal incidence in the absence of acoustic diffraction. Even a small amount of bowing of the mylar window can cause serious errors.

The estimated accuracy of the radiation pressure measurements is about 10% and hence the velocity amplitude in aqueous electrolytes should be known to within 5%. The

IVP probe assembly, however scatters the sound field and hence perturbs the ultrasonic field. Thus the absolute accuracy for a is probably not this good.

7. False effects

a) Pure Liquids. In 1958, Hunter[38] called attention to the existence of acoustically produced alternating potentials observed with glass-mounted platinum probes in conductivity water. With pulse-modulated waves at a frequency of 465kHz, Hunter found an effect for pure water of approximately 50 μV per unit velocity amplitude, a value an order of magnitude greater than that for alkali halide solutions such as 0.01 N KCl. Even more alarming were the results of Rutgers and Rigole[39] who, using standing waves at 1MHz, observed an apparent effect not only in distilled water, but also in pure organic liquids such as methanol, ethanol, 2-propanol, nitrobenzene and even n-heptane. While a satisfactory explanation for these potentials in nonionic solutions was not advanced by either Hunter or Rutgers and Rigole, both suggested that such effects might cause serious complications in the quantitative interpretation of ultrasonic vibration potentials in electrolyte solutions. Weinmann[40] has considered, as a possible explanation for the effects observed by Hunter[38] and also Rutgers and Rigole[39] in pure liquids, the interaction of the sound waves with solvent dipoles, but Weinmann's treatment does not establish the absolute magnitude of such an effect. Another study of IVP in pure liquids was reported by Hunter and Jones[41] in 1961.

Using pulse modulated ultrasonic waves at 200 kHz, Millner[42] also observed an effect in distilled water with a single probe consisiting of platinum sealed in glass capillary tubing but the effect was only about 2μVs/cm.

The authors[6,43] have concluded that the effect observed in pure water and pure organic solvents is an artifact associated with glass mountings in which the probe electrodes are sealed. Measurements were carried out with

probe assemblies in which only the platinum probes entered the liquid under examination. Under these conditions, ac signals were observed only in ionic solutions. When glass or Teflon mounted platinum probes were slowly lowered into a pure liquid with ultrasonic waves at a frequency of 200 kHz, no effect was observed (<1 μV s cm^{-1}) even with high input impedance amplifiers, until the glass mounting contacted the liquid, at which instant a large signal abruptly appeared. Thus the experimental evidence indicates that any effect associated with the interaction of the sound waves with solvent dipoles in pure liquids is well below 1 μV s cm^{-1}

b) Electrolyte solutions. The extent to which this false effect interferes with IVP measurements in aqueous electrolytes is illustrated in Figures 7 and 8. With fully submerged probes (arrangement a in Figure 7) the observed signal approaches the value with the partially submerged probe assembly only at concentrations above 10^{-3}M, where the resistance in the electrolyte between the probes becomes sufficiently small to short out the high impedance false effect. Arrangement c in Figure 7 yields the same results as arrangement b (within a few percent) when a correction factor is applied to take into account the difference in the average acoustic velocity amplitude.

The abnormal acoustical response associated with the glass probe mounting may be caused by pseudo-piezoelectric properties of the strained glass, some type of streaming potential, or a condenser microphone effect in which the capacity between the platinum wire and the glass liquid interface is modulated by the sound waves. In any event, the a.c. response associated with the mounting for the probe wires should be characterized by a high internal impedence. At reasonable ionic concentrations (e.g., greater than 10^{-3} M) in aqueous solutions, the internal impedance associated with the ionic vibration potentials is quite low. As a result, the observed response in ionic solutions should be predominantly the ionic vibration potentials and not any false microphonic effects associated with the probe mounting.

If solutions of ionic strength much less than 10^{-3} are used, serious complications may arise unless precautions are taken to prevent such false effect.

Several procedures have been used to minimize or eliminate this mounting effect. For instance, Millner[44] has built a probe assembly consisting of four platinum wires sealed in glass with two wires extending into the solution and two wires "buried" in the glas seal (see Figure 2 in ref. 6). This procedure suffers from the uncertainty as to whether the buried electrodes fully cancel out the false effect. Since this effect can be large, partial cancellation can still lead to substantial errors. A small residual IVP of about 1.6μV s cm^{-1} was indeed found by Millner et al.[44] for pure water.

The easiest procedure to nearly fully eliminate the mounting effect consists in positioning the two probe wires approximately at the center of the cell and filling the cell up to a level of about 1mm below the probe seal[6]. This procedure which results in a residual IVP of less than 0.2 μV s cm^{-1} was adopted in all studies performed by the authors since 1966 [6,8-16]. It has permitted the establishment of the concentration dependence of the IVP at low concentrations, in the range 10^{-5}-10^{-3} M, where the impedance of the solution is still small compared with the input impedance of the measurement system. Some results for the concentration dependence of the IVP are shown on Figure 9[23]. The experimental points fall fairly close to the theoretical curve calculated on the basis of equation (21). This result constitutes further evidence that all of the possible false effects discussed in reference 6 have been either eliminated or reduced to a level where they have very little effect on the measurements and that the measured potentials represent the true IVP's, at least in the concentration range over which $\Phi_{\lambda/2}$ remains constant.

IV. REVIEW OF IVP STUDIES

1. Aqueous solutions

The quantitative studies of IVP in water include 1-1, 1-2, 2-1 and 2-2 classical electrolytes as well as binary mixtures of 1-1 electrolytes[6], tetraalkylammonium halides[8], alkali metal salts of alkylcarboxylic acids with an alkyl chain containing 1 to 13 carbon atoms[9] and salts of typical amphiphilic ions[10].

1.1. Effect of concentration

If we exclude the salts containing large hydrophobic ions, such as tetraalkylammonium ions or typical amphiphilic ions with an alkyl chain containing ten or more carbon atoms, there is usually a large range of concentration, starting from about 10^{-3}M and extending up to 10^{-1}- 1M, where the measured IVP is independent of the electrolyte concentration $\underline{C}$ or varies only very slightly with $\underline{C}$, as predicted on the basis of equation (21).

Typical results at 220 kHz for 1-1, 1-2, 2-1, 2-2 electrolytes as well as for some potassium alkylcarboxylates with a short alkyl chain, and tetramethyl and tetraethylammonium bromides are listed in Table II[6,8,9]. For many of these salts measurements at 400 kHz yielded identical value of Φ/a indicating no effect of frequency in this range, in accord with theory. Millner and Muller[44] have observed for some 2-1 electrolytes changes of IVP with $\underline{C}$ much larger than those reported in ref.6, in the range 10^{-3}-1 $\underline{M}$. These variations may have their origin in the probe assembly used by these authors, where it is doubtful that the junction effect is fully eliminated, as well as in the complex focused ultrasonic beam used in these experiments.

At $\underline{C}$ below $10^{-3}\underline{M}$, the IVP decreases with $\underline{C}$. For systems with a large value of Φ/a, this decrease closely follows the dependence predicted by the concentration dependent term of equation (21), down to concentrations of 10^{-4} - $3\cdot10^{-5}\underline{M}$, as was pointed out at the end of Section III and illustrated by the results of Figure 9[23]. The agreement is not as good with salts having a small IVP, probably because of

small spurious effects, which cause an insignificant error in the calculation of ionic partial molal volumes from data at higher concentration but which contribute significantly at low concentrations.

Small changes of IVP at $\underline{C}>10^{-3}\underline{M}$ have been found[6] for some electrolytes having a small IVP, or where hydrolysis, extensive ionic association, or spontaneous evolution are known to occur.

1.2. Binary mixtures of 1-1 electrolytes

Such mixtures have been investigated[6] at concentrations where the IVP of each salt alone is independent of $\underline{C}$. The results are shown on Figure 10[6], where the various symbols represent the experimental results and the solid lines the curves calculated on the basis of equation (37). The agreement is excellent and constitutes further evidence, if need be, that the measured potential represent the true IVP effect.

1.3. Effect of the solvent viscosity

Equation (17) predicts that the IVP should have very little dependence on the solvent viscosity η_o since the frictional coefficients ρ_i which are proportional to η_o appear in both the numerator and denominator of the expression of the IVP. This prediction has been first checked by studying the IVP of KI solutions in the presence of increasing amounts of a water soluble polyacrylamide, added to the solution in order to increase its viscosity[6]. A 21-fold increase of the solution viscosity resulted in a less than 20% decrease of the IVP of the most concentrated KI solution. Given that the polyacrylamide solution alone showed a small vibration potential, this result was taken[6] as a good evidence that indeed IVP's are independent of the solvent viscosity. Since then, however, several studies[45] have shown that the presence of polymers in solution does not affect much the motion of ions in electrical fields or their diffusion, because these effects are sensitive to the microviscosity of the solution which is very close to the viscosity of the solvent, even though the presence of polymers greatly increases the macroviscosity of the solution. The effect of polymer on the IVP is, therefore, not a good way to

assess the dependence of the IVP on viscosity. A much better way is to compare the IVP's of a given salt in two solvents with very different viscosities but where ions behave similarly. Water and ethylene glycol give a good basis for this comparison . Their viscosities are in a ratio of about 1/17 at 25°C. Moreover, simple ions appear to have similar behaviors in these two solvents, as far as volumes and transport numbers are concerned. For instance, for KI the values of $\bar{V}_2^\circ$ and t_+ are respectively 45.4 cm^3/mol. and 0.488[6] in H_2O and 45.6 cm^3/mol and 0.499[16] in ethylene glycol. The values of the IVP were found to be -4.0 ± 0.2[6] and -3.9 ± 0.2 $\mu V\ s\ cm^{-1}$ in H_2O[6] and ethylene glycol[16], respectively.

1.4. Solutions containing large hydrophobic ions

A dependence on concentration was observed for solutions containing tetraalkylammonium (TAA^+) ions[8]. This effect was attributed to TAA^+ - TAA^+ interactions.

A dependence on concentration was also observed with salts of long chain alkylcarboxylates[9] and of typical amphiphiles[10], in the concentration range where micelles are known to be formed (cmc or critical micelle concentration). For laurylpyridinium iodide and bromide the absolute magnitude of the IVP passes through a maximum at the cmc, and shows very large changes with concentration, particularly for lauryl pyridinium iodide where a change of sign of the IVP (180° phase change) is observed. The IVP results also suggest a premicellar association of the amphiphile ions. For sodium dodecylsulfate[10], an attempt to account for the IVP changes with concentration in the submicellar range in terms of dimerization of the dodecylsulfate ion proved unsuccessful. This was interpreted as indicating that premicellar aggregation exceeds the dimerization stage. At concentrations well above the cmc, it was not possible to account for the change of the vibration potential with concentration, on the basis of the equations valid for colloidal vibration potentials (see next Section).

1.5. Calculations of ionic partial molal volumes

The values of the partial molal volumes of individual ions can be calculated from $\Phi_{\lambda/2}$ data provided that values of t_i, $\overline{V_2^\circ}$ and a are available from other measurements. The values of t_+ and t_- have been calculated from the tabulations of ionic limiting equivalent conductivities given in literature compilations (e.g. ref. 34). The values of $\overline{V_2^\circ}$ are either from tabulations[46], obtained by using the additivity law[46], or directly determined from density measurements. In studies of aqueous electrolytes[6,8-10], the velocity amplitude a was obtained using the hydrophone technique described in Section III6. Note that a is probably the quantity which is the least accurately known in ionic partial molal volume calculations when $\Phi_{\lambda/2}/a$ is greater than $1\mu V\ s\ cm^{-1}$.

In Table III, based on results reported in references 6,8, 9 and 10 are listed the values of Φ/a, t_+, $\overline{V_2^\circ}$, $\overline{V_+^\circ}$ and $\overline{V_-^\circ}$ for various 1-1 electrolytes. The signs indicated for Φ/a have been assigned in such a way as to render the data self-consistent. For electrolytes with small values of Φ/a, a possible confusion concerning sign has been avoided by studying mixtures of the electrolyte in question with a second electrolyte for which no ambiguity exists as to the sign of the effect[6]. The results of Figure 10 show that if the two electrolytes have IVP's of the same sign Φ_M remains positive or negative in the whole range of concentration while it goes through zero if the two IVP's have opposite signs. Both a and $\Phi_{\lambda/2}$, were obtained at 22°C, Panckhurst[47] has criticized the use of $\overline{V_2^\circ}$ and t_+ data at infinite dilution and 25°C, in conjunction with IVP data at finite, although small concentrations (10^{-3} - 10^{-2}M), and 22°C to obtain the partial molal volumes of ions. These criticisms were shown to be largely unfounded on the basis of the known concentration and temperature dependence of both transport numbers, $\overline{V_2^\circ}$ and IVP[48].

The results of Table III show that for a given anion (or cation), Cl^- for instance, all of the investigated chlorides yield very consistent values of $\overline{V^\circ}(Cl^-)$, with an average of 23.7 ± 1.2 cm^3/mol. The same is true for other univalent anions and cations. Salts involving multivalent ions yield less consistent values of $\overline{V^\circ}$(anion)[6] probably because

of ionic association. The IVP's should therefore not be used to determine the partial molal volumes of multivalent ions. For this purpose, it is easier and more accurate to calculate the partial molal volumes of monovalent ions from IVP measurements on as many 1-1 electrolytes as possible and to obtain the partial molal volumes of multivalent ions from the $\overline{V}_+^\circ$ (or $\overline{V}_-^\circ$) values of monovalent ions together with $\overline{V}_2^\circ$ data for salts containing the multivalent ions, using the additivity law.

A number of methods have been proposed in past years to determine the partial molal volumes of individual ions in water from $\overline{V}_2^\circ$ data. All of these involve extrathermodynamic assumptions. The best known of these non-experimental methods are the following :

(i) Bernal and Fowler[49] assume that the ratio of the ionic partial molal volumes for a given electrolyte is equal to the cube of the ratio of the crystallographic radii of the ions.

(ii) Fajans and Johnson[50] assume that $\overline{V}^\circ(NH_4^+) = \overline{V}^\circ(Cl^-) = \overline{V}^\circ(NH_4Cl)/2$.

(iii) Stokes and Robinson[51] assume that the electrostriction of solvent surrounding a large ion, I^- for instance, is negligible and that the partial molal volume of such an ion is that anticipated from "random close packing" of water molecules around a hard sphere with a radius corresponding to the crystallographic radius of the ion.

(iv) Mukerjee[51] assumes that the ionic partial molal volumes depend only on the ion radii r_i. The $\overline{V}^\circ$(ion)'s are then obtained by setting the value of the partial molal volume of one ion (H^+) such that the ionic partial volumes of monovalent anions and cations calculated from $\overline{V}_2^\circ$ data fall on a smooth curve when plotted as a function of r_i, as predicted by Hepler's[53] semi-empirical equation.

(v) Conway, Verrall and Desnoyers[54] obtain the partial molal volume of one halide ion X by extrapolating to zero cation molecular weight the linear plot of the $\overline{V}^\circ$(tetraalkylammonium halide) versus cation molecular weight.

(vi) $\overline{V}^\circ(Ph_4B^-)/\overline{V}^\circ(Ph_4As^+)$ is equal to the ratio of the van der Waals volumes of these ions.

(vii) Jolicoeur and Mercier[56] assume that pentaerythritol ($(HOCH_2)_4C$) has the same partial molal volume as the tetrakis (hydroxymethyl) phosphonium ion $(HOCH_2)_4P^+$. The difference between the values of $\overline{V}°[(HOCH_2)_4C]$ and $\overline{V}°[(HOCH_2)_4P^+Cl^-]$ readily yields $\overline{V}°(Cl^-)$.

Before comparing numerical values, it should be noted that all these non-experimental methods calculate the partial molal volume of one ion and obtain the partial molal volumes of all other ions from $\overline{V}_2^o$ data using the additivity law. The comparison of the various methods can, therefore, be made on any one ion, the difference between the results for any two methods being the same for all ions. This fact may be misleading when assessing the degree of validity of a given non-experimental method with respect to the IVP method. A difference of say 10 cm^3/mole between the two methods may be considered as small with respect to the partial molal volume of very large ions such as $(C_4H_9)_4N^+$, Ph_4As^+ or Ph_4B^- (300 to 400 cm^3/mole) and the non-experimental method may be said to be accurate to within 2 to 3%. The trouble, however, is that this difference remains the same whatever the value of the ionic partial molal volume. For ions with fairly small volumes this can easily result in positive $\overline{V}°$(ion) while the true values are negative.

In Table IV are listed the values of $\overline{V}°(H^+)$ obtained by the above methods. Method (ii) is the only one yielding a value not consistent with the IVP result while all the other methods yield values close to that obtained from IVP. This result may be taken as indicating that the assumptions underlying these various methods are essentially equivalent when considering volumic properties of ions in water.

2. Solutions in organic solvents

The IVP measurements in organic solvents involve principally alkali halides of sufficient solubility and, in a few instances, other 1-1 electrolytes selected on the basis of their solubility and low tendency for ion-pairing (small association constant K_A, as obtained from conductivity measurements for instance). Although IVP's are fairly insensitive to ionic association as long as neutral ion-pairs are formed, the

formation of charged aggregated species, such as triple ions, will modify the IVP of the solution because these new species contribute to the generation of the IVP. Salts with a large K_A value will more readily give rise to triple ions and other charged species and therefore present problems.

Apart from solubility and ionic association problems another difficulty arises in studies with organic solvents: the determination of the velocity amplitude a. As indicated earlier a cannot be determined without serious error from radiation pressure measurements in the water. Calibrated hydrophones cannot be used either because they are calibrated in water and would need recalibration in each of the investigated organic solvent. This would be very difficult if not totally impossible given the calibration procedure and setup. The following method was used[12-16] to obtain the velocity amplitude a_x in the investigated organic solvent. First, an approximate value of a_x in the cell filled with the solvent was calculated with equation (38) from the velocity amplitude in water determined in turn using an electrolyte of known IVP and calculating back to a_w. The a_x values so calculated are only approximate for the reasons discussed earlier. Nevertheless they help to establish the range of velocity amplitude over which the partial molal volumes of ions are calculated, using a_x as an adjustable parameter. Once the values of $\phi_{\lambda/2}$ for a series of n salts CX_i with a common ion C and counterion X_i have been measured, the values of $\overline{V}^\circ(C)_{CX_i}$ are calculated for each salt CX_i as a function of a_x using equation (27) over this range of a_x values. Then, for a given value of a_x, the average value $\langle\overline{V}^\circ(C)\rangle$ and the root mean square deviation $\sigma(C)$, given by :

$$\langle\overline{V}^\circ(C)\rangle = \sum_i \overline{V}^\circ(C)_{CX_i}/n \qquad (39)$$

$$\sigma(C) = \left[\frac{\left[\overline{V}^\circ(C)_{CX_i} - \langle\overline{V}^\circ(C)\rangle\right]^2}{n}\right]^{1/2} \qquad (40)$$

are calculated. The plot $\sigma(C)$ vs a_x usually shows a fairly sharp minimum for a value a_m of the velocity amplitude. This procedure is repeated for all ions for which a sufficient number of salts have been investigated (4 or more), and the

different a_m values minimizing the rms deviations are once more averaged to yield $\langle a_x \rangle$ which may be considered as the effective velocity amplitude during the IVP measurements. The values of the partial molal volumes of ions and of the σ's are then directly obtained from the plots of $\langle \overline{V}^\circ(C) \rangle$ and $\sigma(C)$ vs a_x. The method is illustrated by the results of Figure 11 relative to the determination of $\overline{V}^\circ(Br^-)$ and $\sigma(Br^-)$ in ethylene glycol[16].

Table V lists the IVP's of alkali metal iodide solutions, in all of the organic solvents investigated thus far[12-16] and in a large range of concentration. As for H_2O, there is a certain range of concentration where the IVP's depend only little on concentration. The concentration dependence at lower concentration is nevertheless clearly evident for solutions in methanol[12], ethanol and DMF[13]. Note, however, that other salts such as the alkali metal chlorides showed much smaller variations of Φ/a in these three solvents. It cannot be said with certainty whether this observation is specific to these solvents or is the result of some unknown difficulty experienced during the measurements, because practically no change of IVP with C was observed for all of the salts investigated in DMSO[14], acetonitrile[15] and ethylene glycol[16]

The partial molal volumes of ions have been determined using the measured IVP's, together with $\overline{V}_2^\circ$ data where available from the literature or determined in the same studies as the IVP's and the t_+ values calculated from literature data. The values are listed in Table VI. Note that all these values are not those directly obtained from the calculations based on IVP and $\overline{V}_2^\circ$ data. Once these calculations were done, one or several of the $\overline{V}^\circ$(ion) so determined were selected on the basis of the number of electrolytes including these ions which had been investigated and their low σ(ion) value. Another criteria of choice is a small change of $\langle \overline{V}^\circ(\text{ion}) \rangle$ with a_x. This is generally the case for ions such as Br^-, for instance, whose alkali metal salts show IVP's both positive and negative depending on the counterion. Figure 11 clearly shows that there is then a compensation in the

variations of the values of the $\overline{V}°(Br)_{MBr}$ when a_x is increased which results in an almost constant $\langle\overline{V}°(Br^-)\rangle$ in the whole range of velocity amplitude.

In Table VII, the partial molar volumes of Cl^- in various solvents, obtained from IVP measurements are compared with the values obtained from the methods of Mukerjee[52], Conway et al.[54] and Millero[55]. The extrapolation method of Conway et al.[54] which yields good results in water does not hold in organic solvents. This probably results from contributions of various extraneous effects which cancel out in water[57] but no longer do so in the organic solvents, thereby yielding an intercept which no longer just corresponds to the partial molal volume of the anion, but also some unknown contributions of these various effects[29]. On the other hand, Mukerjee's method[52] yields values which agree with the ones obtained from IVP except for the two sterically hindered solvents, DMF and DMSO. The same remark seems to hold for Millero's method.

In any case the results of Table VII clearly indicate that considerable caution must be exercised when determining the partial molal volumes of ions by means of non-experimental methods, and discussing these data because the degree of validity of these methods greatly varies from solvent to solvent *.

3. Factors which determine the partial molal volumes of ions

The partial molal volume $\overline{V}°_i$ of an ion i is usually considered as including a geometric contribution (intrinsic volume of the ion plus the volume of the void space around the ion owing to the molecular structure of the solvent) and a

---

* The determination of ionic partial molal volumes of monovalent ions from IVP measurements is in progress in water-t-butanol mixtures[17]. This system has been selected for the first investigation of IVP in binary solvents because it is probably one of the best characterized at the present time.

contribution due to ion-solvent interactions (electrostriction, hydrophobic hydration, etc.). For a rather qualitative discussion restricted to the alkali metal and halide ions it is sufficient [12-16] to consider only the geometric contribution and the electrostrictive effect of the ion on the surrounding water molecule, so that :

$$\bar{V}^{\circ}_{\underline{i}} = \bar{V}^{\circ}_{\underline{i}}(\text{ geom.}) + \bar{V}^{\circ}_{\underline{i}}(\text{ elect.}) \qquad (41)$$

Several treatments have been proposed concerning these two contributions. The geometric contribution has been dealt with by Hepler[53], Glueckauf[58], Conway *et al*[54] and more recently by Hirata *et al*.[59]. Hepler's[53] treatment expresses $\bar{V}^{\circ}_{\underline{i}}(\text{ geom})$ as proportional to the crystallographic volume of the ion $\underline{i}$ of radius $r_{\underline{i}}$; that is :

$$\bar{V}^{\circ}_{\underline{i}}(\text{ geom}) = Ar^{3}_{\underline{i}} \qquad (42)$$

The expressions for $\bar{V}^{\circ}_{\underline{i}}(\text{ geom})$ from the other treatments are more complex.

The electrostrictive effect has been dealt with by Hepler[53], Mukerjee[52], Padova[60], Desnoyers *et al*[61] and Glueckauf[58]. Hepler's equation, adapted to the treatment of ionic partial molal volumes[8,12-16] gives

$$\bar{V}^{\circ}_{\underline{i}}(\text{ elect}) = -B/r_{i} \qquad (43)$$

Benson and Copeland[62] have presented a detailed discussion and justification of Hepler's equations (42) and (43) and of Mukerjee's method. Note that the Drude-Nernst[63] equation, which is based on Born's treatment of an ion in a solvent continuum, leads for monovalent ions to the following expression

$$B = \frac{6.9\times10^{12}}{D} \cdot \frac{d\ \ln D}{dp} \qquad (44)$$

where B is in cm^3 Å/mole and the pressure p in dyne/cm^2. This equation provides a theoretical basis for the discussion of the experimental values of B[12-16].

Equations (42) and (43) indicate that the plot of $\bar{V}_i^\circ \cdot r_i$ vs r_i^4 should yield a straight line whose slope and intercept give the values of A and B. This prediction has been verified for most solvent systems[8,12-16], as is shown by the plots in Figure 12. It has been found that in water[8], alkali metal and halide ions fall on a single straight line. In DMF[13], DMSO[14] and ethylene glycol[16], two distinct straight lines are obtained for these two types of ions. Methanol[12] and ethanol[13] constitute border cases where alkali metal and halide ions fall on two distinct, although fairly close straight lines. Finally acetonitrile shows a slightly curved $\bar{V}_i^\circ \cdot r_i$ vs r_i^4 plot with a positive curvature[15].

Table VIII lists the value of A and B for alkali metal and halide ions in the various solvents investigated thus far[6,12-16]. Also listed are the values of B calculated according to equation (44). For the solvents where the values of d ln D/dp were not known, this derivative was approximated by the isothermal compressibility κ_T[13] of the solvent. This approximation holds to within 10% for water and methanol[13]. It should be noted, as pointed out by Millero[64], that the comparison of the B values obtained from the $\bar{V}_i^\circ \cdot r_i$ vs r_i^4 plots may not be correct if the geometric contribution is not proportional to r_i^3 in all solvents. This fact, together with the possible errors on $\bar{V}^\circ$(ion) incurred by omitting the non-isothermal propagation correction term, call for caution when comparing the A and B values in different solvents. Nevertheless from such a comparison it has been inferred[12-16] that electrostriction is a short range effect, in agreement with theoretical calculations[60,61], which is mainly determined by the nature of the local dipoles in contact with the ion, the degree of steric hindrance at the poles of the solvent molecule dipoles, and possibly, other specific interactions between ions and solvent molecules. On the other hand the A values appear to reveal that the geometric contribution decreases as the molar volume or van der Waals volume of the solvent increases and that this contribution also depends on specific packing effects, as well as on the degree of steric hindrance of the poles of the solvent molecule dipoles[12-16].

4. IVP's and solvation numbers

Bockris and Saludja[65] have reported a method by which ionic solvation numbers are obtained from the combination of compressibilities and ionic vibration potentials. In its principle this method is very similar to that by which ionic partial molal volumes are obtained. Note that Bockris and Saludja[65] distinguish between solvational and non-solvational coordinated water molecules on a kinetic basis, the former being those water molecules which remain associated with the ion during its movement through the solution. Several aspects of this work, both theoretical[66] and numerical[67], have been criticized. In particular, contrary to Bockris and Saludja claim, it has been shown[67] that the compressibility - IVP method[65] yields the same solvation numbers as the density - IVP method[67] provided the volumes of the solvated ions used in the calculation are obtained using a calibration curve prepared by using for the radii of the tetraalkylammonium ions the values obtained from their partial molal volumes and not from bond lengths and bond angles.

V. MISCELLEANOUS STUDIES

1. Colloidal vibration potentials

In 1938, Hermans[18,19] and Rutgers[20] simultaneously reported that alternating potentials should be produced when ultrasonic waves are propagated through colloidal suspensions. This effect is closely related to IVP. Its generation, however, involves differences in displacements of the colloidal particles and their surrounding diffuse atmospheres in the ultrasonic field. The diffuse ionic atmosphere surrounding each colloidal particle is periodically distorted by the sound waves and thus gives rise to dipoles of periodically varying moment (see Figure 13). The net result is a periodic excess of positive and negative charge on a macro-scale at various points in the colloidal suspension. Therefore, as for IVP's, if two inert metal probes are placed in the suspension, an alternating potential difference with the same frequency as the ultrasonic wave will develop between them, provided that they are separated by a distance other than a multiple of the wavelength.

This effect was considered by Hermans[19] to hold much promises for the study of the diffuse ionic atmosphere surrounding colloidal particles. With other methods available at that time, the ionic atmosphere is involved only as a second order correction term, while colloid vibration potentials (CVP) are directly sensitive to the distribution of ions around the colloidal particles.

1.1. Theory of CVP

Theoretical treatments of CVP's have been presented by Hermans[18,19], Rutgers[20], Enderby[68] and Booth and Enderby[69]. The last two authors have developed an equation of a somewhat more general nature for CVP's, based on the periodic dipole concept. For a uni-univalent suporting electrolyte where anions and cations have the same frictional coefficient ρ, Enderby gives an expression equivalent to the following for the amplitude of the potential between two points separated by a phase difference of one half wavelength :

$$\frac{\phi_{\lambda/2}}{a} = \frac{c\rho n_K W_K B(b)\zeta\mu}{72kT\eta_o \kappa^2} \qquad (45)$$

where a, c, ρ, η_o, k and T have the same meaning as in Section II. n_K is the number of colloidal particles of radius R_K and apparent mass W_K per cm^3, ζ is the zeta potential of the colloidat particle and $1/\kappa$ the effective thickness (Debye length) of the diffuse ionic atmosphere surrounding each colloidal particle. The quantities B(b) and μ are given by the equations :

$$B(b) = 96+6b^2-10b^3-b^4+b^5+(12b^4-b^6)e^b\, E(b) \qquad (46)$$

where

$$E(b) = \int_b^\infty (\exp - b)\, d\ln b \qquad (47)$$

$$b = \kappa R_K \qquad (48)$$

and

$$\mu = \kappa^2 \Big/ \left[\kappa^4 + (\omega\rho/kT)^2 \right]^{1/2} \qquad (49)$$

The zeta potential is related to the charge of the colloidal particle Q_K by the equation

$$Q_K = \zeta \, DR_K \, (1 + \kappa R_K) \qquad (52)$$

Equations (45) to (52) indicate that the CVP is dependent on the zeta potential, colloid concentration and apparent mass, nature and concentration of the supporting electrolyte and frequency. The CVP becomes essentially independent of frequency when $\kappa^2 >> \omega\rho/kT$. Order of magnitude calculations yield values of $\phi_{\lambda/2}/a$ of typically 10^{-4} to 10^{-2} V s/cm.

Booth and Enderby[69] have examined the more general situation where the frictional coefficients of the anion and cation of the supporting electrolyte are not equal. The calculations show that this usually results in a smaller calculated value of the CVP than in the assumption of equal mobilities. Note that the restrictive assumptions made by Booth and Enderby[68,69] are that the separation of the colloidal particles is much greater than the thickness of the ionic atmosphere and that the particles are not conducting.

1.2. Results

The existence of CVP was established much earlier than that of IVP owing to its much larger magnitude. Already in 1938, Rutgers[20] reported the detection of this effect in silver iodide suspensions, using the standing wave technique. Following World War II, Vidts[21], Rutgers and his students[22,39,70,71] continued the studies of CVP's in silver iodide and arsenic trisulfide suspensions using the same technique. Other work on CVP included that of Yeager and co-workers[5,72] (silica suspensions investigated first with a standing wave technique[72], then with pulse modulated ultrasounds[5]), Causse[73] (silver iodide suspensions) and Dérouet and Denizot[4] (arsenic trisulfide sols). These studies were qualitative or at the best semiquantitative. It was only in 1960 that Yeager et al.[74] reported the first reasonably quantitative investigation of CVP performed on deionized silica suspensions using pulse-modulated ultrasonic waves and a single probe to detect the effect. These authors verified

the predictions of the theory concerning the dependence of CVP's on ultrasonic frequency and colloidal concentration. Under the experimental conditions involved in this study the effect was found to be independent of frequency in the range 200-1000 kHz, and to become independent of the colloidal concentration at sufficiently large concentration, as is to be expected from theory. The CVP's also were found to be relatively constant for a given ratio of the colloid concentration to specific conductance at a given frequency, over a fairly large range of colloid concentrations. Finally, the agreement between calculated and experimental values was always within an order of magnitude and in many cases surprisingly good. The main difficulty in this study was associated with the low conductivities of the solutions, the magnitude of the internal impedance for the CVP at the platinum probe was often comparable with the input impedance of the measuring equipment. This resulted in a sizeable loading effect for which it was difficult to correct.

This brief review shows that the investigations of CVP's reported so far have been essentially directed to checking the theory of this effect. The CVP effect has not yet been used to gain new basic informations on colloidal suspensions. This should be the task for the coming years. CVP studies on well characterized systems such as silica, titanium oxide and latex suspensions with the equipment now available should prove extremely interesting and useful.

1.3. Application of CVP to ζ-potential monitoring in industrial processes

In many industrial processes involving colloidal suspensions, the desired quality of the end product is obtained throught the addition of sizeable amount of various compounds to the raw product. This is the case in paper processing where the starting material is a suspension of cellulose fibers[75]. There, the retention of the additives by the fibers is governed by the value of their ζ potential. Retention agents which modify this potential are often added in order to increase the retention of the additives by the fibers. For this purpose it is desirable to know the effect of the retention agents on the

ζ-potential as soon as possible after adding them to the system. Unfortunately, the usual methods of measuring ζ-potential require more than fifteen minutes and cannot be performed in a continuous fashion. This may result in losses of additives and in lower quality products. Equation (45) indicates that the CVP of colloidal suspensions is proportional to their ζ-potential. A determination of this quantity through CVP measurements with ill defined cellulose fibers would prove far too inaccurate. The idea has been put forward, however, to use CVP to follow changes of ζ of the colloidal suspensions upon addition of various compounds. The validity of this approach has been verified for such fibers[75] by comparing CVP measurements with other techniques for measurements of ζ potentials. The CVP measurement should facilitate ζ-potential measurements but require some calibration before a full use. The possibility of building smaller and more rugged equipments, specific to industrial use, is presently being investigated.

2. Polyelectrolyte vibration potentials

Polyelectrolytes incorporate features of simple electrolytes and colloidal systems and yet possess additional features associated with the linkage of charged groups together in an appended structure. For this reason, one of the problems in investigating polyelectrolyte solutions was to determine whether the vibration potential which would arise upon propagation of ultrasonic waves in these systems would be of a nature similar to IVP or CVP, or eventually more complex than either of these two effects.

The first evidence for the existence of a vibration potential in polyelectrolyte solutions (PVP) was reported by Booker et al.[24] in 1962. The authors investigated the effect of the degree of neutralization on the vibration potential of aqueous solutions of polyacrylic acid, using pulse modulated ultrasonic waves and a single probe to measure the effect. This study was of a qualitative character and the results were interpreted in terms of CVP.

In 1967 was reported the first quantitative investigation of PVP's[27]. The measurements involved the dependence of the PVP on the nature of the polyelectrolyte and its concentration and degree of neutralization, as well as on the nature of the cation of the base used for the neutralization and the nature and concentration of the supporting electrolyte. Most of the measurements were performed on samples of polyacrylic acid of different molecular weights. Typical neutralization curves are shown on Figure 14. All the data reported in this study were in quantitative or semi-quantitative agreement with a model where PVP's are assumed to arise by a mechanism identical with IVP's. The Debye bead model[76] for describing the dynamic properties of polymers, has been used[27]. This model is particularly appropriate for interpreting the dynamic behavior of polyions in ultrasonic fields. At the frequencies of the measurements the periodic displacements of the polymer molecules relative to solvent as well as one part of the polymer relative to the other parts of the same polymer molecule are very small. Consequently, the various segments or beads of the polyion can be viewed as moving independently in considering only first order dynamic effects. The polyelectrolyte solution is then treated as a solution of a simple electrolyte consisting of polymer beads, protons due to the self ionization of the polyacid, monovalent metal ions G^+ from the hydroxyde used for the neutralization and a supporting 1-1 electrolyte C^+A^-. The general equation (17) without the concentration dependent term is then applied to this system. The unknown number of monomer units per polyion bead drops out in the calculations and the PVP of a polyacid solution at neutralization degree α and in the presence of a supporting electrolyte at the concentration $\underline{C}_s$ is [27] :

$$\Phi_{\alpha,\underline{C}_s} = \frac{\Phi_P}{1+K} + \frac{\Phi_s}{1+1/K} \qquad (51)$$

Note that this expression is formally identical to that for a binary mixture of 1-1 electrolytes (see equation 37). The full expressions for Φ_P, Φ_s and K are complicated in the case where the ions G^+ and C^+ are different.[27] When only one kind of counterions is present, the term K can be shown to be the

ratio of the conductivity of a solution containing only the salt G^+A^+ at the concentration C_s to the conductivity of the polyelectrolyte solution without the salt present.[27] Let Φ_s be the IVP for a G^+A^- solution and Φ_P be the vibration potential of the solution of polyacid P at the neutralization degree α in the absence of supporting electrolyte. Then, in water

$$\Phi_P = 0.155a \frac{(\theta-\alpha)W_H u_H + (\alpha-\theta\beta)W_G H_G - W_M u_M}{(\theta-\alpha)u_H + (\alpha-\theta\beta)u_G + (1-\beta)\theta u_M} \qquad (52)$$

The subscripts H,G and M refer to protons, counterions and monomer units, respectively. θ is the fraction of ionized acid groups and β is the fraction of the charge of the polyion which is compensated by associated counterions. The u's are the mobilities (ratio of the charge to the frictional coefficient) and the W's the apparent molar masses of the various species, given by equation (25).

The experimental results[27] and in particular the neutralization curves (see Figure 14)) were fitted to the equations (51) and (52) by making use of the values of W_H and W_G obtained from IVP measurements on classical electrolytes[6], and of the transport numbers and conductivities of polyacrylic acid solutions reported in the literature. The only unknown in equation (52) was W_M which was obtained[27] from the value of Φ_P at $\alpha=0$. This quantity was found equal to 25.6 g/mol., which yields $\overline{V}_M^\circ$ = 46.4 cm^3/mole. This value is in excellent agreement with that obtained from direct density measurements[77] a few years later : 46.7 cm^3/mole. This result gives a strong support to the model used for the interpretation of the PVP measurements.

The rather complicated features of the curves in Figure 14 were explained as follows[27]. The maximum in the plot of $-\Phi$ vs α at low θ values, which is evident for small counterions, is due to the competition between two effects : (i) the rapid disappearance of the protons (which have a large mobility) which makes the potential more negative and (ii) the increase of number of counterions (which have a smaller mobility than protons) with α, which makes the potential less

negative. With heavier cations, the second effect becomes predominant at lower α's. This shifts the maximum to lower α's and explains why the maximum disappears completely with the heaviest metal ion, Cs^+ ; then the effect of mass overcomes the effect of mobility. The minimum in $-\Phi$ in Figure 14 found at intermediate α values was attributed to the binding of counterions to polyions. Indeed it does not occur with the tetraalkylammonium ions because of their very small apparent masses[8] but becomes very pronounced with heavy metal ions. From these results it has been inferred that PVP's are sensitive to the total fraction of bound counterions, i.e., with and without dehydration. The method is not thought to be sufficiently sensitive, however, to permit a distinction between these two types of counterions.

Results very similar to those for polyacrylic acid have been obtained with carboxymethyl cellulose samples of various substitution degrees[78].

The above results did not provide much evidence for sensitivity of PVP's to the polymer conformation as was originally hoped[24]. This is probably because the polymers investigated are rather extensively solvated and extended, even at low neutralization degree. In a study of the effect of pH on poly-L-glutamic acid, which undergoes a transition from a helix (low pH) to coil (high pH), however, a change in PVP of about 5 $\mu V\ s\ cm^{-1}$ was found to accompany this transition[26]. This effect arises mostly from changes of monomer mobility, rather than of apparent mass since the volume change for the transition is only 1 to 2 cm^3/monomole.

Finally it should be noted that preliminary measurements of vibration potentials have been performed on aqueous solutions of a well characterized globular protein, lysozyme, which was thought to represent a good model of a highly charged quasi spherical particle[23]. The measured effects which were of the order of 10 $\mu V\ s\ cm^{-1}$ and strongly dependent on the ionic content of the solution, did not reveal any significant feature in the pH range between 5 and 10 but showed a large decrease of Φ above pH 10.

CONCLUSIONS

Accurate measurements of vibration potential can be now performed on a routine basis, using pulse modulated ultrasonic waves for the generation of the effect and a double probe assembly with driven shields, connected to a differential cathode follower for the detection of the effect, in a variety of solvents and solvent mixtures. The results obtained thus far have been used to check the theoretical treatments of the ultrasonic vibration potentials. Moreover the combination of vibration potential and density data has provided us with the partial molal volumes of ions in a series of solvents. These data should prove useful in checking theories dealing with electrostriction once they can accurately be split into a geometric contribution, and a contribution due to ion-solvent interactions.

There have been relatively few investigations of polyelectrolyte solutions and colloidal systems by means of vibration potentials, although the study of these systems should prove interesting. Vibration potentials may be useful for the monitoring of changes of ζ-potential of colloidal suspensions upon addition of various agents, in some industrial processes of major importance such as paper processing.

Acknowledgements

The authors acknowledge the support which has been provided by the CNRS and the US Office of Naval Research for much of the research on ionic and colloidal vibration potentials and the preparation of this manuscript.

LIST OF SYMBOLS

A - coefficient m eq. 42

a_i - velocity amplitude of i^{th} ion

a_o, a - velocity amplitude of solvent

a_x - velocity amplitude in solvent x

B - coefficient in eq. 43

$B(b)$ - see eq. 46

b - κR_K

C - molar concentration

C_p - specific heat at constant pressure

c - velocity of sound

D - dielectric constant

D_ω - dielectric constant at frequency ω

d_o - density of solvent

$E(b)$ - see eq. 47

e - elementary charge

e_i - charge of $i^{\underline{th}}$ ion

h_i - number of solvent molecules transferred with the $i^{\underline{th}}$ ion

k - Boltzmann constant

L_o - specific conductance at zero frequency

L_w - specific conductance at frequency w

$M_{i,s}$ - molar mass of $i^{\underline{th}}$ solvated ion

$m_{i,s}, m_+, m_-$ - mass of $i^{\underline{th}}$ ion

N_A - Avogadro's number

n - number of salts

n_i - number of $i^{\underline{th}}$ ion per unit volume

$\bar{n}_i$ - average number of $i^{\underline{th}}$ ions per unit volume

n_K - particle concentration of colloid

p - pressure

Q_i^* - heat transferred by $i^{\underline{th}}$ ion

Q_K - charge on colloidal particle

q - see eq. 4

R - gas constant

R_K - radius of colloidal particle

r - see eq. 19

S - molar mass of solvent

S_i^* - entropy of transfer for $i^{\underline{th}}$ ion

$\bar{S}_i$ - ionic partial molal entropy

$(\bar{S}_t)_i$ - transported entropy for $i^{\underline{th}}$ ion

$(\bar{S}_t)_e$ - transported entropy of electron in probe metal

T - absolute temperature

t - time

t_i, t_+, t_- - ionic transport numbers

u_G, u_H, u_M - mobilities for counterions, protons, and monomer units

$\bar{V}_e$ - partial molal volume of electron in metal

$V_{i,s}$ - molar volume of $i^{\underline{th}}$ solvated ion

$\bar{V}_{i,+,-}$ - ionic partial molal volumes

$\bar{V}_2$ - standard partial molal volume of electrolyte

v_o - velocity of solvent

v_i - velocity of $i^{\underline{th}}$ ion

$v_{i,s}$ - volume of $i^{\underline{th}}$ ion

W_i, W_+, W_- - apparent molar mass (see eq. 18)

W_G, W_H, W_M - apparent masses of counterions, protons and monomer units

W_K - apparent mass of colloidal particle

X - electric field

x - distance in direction of propagation

z_i, z_+, z_l - ionic valences

α - degree of neutralization of polyelectrolyte

α_E - thermal coefficient of expansion

β - fraction of charge of polyion compensated by associated counterions

β_i - see eq. 11

γ_i, γ_i^o - see eq. 8

Δ - phase angle

δp - acoustical pressure

ξ - zeta potential

η_o - viscosity of solvent

relaxation time of ionic atmosphere

θ - fraction of ionized end groups in polyelectrolyte

κ - reciprocal of ionic atmosphere thickness

Λ^o - limiting equivalent conductance of electrolyte

$\lambda_i, \lambda_+, \lambda_-$ - equivalent ionic conductance

μ_e - chemical potential of electron in metal

ρ_i - friction coefficient of $i^{\underline{th}}$ ion

σ - propagation constant $(2\pi/\lambda)$

$\sigma(C)$ - see eq. 40

Φ - potential

Φ_o - potential amplitude

$\Phi_{o,\lambda/2}$ - potential difference between two points with phase distance of $\lambda/2$

Φ_P, Φ_S - see eq. 51

ω - angular frequency

REFERENCES

1. E. Yeager and F. Hovorka, J.Acoust.Soc.Am., 25, 443 (1953)
2. P. Debye, J.Chem.Phys., 1, 13 (1933)
3. E. Yeager, J. Bugosh, F. Hovorka and J. McCarthy, J.Chem.Phys. 17, 411 (1949)
4. B. Derouet and F. Denizot, C.R.Acad.Sci., (Paris), 233,368(1951)
5. E. Yeager, H. Dietrick and F. Hovorka, J.Acoust.Soc.Am., 25, 456 (1953)
6. R. Zana and E. Yeager, J.Phys.Chem., 70, 954 (1966) ; 71, 521 (1967)
7. J. Bugosh, E. Yeager and F. Hovorka, J.Chem.Phys., 15, 592 (1947)
8. R. Zana and E. Yeager, J.Phys.Chem., 71, 4241 (1967)
9. R. Zana and E. Yeager, J.Chim.Phys. Physicochim.Biol., 65, 467 (1968)
10. R. Zana and E. Yeager, J.Chim.Phys.Physicochim.Biol., 66, 252 (1969)
11. F. Kawaizumi and R. Zana, C.R.Acad.Sci.,(Paris) Ser.C, 277, 609 and 667 (1973).
12. F. Kawaizumi and R. Zana, J.Phys.Chem., 78, 627 (1974)
13. F. Kawaizumi and R. Zana, J.Phys.Chem., 78, 1099 (1974)
14. K. Kale and R. Zana, J.Solution Chem., 6, 733 (1977)
15. G. Perron, J. Desnoyers and R. Zana, in preparation
16. G. Lange, C. Criss and R. Zana, in preparation
17. N. Dollet, J. Juillard and R. Zana, in preparation
18. J. Hermans, Phil.Mag., 25, 426 (1938)
19. J. Hermans, Phil.Mag., 26, 674 (1938)
20. A. Rutgers, Physica, 5, 46 (1938)
21. J. Vidts, Meded.Koninkl.Vlaam.Acad.Wetenschap, Letteren,Belg., Kl.Wetensch. , N°3, 5 (1945)
22. A. Rutgers, Nature, 157, 74 (1946). This letter to the Editors appears to be based on the work described in ref.21.
23. R. Zana and E. Yeager, unpublished results
24. J. Booker, E. Yeager and F. Hovorka, Proceedings of the Fourth International Congress on Acoustics, Copenhagen 1962, paper J42
25. R. Zana and E. Yeager, Proccedings of the Fifth International Congress on Acoustics, Liège 1965, paper D 31.

26. R. Zana and E. Yeager, Polym.Lett., 4, 947 (1966)
27. R. Zana and E. Yeager, J.Phys.Chem., 71, 3502 (1967)
28. S. Oka, Proc.Phys.Math.Soc. Jpn, 13, 413 (1933)
29. B. Conway, submitted for publication
30. H.S. Harned and B.B. Owen, "The Physical Chemistry of Electrolyte Solutions", 3rd Edition, Rheinhold Publ.Corp., New York, 1958, pp.39-41, 278-282
31. G. Lewis, M. Randall, K. Pitzer and L. Brewer, "Thermodynamics", 2nd edition, Mc Graw Hill Book Co., New York, 1961, pp. 464-469
32. M.I. Temkin and A.V. Khoroshin, Zhur.Fiz.Khim., 26, 500 (1952)
33. J.C. Goodrich, F.M. Goyan, E.E. Morse, R.G. Preston and M.B. Young, J.Amer.Chem.Soc., 72, 4411 (1950)
34. R. Parsons, "Handbook of Electrochemical Constants", Butterworths and Co.Ltd., London, 1959, pp. 60, 85
35. "Handbook of Chemistry and Physics", R.C. Weast, Ed., 52nd Edition, The Chemical Rubber Co., Cleveland, Ohio 1972
36. E. Herrey, J. Acoust .Soc.Amer., 27, 89 (1955)
37. E. Yeager, H. Dietrick and F. Hovorka, J.Acoust.Soc.Am., 25, 456 (1953)
38. A.N. Hunter, Proc.Phys.Soc., 71, 847 (1958)
39. A.J. Rutgers and W. Rigole, Trans.Faraday Soc.,54, 139 (1958)
40. A. Weinmann, Proc.Phys.Soc., 73, 345 (1959) and 75, 102 (1960)
41. A.N. Hunter and T. Jones, Proc.Phys.Soc., 79, 795 (1961)
42. R. Miller, Zeit.Elektrochem., 65, 639 (1961)
43. E. Yeager, J.Booker and F. Hovorka, Proc.Phys.Soc., 73,690 (1959)
44. R. Millner, private communication (1966) ; R. Millner and H.D. Muller, Ann.Physik., 17, 160 (1966)
45. J. Komiyama and R. Fuoss, Proc.Nat.Acad.Sci. US, 69, 829 (1972) ; P. Turq, B. Brun and M. Chemla, J.Chim.Phys. Physicochim.Biol., 70, 661 (1973)
46. F. Millero, Chem.Revs., 71, 147 (1971) ; see also, "Water and Aqueous Solutions", R.A. Horne Ed., Wiley-Interscience, New York, 1972.
47. M.H. Panckhurst, Rev.Pure Appl.Chem., 19, 45 (1969) ; J. Phys.Chem., 75, 3035 (1971)
48. E. Yeager and R. Zana, J.Phys.Chem., 76, 1086 (1972)
49. J. Bernal and R. Fowler, J.Chem.Phys., 1, 515 (1933)
50. K. Fajans and D. Johnson, J.Am.Chem.Soc., 64, 668 (1942)

51. R. Stokes and R. Robinson, Trans.Faraday Soc., 53, 301 (1957)
52. P. Mukerjee, J.Phys.Chem., 65, 740 (1961) ; 65, 744 (1961)
53. L.G. Hepler, J.Phys.Chem., 61, 1426 (1957)
54. B. Conway, R. Verrall and J. Desnoyers, Trans.Faraday Soc., 62, 2738 (1966) ; Z.Phys.Chem., 230, 157 (1965)
55. F. Millero, J.Phys.Chem., 75, 280 (1971)
56. C. Jolicoeur and J.C. Mercier, J.Phys.Chem., 81, 1119 (1977)
57. B. Conway, J.Desnoyers and R. Verrall, J.Phys.Chem., 75, 3031 (1971)
58. E. Glueckauf, Trans.Faraday Soc., 61, 1 (1965) and 64, 2423 (1968)
59. F. Hirata and K. Arakawa, Bull.Chem.Soc. Jpn, 46, 3367(1973)
60. J. Padova, J.Chem.Phys., 39, 1552 (1963)
61. J. Desnoyers, R. Verrall and B. Conway, J.Chem.Phys., 43, 243 (1965)
62. S. Benson and C. Copeland, J.Phys.Chem., 67, 1194 (1963)
63. P. Drude and W. Nernst, Z.Phys.Chem., 15, 79 (1894)
64. F. Millero, J.Phys.Chem., 72, 3209 (1968)
65. J. O'M Bockris and P. Saludja, J.Phys.Chem.,76,2140(1972) and 79,1230, (1975)
66. E. Yeager and R. Zana, J.Phys.Chem., 75, 1228 (1975)
67. R. Zana and E. Yeager, "L'eau et les systèmes biologiques" Editions du CNRS, 1976, p. 155
68. J. Enderby, Proc.Phys.Soc., 207 A, 329 (1951)
69. F. Booth and J. Enderby, Proc.Phys.Soc., 208 A, 321 (1952)
70. A. Rutgers and J. Vidts, Nature, 165, 109 (1950)
71. A. Rutgers and G. Jacobs, Acad.Weten.Let.Sch. Kunst, Belgie, 210 (1951)
72. E. Yeager, J. Bugosh, F. Hovorka, and J. Mc Carthy, J.Chem. Phys., 17, 416 (1949)
73. J. Causse, C.R.Acad.Sci. (Paris), 230, 806 (1950)
74. J. Dereska, E. Yeager and F. Howorka, Tech.Rep.23, Ultrasonics Res.Lab., Western Reserve Univ., Cleveland, 1960
75. U. Beck, R. Zana and E. Rohloff, Wochenblatt fur Papierfabriken, 106, S 181 (1978) ; TAPPI, 61, 63 (1978)
76. P. Debye, J.Chem.Phys., 14, 636 (1946)
77. C. Tondre and R. Zana, J.Phys.Chem., 76, 3451 (1972)
78. M. Milas and R. Zana, unpublished results

Table I. Estimated errors in $(t_+/z_+)\bar{V}^\circ_+ - (t_-/z_-)\bar{V}^\circ_-$ for alkali metal bromides in water at 25°C, caused by assuming isothermal propagation of sound[a].

Electrolyte	LiBr	NaBr	KBr
t_+	0.331	0.392	0.485
$\bar{S}_2$ [b,c]	22.7	33.7	43.8
$\bar{S}_+$ [b,d]	0.9	11.9	22.0
$\bar{S}_-$ [b,d]	21.8	21.8	21.8
$\bar{S}^*_+$ [b,d]	-10.15	-6.04	-5.2
$\bar{S}^*_-$ [b,d]	0.52	0.52	0.52
$(\bar{S}_t)_+$ [b,d]	-9.3	5.9	16.8
$(\bar{S}_t)_-$ [b,d]	22.3	22.3	22.3
$\Sigma t_i(\bar{S}_t)_i/z_i$ [b]	-17.8	-11.3	-3.4
error in $t_i\bar{V}^\circ_i/z_i$ [e]	-1.1	-0.7	-0.2
error in $\bar{V}^\circ(Br^-)$ [e]	+1.1	+0.7	+0.2

(a) The calculations assume $\alpha_E = 2\times10^{-4}$/deg ; (b) in entropy unit ; (c) from refs. 34 and 35 ; (d) from ref. 33 ; (e) in cm^3/mole.

Table II Values of Φ/a (in $\mu V\ s\ cm^{-1}$) for aqueous solutions of typical electrolytes at 22°C and 220 kHz

	Concentration (mole/liter)						
Salt	10^{-3}	3.10^{-3}	10^{-2}	3.10^{-2}	10^{-1}	3.10^{-1}	1
HCl (a)	0.2	0.3	0.5	0.6	0.6	0.5	-
LiCl (a)	0.3	0.1	0.05	0.1	0.05	0.05	0.05
NaCl (a)	1.15	1.0	0.8	0.7	0.6	0.6	0.5
KCl	1.9	1.8	1.7	1.7	1.7	1.7	-
RbCl (a)	5.2	5.2	5.2	5.2	5.2	5.2	-
CsCl (a)	8.1	8.1	8.1	8.1	8.1	8.1	-
$MgCl_2$ (a)	1.1	1.1	1.1	1.1	1.1	1.1	1.0
$CaCl_2$ (a)	1.2	1.2	1.2	1.2	1.2	1.1	1.0
$SrCl_2$ (a)	2.5	2.4	2.4	2.4	2.3	2.1	-
$BaCl_2$ (a)	4.0	4.1	4.1	4.0	4.0	3.9	3.5
Li_2SO_4 (a)	2.4	2.4	2.4	2.4	2.4	-	-
Na_2SO_4 (a)	1.7	1.7	1.7	1.7	1.7	-	-
K_2SO_4 (a)	0.3	0.3	0.3	0.3	0.2	-	-
$ZnSO_4$ (a)	0.5	0.4	0.3	0.3	0.3	-	-
$KHCO_2$ (b)	2.1	2.1	2.0	2.0	1.9	1.8	-
KCH_3CO_2 (b)	2.7	2.7	2.7	2.7	2.7	2.7	-
KCH_2ClCO_2 (b)	1.6	1.5	1.5	1.5	1.5	1.5	-
$KCHCl_2CO_2$ (b)	-	0.7	0.6	0.6	0.6	0.6	-
$KCCl_3CO_2$ (b)	-	0	0	0	0	0	-
$KC_2H_5CO_2$ (b)	2.8	2.8	2.8	2.8	2.8	2.8	-
$KC_3H_7CO_2$ (b)	3.1	3.1	3.1	3.1	3.1	3.1	-
$KC_5H_{11}CO_2$ (b)	3.4	3.4	3.4	3.4	3.4	3.3	-
$(CH_3)_4NBr$ (c)	-5.2	-4.8	-4.8	-4.4	-4.0	-	-
$(C_2H_5)_4NBr$ (c)	-6.5	-5.9	-5.6	-5.1	-4.8	-	-

(a) from ref. 6 ; (b) from ref. 9 ; (c) from ref. (8)

Table III Partial molal volumes of monovalent ions calculated from the values of the vibration potentials Φ/a, partial molal volume of salts $\overline{V}_2^\circ$ and cation transport number t_+ in these salts, from reference 6 (a)

Electrolyte	Φ/a	$\overline{V}_2^\circ$	t_+	$\overline{V}_+^\circ$	$\overline{V}_-^\circ$
	(μV s cm^{-1})	cm^3/mole		cm^3/mole	cm^3/mole
NaF	0.8	-3.5	0.476	-6.1	2.6
KF	2.0	6.6	0.570	4.0	2.6
RbF	5.8	12.8	0.585	9.7	3.1
CsF	9.4	20.1	0.580	15.1	5.0
HCl	0.4	17.8	0.820	-5.6	23.4
LiCl (b)	0	17.0	0.336	-9.5	26.5
NaCl	0.6	16.4	0.396	-6.4	22.8
NH_4Cl	-0.1	36.0	0.490	9.6	26.4
KCl	1.7	26.5	0.490	3.7	22.8
RbCl	5.2	31.9	0.511	8.4	23.5
CsCl	8.1	39.2	0.500	15.7	23.5
NaBr	-3.1	23.5	0.392	-6.5	30.0
KBr	-1.3	33.7	0.485	3.4	30.3
LiI (b)	-7.2	35.5	0.344	-12.0	47.5
NaI	-6.4	35.1	0.395	-5.4	40.5
KI	-4.0	45.4	0.488	3.1	42.3
LiOH (b)	-0.5	-4.0	0.164	-12.6	8.6
NaOH	-0.4	-4.6	0.202	-9.5	4.9
KOH	-0.2	5.4	0.271	3.6	1.8
$LiIO_3$ (b)	-9.7	24.8	0.487	-11.6	36.0
$NaIO_3$	-6.8	24.2	0.554	-10.4	34.6
KIO_3	-4.4	34.3	0.644	3.1	31.2
HNO_3	0	29.8	0.830	-5.2	35.0
KNO_3	0.7	38.3	0.507	3.6	34.6

(a) The values of Φ/a have been obtained at 22°C while those of $\overline{V}_2^\circ$ and t_+ are at 25°

(b) The values of $\overline{V}^\circ$(anion) found with Li^+ salts are all larger by 3 to 4 cm^3/mole than with the other alkali metal ion salts. Such a result indicates a particuliar behavior of Li^+ salts in aqueous solution, as far as IVP's are concerned, and for which no definite explanation has been found (6).

Table IV Values of $\overline{V}^{\circ}(H^{+})$ in cm^3/mole obtained by means of various methods[a]

Method	$\overline{V}^{\circ}(H^{+})$
Bernal and Fowler[49]	-3.8
Fajans and Johnson[50]	-0.2
Stokes and Robinson[51]	-7.6
Mukerjee[52]	-4.5
Conway, Verrall and Desnoyers[54]	-5.7
Millero[55]	-5.0
Jolicoeur and Mercier[56]	-4.8
Zana and Yeager[6] (IVP)	-5.4

(a) A more extensive compilation is given in reference 46.

Table V Values of ϕ/a in $\mu V\ s\ cm^{-1}$ for alkali metal iodides in Methanol (I)[12], Ethanol (II)[13], DMF (III)[13], DMSO (IV)[14], Acetonitrile (V)[15] and Ethylene Glycol (VI)[16] at 22° (a)

Solvent	C(M)	Salt LiI	NaI	KI	RbI	CsI
I		-	-2.2	-1.6	-	0.7
II		-	-2.8	-1.9	-0.6	0.4
III	3.10^{-4}	-	-2.6	-2.5	-1.0	-0.2
IV		-4.6	-4.6	-4.1	-1.7	0.4
V		-	-	-	-	-
VI		-	-	-	-	-
I		-	-2.3	-2.0	-	0.7
II		-	-3.0	-2.1	-0.7	0.4
III	10^{-3}	-	-2.5	-2.5	-1.0	-0.2
IV		-6.2	-5.6	-5.1	-2.0	0.4
V		-6.6	-5.9	-5.1	-2.1	0.5
VI		-	-	-	-	-
I		-	-2.4	-2.1	-	0.6
II		-	-3.2	-2.1	-0.9	0.3
III	3.10^{-3}	-	-2.8	-2.8	-1.3	-0.4
IV		-6.2	-5.6	-5.0	-2.3	0
V		-6.9	-5.9	-5.1	-2.2	0.6
VI		-7.8	-6.1	-3.7	0	3.0
I		-	-2.8	-2.3	-	0.3
II		-	-3.3	-2.3	-1.1	-
III	10^{-2}	-	-3.0	-3.0	-1.6	-0.6
IV		-6.3	-5.6	-5.2	-2.4	0
V		-7.0	-5.9	-5.1	-2.3	0.5
VI		-8.3	-6.1	-3.7	0	3.0
I		-	-3.1	-2.7	-	0.2
II		-	-3.5	-2.7	-	-
III	3.10^{-2}	-	-3.2	-3.1	-	-0.8
IV		-6.3	-5.6	-5.2	-2.5	0
V		-7.4	-6.3	-5.3	-	-
VI		-8.3	-6.1	-3.7	0	3.0

(a) The values of Φ/a have been calculated from the $\Phi_{\lambda/2}$ values listed in various Tables of references 12 to 16 and the values of the velocity amplitude a determined by the procedure given in reference 12 and Section IV 2.

Table VI. Values of the partial molal volumes of monovalent ions obtained from IVP and $\overline{V}_2^\circ$ data, in cm^3/mole [a]

Ion \ Solvent	Water (Ref.6)	Methanol (ref.12)	Ethanol (ref.13)	DMF (ref.13)	DMSO (ref. 14)	Acetonitrile (ref.15)	Ethylene glycol (ref.16)
H^+	-5.9	-17.0	-15.5	-	-	-	-
Li^+	-6.8	-17.9	-19.2	-26.4	-20.2	-22.6	-9.9
Na^+	-7.1	-17.1	- 9.8[b]	-16.3	-9.9	-20.7	-5.0
K^+	3.1	-7.3	-0.4	-9.0	-1.1	-10.3	4.0
Rb^+	8.2	-1.7	5.5	-5.0	4.7	-6.9	9.3
Cs^+	15.9	4.8	13.3	1.5	9.6	-0.1	15.5
NH_4^+	12.0	4.1	8.9	-3.1	-	-	-
F^-	4.7	-1.3	-	-	-	-	-
Cl^-	23.7[b]	13[b]	12.5[b]	22.0	25.3	6.1	26.1
Br^-	30.6	18.3	15.1	22.9	29.7[b]	10.7	31.9[b]
I^-	42.1	28.2	26.7[b]	39.0	43.4	26.1[b]	42.1
NO_3^-	34.9	27.5[b]	23.8[b]	33.3	38.5	-	-

(a) The accuracy on the $\overline{V}^\circ$(ion) values is probably of $\pm$1cm^3/mole in water ; $\pm$ 3 cm^3/mole in DMF and $\pm$ 2 cm^3/mole for all other solvents

(b) Values of $\overline{V}^\circ$(ion) obtained from the IVP-$\overline{V}_2^\circ$ data used to recalculate all other $\overline{V}^\circ$(ion) using the $\overline{V}_2^\circ$ data reported in references 6-12 and the additivity law

THIS PAGE IS BEST QUALITY PRACTICABLE
FROM COPY FURNISHED TO DDC

Table VII. Comparison of the values of $\overline{V}^{\circ}(Cl^-)$ in cm^3/mole from IVP's and by three different non-experimental methods

Solvent	IVP	Method		
		Mukerjee[51]	Conway Desnoyers Verrall [54]	Millero[55]
Water[6]	23.7±2	22.3	23.6	22.8
Methanol[12]	13± 2	11	0.7	14.6
Ethanol[13]	12.5±2	15	-	-
DMF[13]	22±3	15	-21	7.6
DMSO[14]	25.3±2	21.5	8	10.4
Acetonitrile[15]	6.1±2	7	-16	3.3
Ethylene-Glycol[16]	26.1±2	23.2	-	-

Table VIII. Values of A (cm^3 $Å^{-3}$ $mole^{-1}$) and B (cm^3 Å $mole^{-1}$) at 25°, obtained from the partial molal volumes of alkali metal and halide ions in various solvents

	Halide Ions		Alkali Metal Ions		
	A	B	A	B	B_{calc}[a]
Water	4.7	10±2	4.7	10±2	4.2
Methanol	3.5	17±2	3.5	17±2	24.2
Ethanol	3.3	12±2	3.3	12±2	32.6
Ethylene glycol	4.1	-3±2	4.1	7±2	7
DMF	3.8	2±5	2.5	18±4	11.7
DMSO	4.2	0±5	3.6	12±3	7.6
Acetonitrile[b]	3.2	24±5	3.2	24±5	22

(a) Values calculated from equation (44) with the literature values of $d \ln D/dp$ or by assuming this quantity equal to κ_T

(b) The values of A and B have been obtained by drawing a straight line through the representative points for all ions but Li^+ and I^-[16].

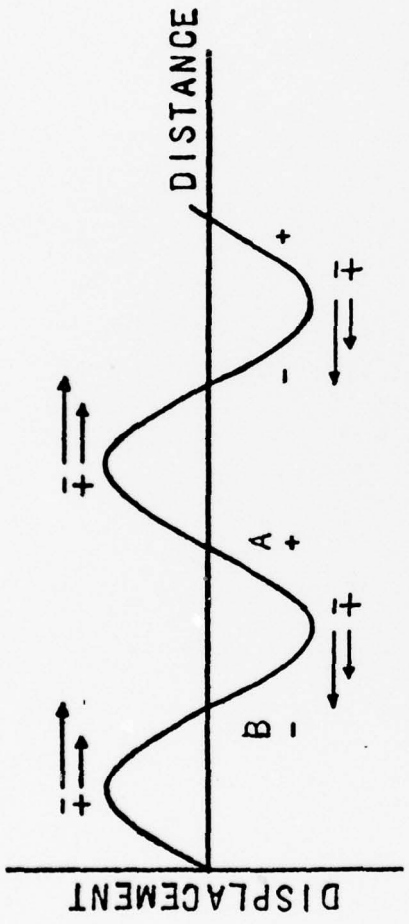


Figure 1 : Mechanism for ionic vibration potentials. Reprinted from ref.6 with permission of the Journal of Physical Chemistry. Copyrights by the American Chemical Society

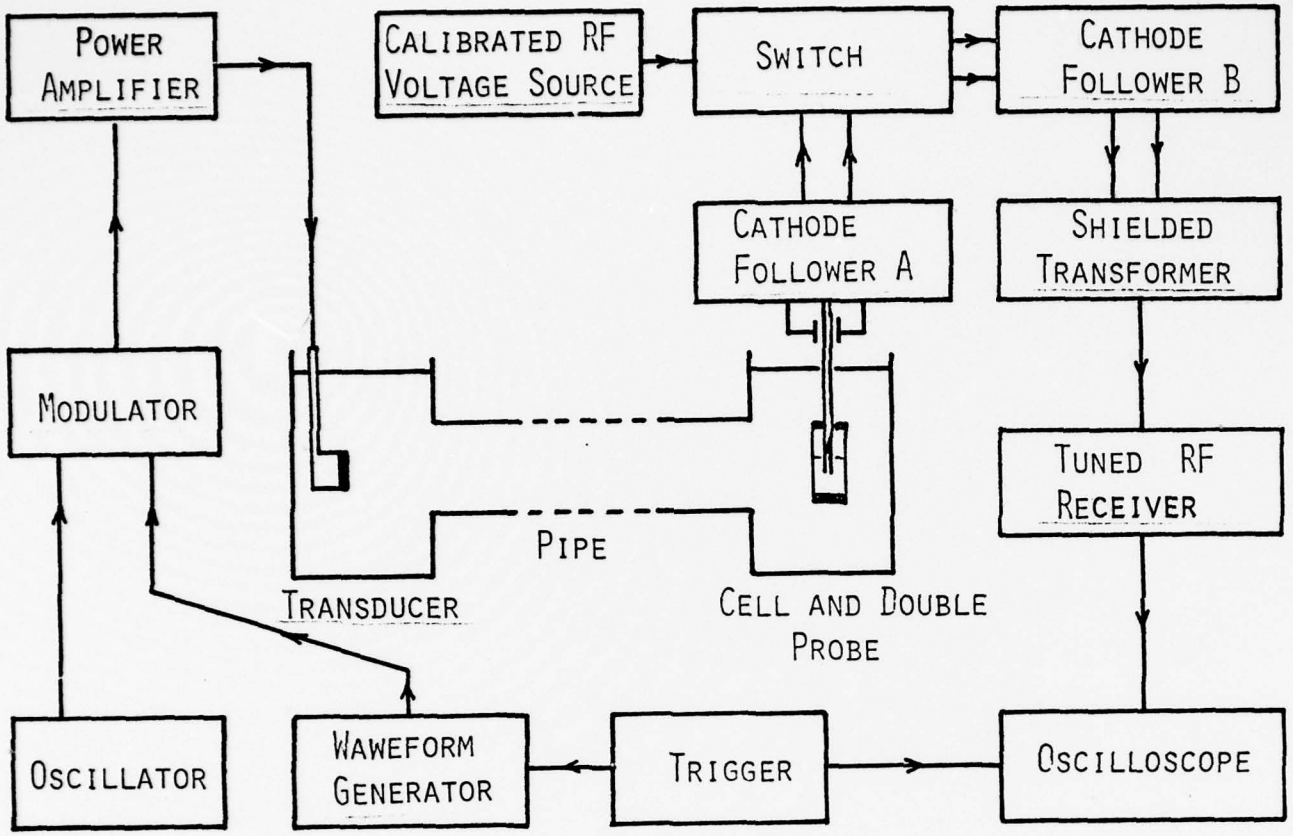


Figure 2 : Block diagram of the apparatus

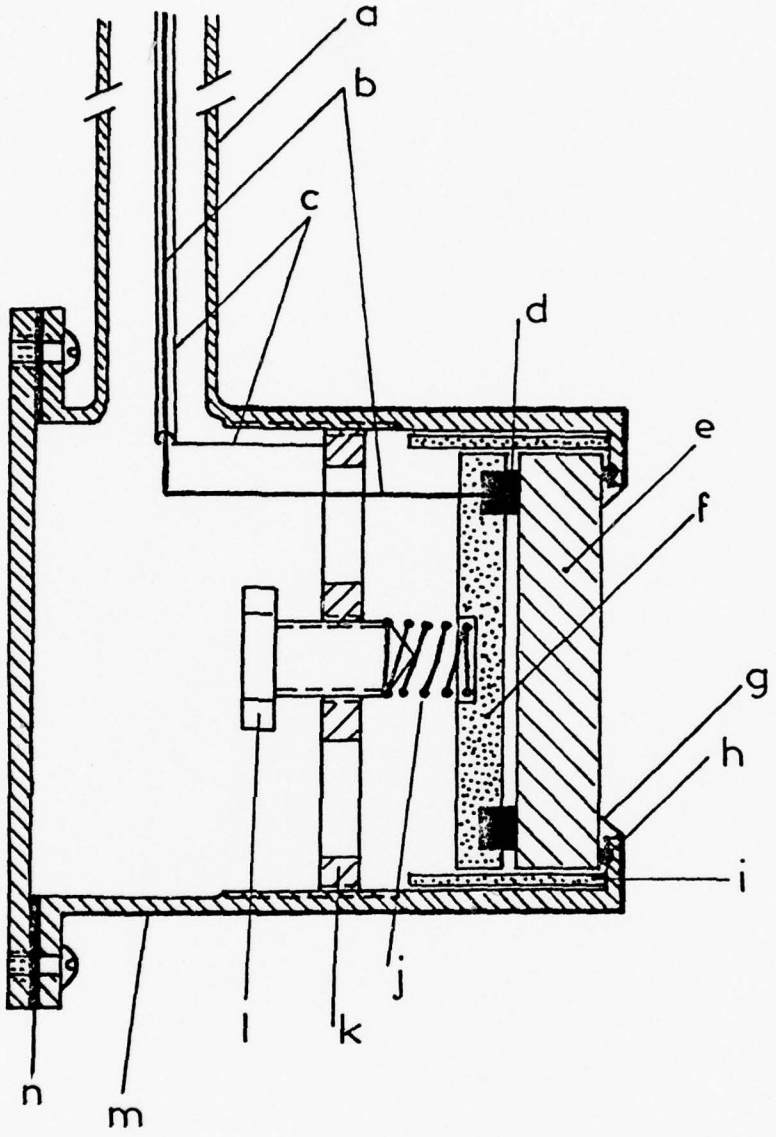


Figure 3 : Transducer housing

(a) Stainless steel tube, 20 mm OD ; (b) live connector from the power amplifier ; (c) ground connector ; (d) brass cylinder connecting the live connector to the backside of the silver plated transducer (e);(f) Plexiglass disk insulator (g) conducting water-resistant glue seal grounding the silver plated front side of the transducer and insuring together with the O-ring (h) the water tightness of the transducer housing ; (i) hollow plexiglass cylinder for insulation ; (j) strong spring (k) brass screw holder ; (l) screw holding the transducer in place through the spring ; (m) stainless steel transducer housing ; (m) flat rubber gasket.

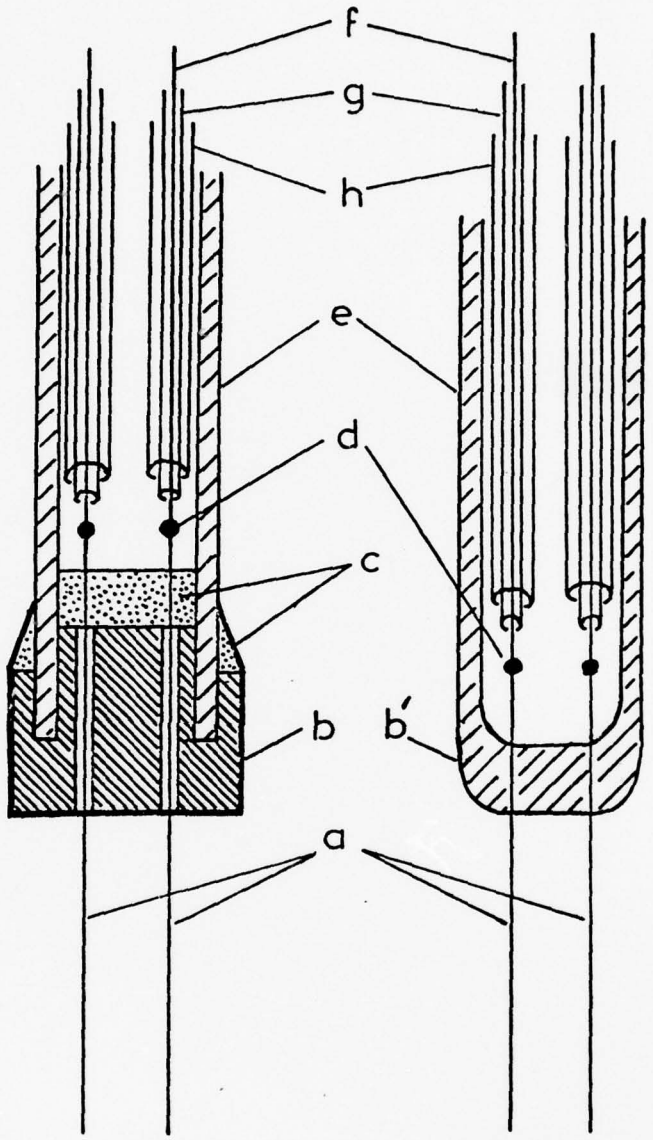


Figure 4 : Design of the tip of the double probe assembly. A. Teflon mounted probes (refs 11-16) ; B : Glass mounted probes (refs 6,8-10). (a) 0.2 mm diameter Pt-wires ; (b) teflon plug ; (b') glass seal ; (c) epoxy glue seals ; (d) soldering of Pt-wires to internal lead of double shielded cables ; (e) glass tubing (9mm OD and 7mm ID) ; (f) internal leads of double shielded cables ; (g) driven shield ; (h) outer shield.

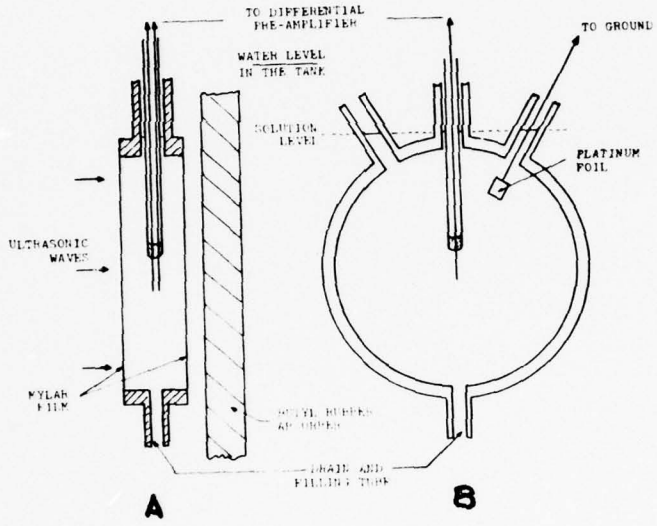
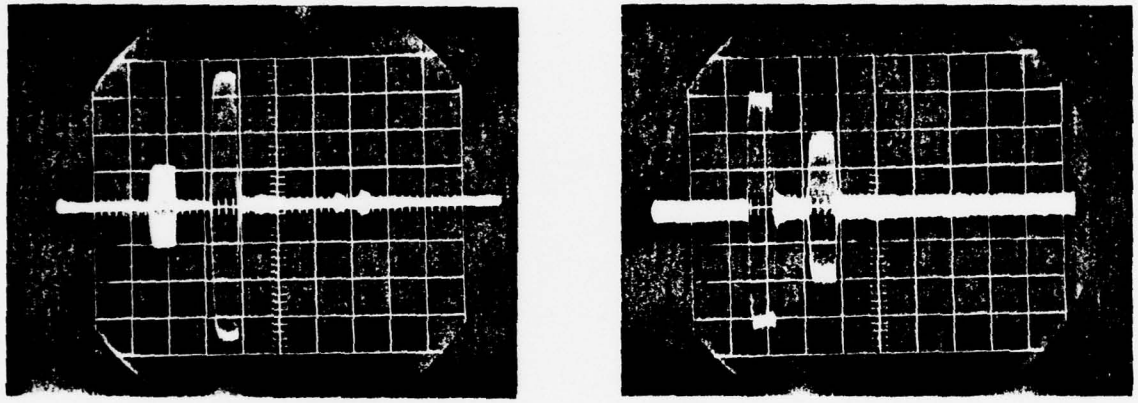


Figure 5 : Cell arrangement for the measurement of ionic vibration potentials. A, side view perpendicular to ultrasonic beam; B, front view parallel to ultrasonic beam. Reproduced from ref.6 with permission from the Journal of Physical Chemistry Copyright by the American Chemical Society.



CsCl NaCl

Figure 6 : Oscilloscope displays for 10^{-2} M aqueous solutions of CsCl and NaCl (Sweep rate : 2 ms per division ; sensitivity 0.1 and 0.02 V per division for CsCl and NaCl, respectively). In both displays the first pulse corresponds to the electromagnetically induced signal and the second one to the vibration potential ($\Phi_{\lambda/2}$ has the values 172 and 23 μV for CsCl and NaCl, respectively).

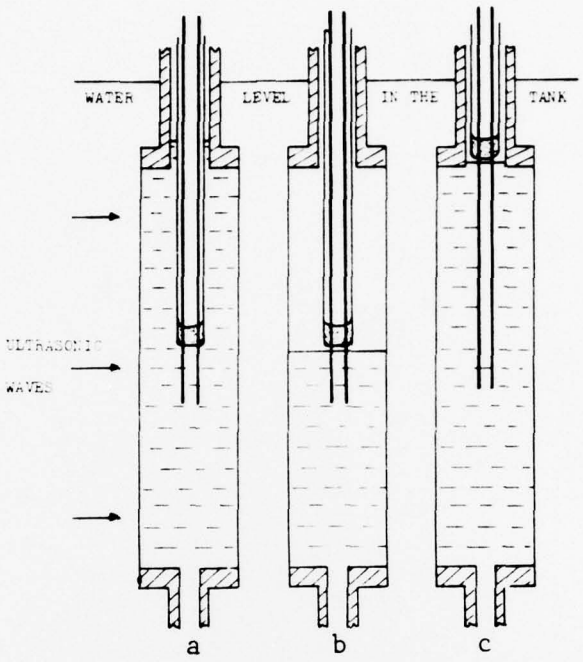


Figure 7 : Cell arrangements used in reference 6
(a) Standard arrangement leading to large probe mounting effects for dilute electrolyte solutions ; (b) arrangement with half-filled cell ; (c) arrangement with long-wire double probe assembly and completely filled cell.
Reproduced from ref.6, with permission from the Journal of Physical Chemistry Copy-rights by the Chemical Society.

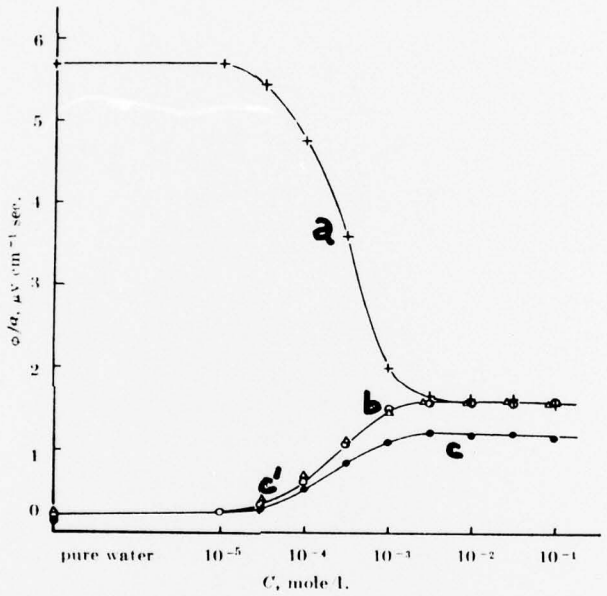


Figure 8 : Terminal responses in KCl solutions at 220 kc with cell arrangements shown in Figure 7 . Curves a,b, and c correspond to cell arrangements a,b, and c, respectively. Curve c' was obtained from curve c by multiplying the ordinates by the factor 1.35 and coincides with curve c. Reproduced from ref.6 with permission from the Journal of Physical Chemistry. Copyrights by the American Chemical Society

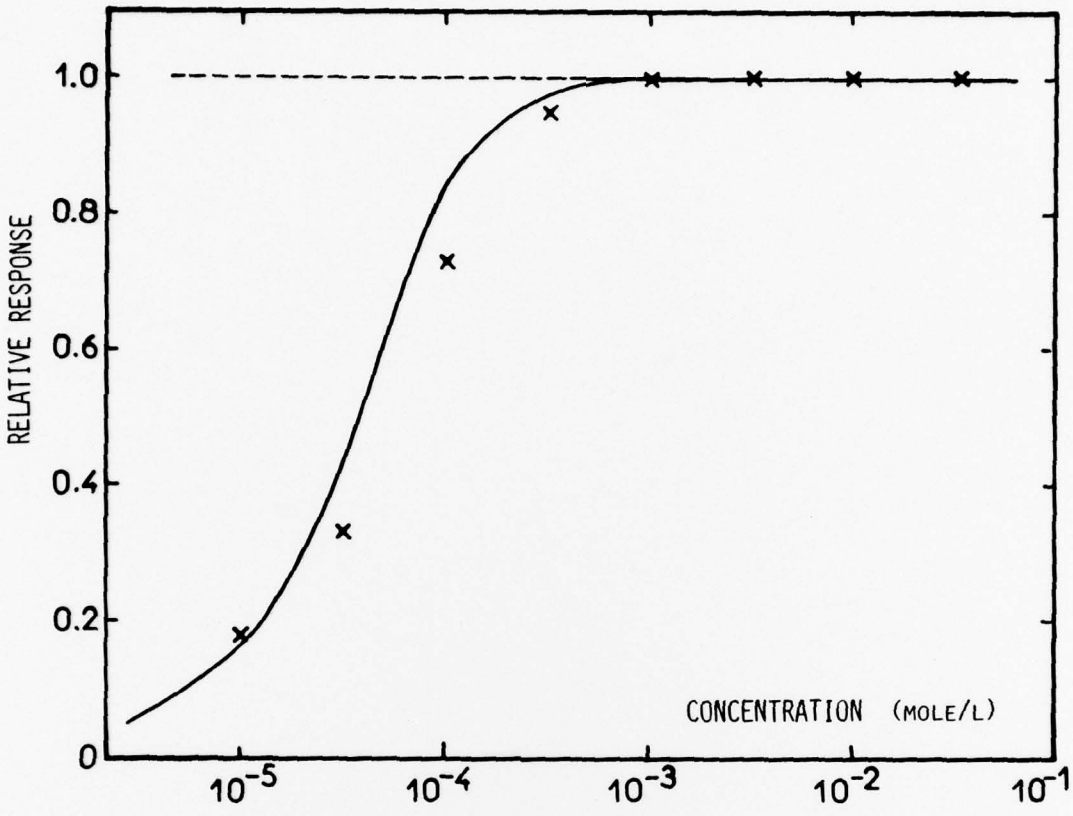


Figure 9 : Concentration dependence of the vibration potential of CsCl solutions at 220 kHz in water from reference 23. The solid line represents the concentration dependent term $R=(4\pi L_o/D\omega)\ \left[1+(4\pi L_o/D\omega)^2\right]^{-1/2}$ in the right hand side of equation (21). The crosses are the values of the ratio of the values of $\Phi_{\lambda/2}$ at concentration $\underline{C}_{CsCl}$ and at a concentration above 10^{-3} $\underline{M}$, where the potential becomes constant (R=1). Similar results have been obtained for RbF, CsF, etc. In most instances the experimental points fall below the calculated curves[23].

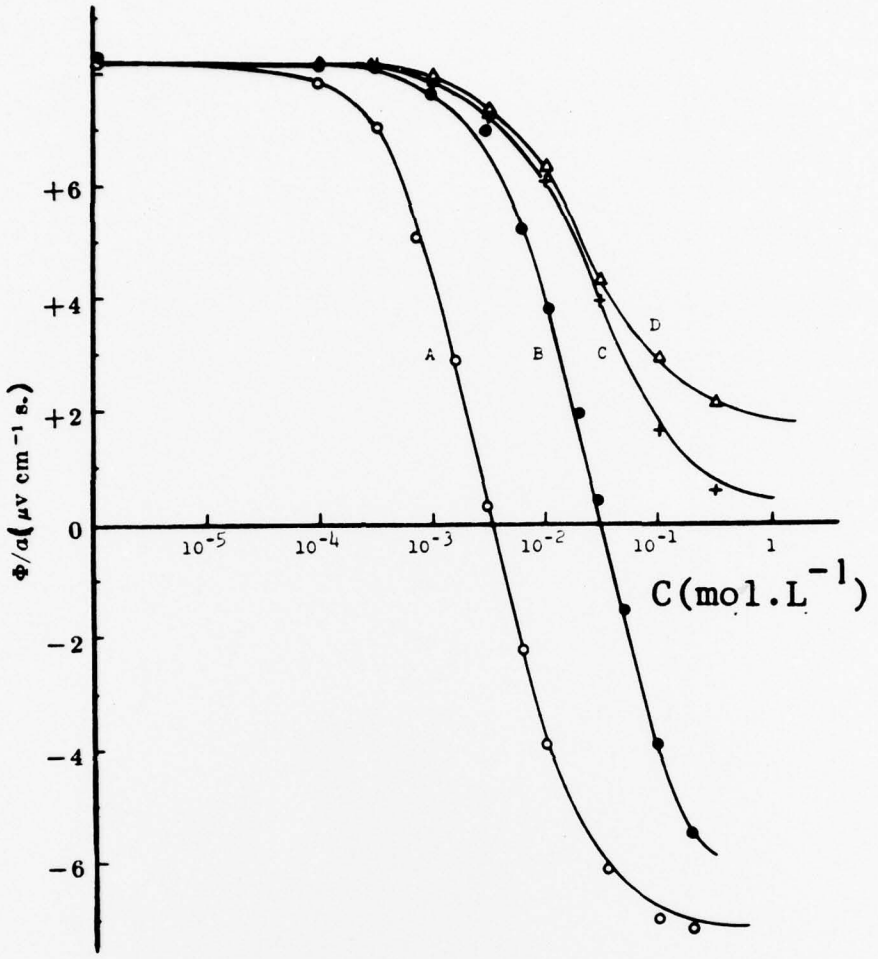


Figure 10 : Vibration potential of binary mixtures of 1-1 electrolytes at 220 kHz, from reference 6. The

obtained using equation (37), the values of $\Phi_{AB/a}$ and Φ_{CD}/a from Table II and the Λ°_{AB} and Λ°_{CD} reported in the literature. Curves A and B : additions of LiI to solutions 2.10^{-3} and 2.10^{-2} M CsCl. Curves C and D : additions of LiCl and KCl to a solution 2.10^{-2}M CsCl, respectively. Reproduced from ref.6 with the permission from the Journal of Physical Chemistry. Copyrights by the American Chemical Society.

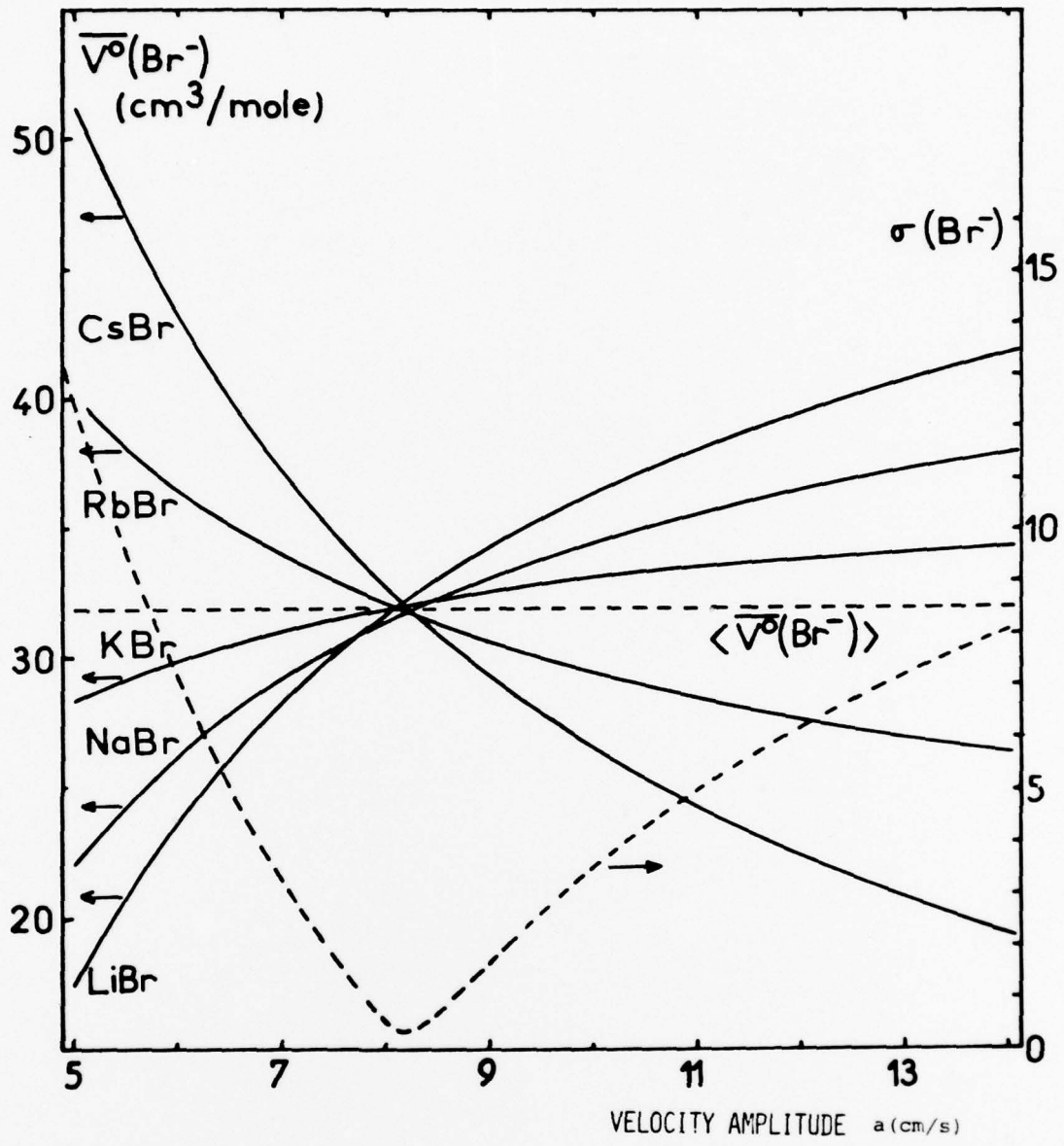


Figure 11 :Illustration of the method used for the determination of the partial molal volumes of ions and their standard deviations in organic solvents. The values of $\overline{V}^o(Br^-)$ calculated using equation (27) and the $\Phi_{\lambda/2}$ and $\overline{V}_2^o$ data for each alkali metal bromides are plotted as a function of the velocity amplitude a. The average value of $\overline{V}^o(Br^-)$ and $\sigma(Br^-)$ as defined by equations (39) and (40) are also plotted as a function of a (curves in dotted lines). The $\sigma(Br^-)$ curve shows a well defined minimum. Note that $\langle\overline{V}^o(Br^-)\rangle$ is almost independent of a, for the reason pointed out in the text.

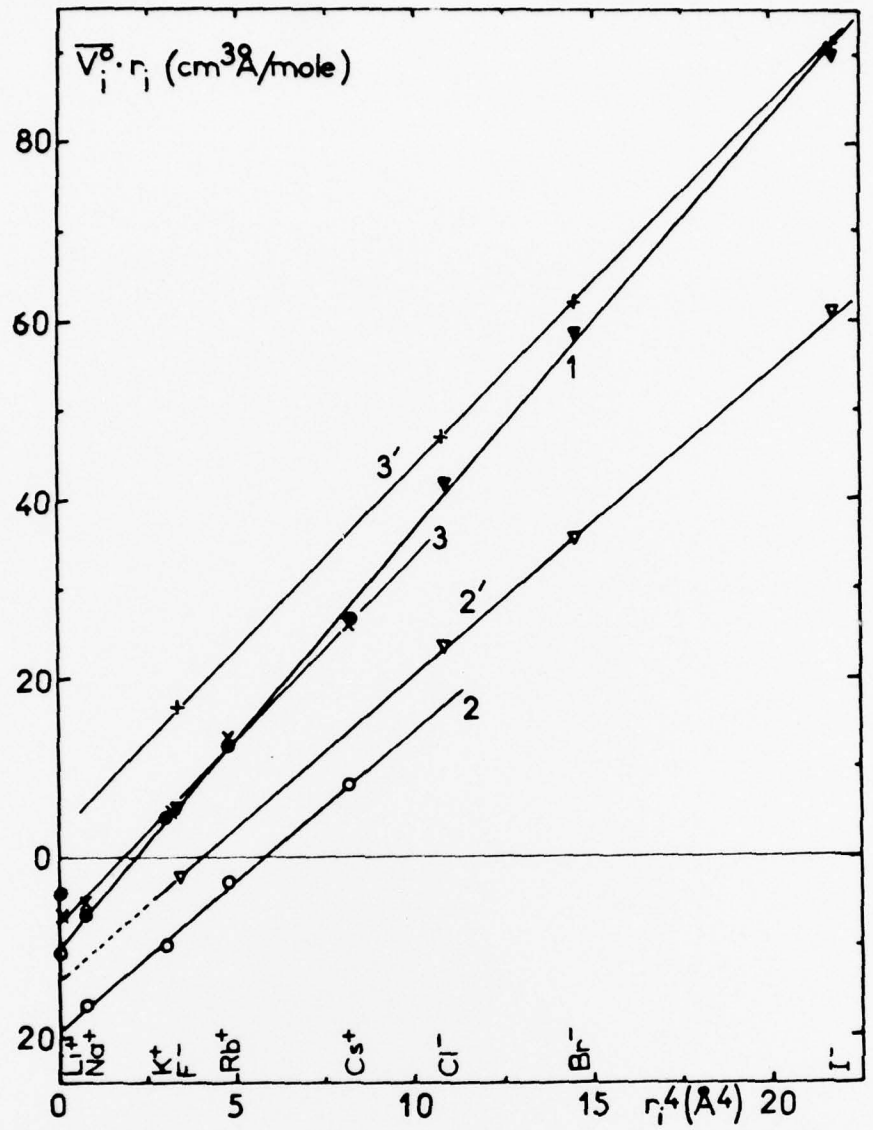


Figure 12 : Plots of $\overline{V}_i^o . r_i$ vs r_i^4 for alkali metal (●,o,x) and halide (▼,▽, +) ions in water (line 1), methanol (lines 2 and 2') and ethylene glycol (lines 3 and 3') prepared from the results reported in references 6,12 and 16. Note that in water and methanol the points for Li^+ fall well above lines 1 and 2 respectively, while in ethylene glycol the result relative to Li^+ fall on the same line as for other alkali metal ions. The distance between lines 2 and 2' for methanol is within the experimental uncertainty quoted for $\overline{V}^o$(ion) data in this solvent[12]. In reference 12 a single line was drawn through the data from which were obtained the values of A and B given in Table VIII.

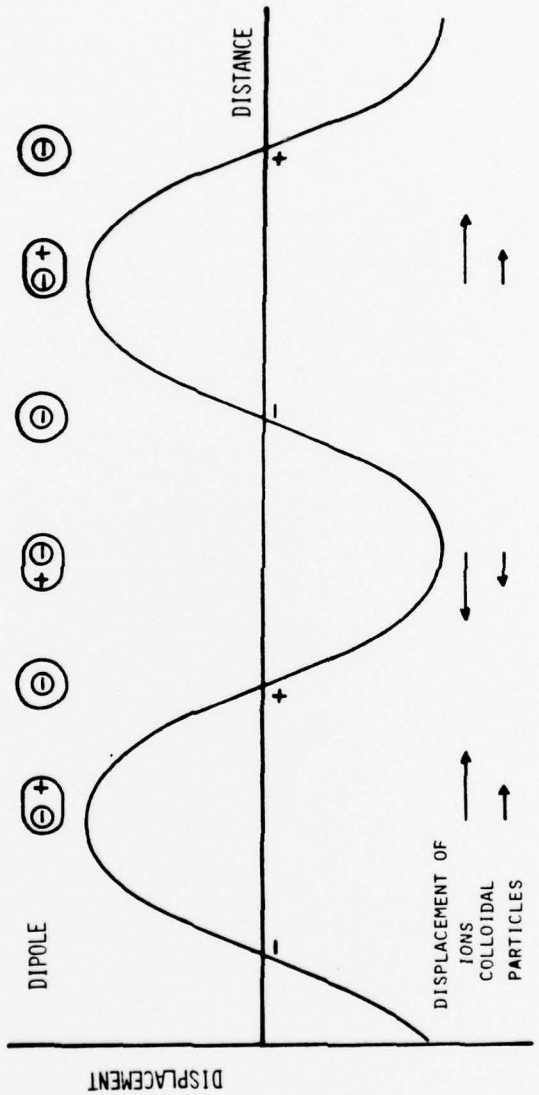


Figure 13 : Mechanism for colloidal vibration potentials : oscillating dipole model.

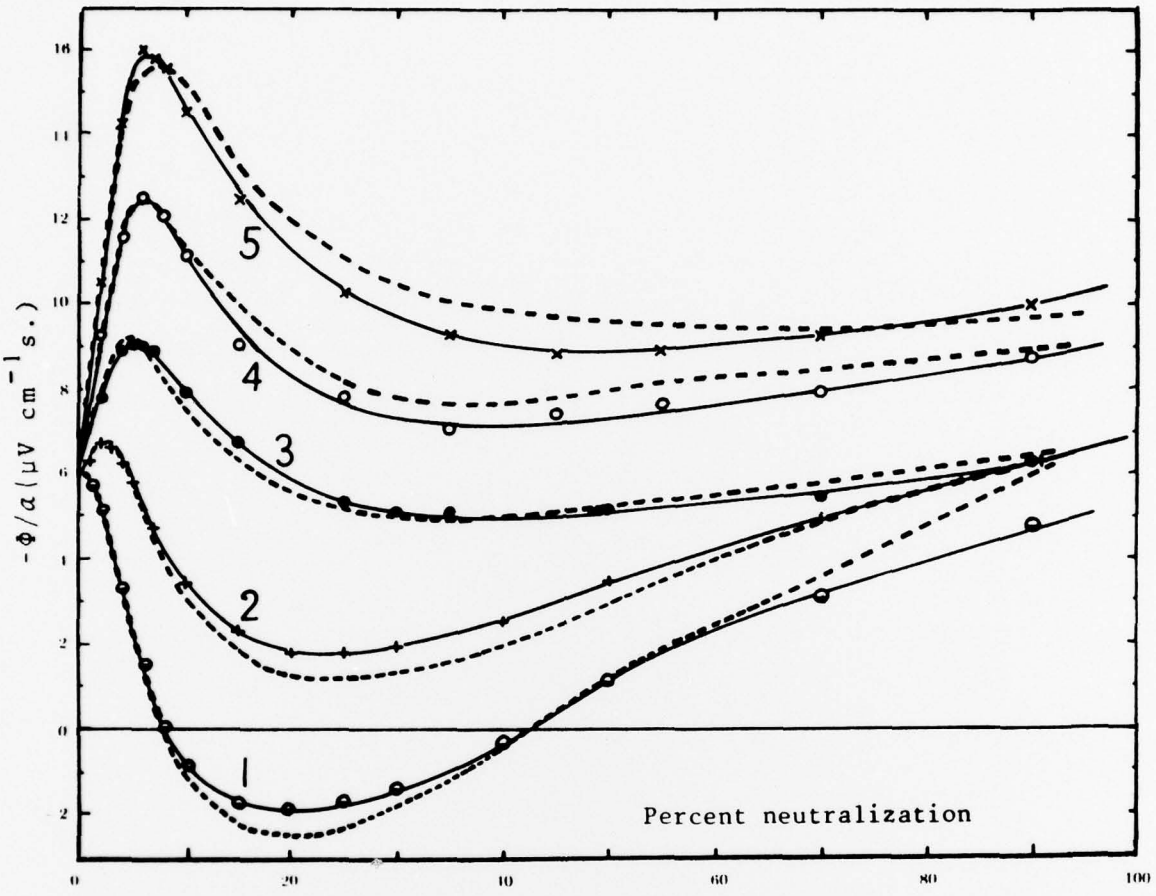


Figure 14 : Variation of the vibration potential of a 3×10^{-2} monomole/l solution of polyacrylic acid (M_η=130,000), upon neutralization by various alkali metal hydroxydes : (O)CsOH ; (+) RbOH ; (o) KOH ; (O) NaOH and (X) LiOH ; (———) Experimental curves and (-----) curves calculated according to equation (52). Reprinted from ref.27 with permission from the Journal of Physical Chemistry. Copyrights by the American Chemical Society.

TECHNICAL REPORT DISTRIBUTION LIST

CASE WESTERN RESERVE UNIVERSITY

Contract N00014-75-C-0557 — Project NR 384-305

Director Defense Advanced Research Projects Agency Attn: Technical Library 1400 Wilson Blvd. Arlington, Virginia 22209	3 copies
Office of Naval Research Physics Program Office (Code 421) 800 North Quincy Street Arlington, Virginia 22217	3 copies
Office of Naval Research Assistant Chief for Technology (Code 200) 800 North Quincy Street Arlington, Virginia 22217	1 copy
Naval Research Laboratory Department of the Navy Attn: Technical Library Washington, D.C. 20375	3 copies
Office of the Director of Defense Research and Engineering Information Office Library Branch The Pentagon Washington, D.C. 20301	3 copies
U. S. Army Research Office Box 12211 Research Triangle Park North Carolina 27709	2 copies
Defense Documentation Center Cameron Station (TC) Alexandria, Virginia 22314	12 copies
Director, National Bureau of Standards Attn: Technical Library Washington, D.C. 20234	1 copy
Commanding Officer Office of Naval Research Branch Office 536 South Clark Street Chicago, Illinois 60605	3 copies
Commanding Officer Office of Naval Research Branch Office 1030 East Green Street Pasadena, California 91101	3 copies

San Francisco Area Office — 3 copies
Office of Naval Research
One Hallidie Plaza
Suite 601
San Francisco, California 94102

Commanding Officer — 3 copies
Office of Naval Research Branch Office
666 Summer Street
Boston, Massachusetts 02210

New York Area Office — 1 copy
Office of Naval Research
715 Broadway, 5th Floor
New York, New York 10003

Director — 1 copy
U. S. Army Engineering Research
and Development Laboratories
Attn: Technical Documents Center
Fort Belvoir, Virginia 22060

ODDR&E Advisory Group on Electron Devices — 3 copies
201 Varick Street
New York, New York 10014

Air Force Office of Scientific Research — 1 copy
Department of the Air Force
Bolling AFB, D.C. 22209

Air Force Weapons Laboratory — 1 copy
Technical Library
Kirtland Air Force Base
Albuquerque, New Mexico 87117

Air Force Avionics Laboratory — 1 copy
Air Force Systems Command
Technical Library
Wright-Patterson Air Force Base
Dayton, Ohio 45433

Lawrence Livermore Laboratory — 1 copy
Attn: Dr. W. F. Krupke
University of California
P. O. Box 808
Livermore, California 94550

Harry Diamond Laboratories — 1 copy
Technical Library
2800 Powder Mill Road
Adelphi, Maryland 20783

Naval Air Development Center — 1 copy
Attn: Technical Library
Johnsville
Warminster, Pennsylvania 18974

Naval Weapons Center — 1 copy
Technical Library (Code 753)
China Lake, California 93555

Naval Training Equipment Center — 1 copy
Technical Library
Orlando, Florida 32813

Naval Underwater Systems Center — 1 copy
Technical Library
New London, Connecticut 06320

Commandant of the Marine Corps — 1 copy
Scientific Advisor (Code RD-1)
Washington, D. C. 20380

Naval Ordnance Station — 1 copy
Technical Library
Indian Head, Maryland 20640

Naval Postgraduate School — 1 copy
Technical Library (Code 0212)
Monterey, California 93940

Naval Missile Center — 1 copy
Technical Library (Code 5632.2)
Point Mugu, California 93010

Naval Ordnance Station — 1 copy
Technical Library
Louisville, Kentucky 40214

Commanding Officer — 1 copy
Naval Ocean Research & Development Activity
Technical Library
NSTL Station, Mississippi 39529

Naval Explosive Ordnance Disposal Facility — 1 copy
Technical Library
Indian Head, Maryland 20640

Naval Ocean Systems Center — 1 copy
Technical Library
San Diego, California 92152

Naval Surface Weapons Center — 1 copy
Technical Library
Dahlgren, Virginia 22448

Naval Surface Weapons Center (White Oak) — 1 copy
Technical Library
Silver Spring, Maryland 20910

Naval Ship Research and Development Center — 1 copy
Central Library (Code L42 and L43)
Bethesda, Maryland 20084

Naval Avionics Facility — 1 copy
Technical Library
Indianapolis, Indiana 46218