

Figure 5 Reflectivity from Co-implanted Si(111) samples with various Co doses (ions/cm²) and from a virgin Si(111) sample is shown. The surface roughness values (σ) are listed. The ordinates of the successive curves have been shifted by a decade for clarity.

Co⁺ implantation was done at a tilt angle of 70°. The samples were not annealed. The reflectivity results are shown in Figure 5. A comparison with the virgin Si(111) sample shows that the surface roughness is significantly enhanced. However, the roughness is not strongly dose-dependent within the range of doses (2×10^{15} – 2.15×10^{16} Co/cm²) studied. The oscillations on the reflectivity curves arise from the interference due to scattering from a carbon layer deposited on the surface during implantation. The thickness of this layer is determined from the periodicity of these oscillations. Independently, we have determined the thickness of this carbon film and the depth distribution of Co atoms by Rutherford backscattering spectrometry¹³. Detailed analysis of the Co-implanted system will be published elsewhere.

X-ray reflectivity from a multilayer system has been worked out by Parrat⁵. For the multilayer system each interface can be represented by a Gaussian of the form given in eq. (6), with σ_i representing the rms roughness of the $(i-1)$ th interface. (The first layer being vacuum, σ_2 represents the roughness of the surface of the second layer or the first interface.)

We believe that now with the availability of this powerful technique in India, further activities will be stimulated in the fast-developing area of surface and interface physics.

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Single-ion activities by a solid ion transmitter bridge and a reference electrode without liquid junction

S. Parthasarathy and K. Ramya

Centre for Electrochemical and Energy Research, SPIC Science Foundation, 110, Mount Road, Madras 600 032, India

It had been shown that it is possible to measure thermodynamic values of single-ion activity using a solid ion conductor to bridge a reference electrode and a test electrode, thus eliminating liquid junction potentials. This led to redefinition of activity of an ion and brought out into sharp focus the crucial role of the charge factor in determining the effective strength of an ion. In this paper, we have measured potentials, free from liquid junction, using chloride ion sensors and the solid-ion transmitter bridge for determining chloride ion activity in zinc chloride solutions, leading to confirmation of definition of activity of an ion already proposed.

THE central paradigm of the theory of ionic solutions of strong electrolytes can be stated as follows:

1. It is impossible to measure the activity of single ion in solutions of strong electrolytes, as any reference

electrode will have to necessarily form a liquid junction with the test solution^{1,2}.

2. Liquid junction potentials cannot be eliminated, but can at best be minimized using devices like a salt bridge^{3,4}.

3. The concept of individual activity coefficients cannot be defined accurately, and such coefficients may not even be determined experimentally without some supplementary definition of nonthermodynamic nature⁵.

Harned⁶ has expressed the point at issue in explicit terms: 'We are confronted with interesting perplexity that it is not possible to compute liquid junction potentials without a knowledge of individual ion activities, and it is not possible to determine individual ion activities without an exact knowledge of liquid junction potentials. For the solution of this difficult problem, it is necessary to go outside the domain of exact thermodynamics'. Correlating the liquid junction potentials and individual ionic activities, Guggenheim⁷ has deduced equations for cell potentials with liquid junction that are free from ionic activities and concluded that the activity coefficient of a single ionic species is not an operational concept and is completely unnecessary for an adequate treatment of the thermodynamics of the cell with liquid junction. Conversely, this type of cell can furnish no exact information regarding the activity of a single ionic species, whereas the meaning and usefulness of single ion activities have been stressed by Bronsted *et al.*⁸, MacInnes⁹ and Kortum¹⁰.

Single-ion activity (SIA) would be a prerequisite for building electrochemical potential series without invoking arbitrary zero potential for the standard hydrogen electrode. Measurement of SIA would provide a tool for direct measurement of free metal ion concentration for studies on metal–ligand interactions instead of the fitment procedure adopted currently, using only ionic strength and pH, by successive iterations to calculate the activity of the species in solution.

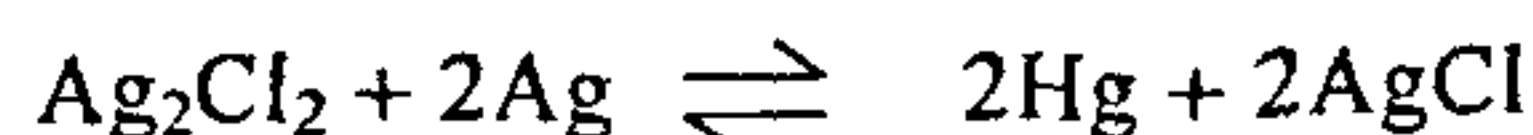
Thermodynamic activities of the electrolyte can be obtained from the potential of an electrochemical cell without liquid junction. For example, in the cell Zn, ZnCl₂/AgCl, Ag system consisting of Zn electrode and an indicator electrode, Ag/AgCl in the same solution is treated as a cell without liquid junction and thermodynamic activities are derived from cell potentials.

The activity of an ionic species is arbitrarily defined as the product of molality and activity coefficient. If SIA can be determined experimentally, this arbitrary assumption can be dispensed with, by comparing it with value calculated using molality and the single-ion activity coefficient (calculated using Debye–Huckel equation and its modifications)^{11–13}. This would enable us to check whether the present mode of calculation of SIA will require any modification about which reservations have already been expressed¹⁴.

It has already been shown¹⁵ that the activity of an ion in a solution of molality m may be redefined as the effective strength of the ion expressed by the term $Z^2 m \gamma_i$ (where Z_i is the valence of the ion), rather than the effective concentration signified by $m \gamma_i$. EMF measurements of the cell Zn/ZnCl₂(m)/bridge/KCl(satd), AgCl/Ag have been carried out for different concentrations (molality) of zinc chloride, using a bridge based on solid silver chloride ionic conductor to avoid liquid junction potential. From the experimental data the activity of zinc ion has been derived for different molal concentrations of zinc chloride and has been found to compare well with the calculated values.

This paper presents a new approach to eliminate liquid junction potential by using a solid ion transmitter bridge for determining single-ion activities (chloride ion) in zinc chloride solutions. The experimental results lend further support to the new definition of activity of an ion proposed earlier¹⁵. The preparation and other details of the solid ionic conductor bridge are also discussed in this paper.

The chloride-ion-selective electrodes are the Ag/AgCl electrodes prepared by dipping a loop of high-purity silver wire into molten high-purity silver chloride. These electrodes are then tested against saturated calomel electrode (SCE) for reproducibility and stability in the cell Ag/AgCl, KCl(satd), Hg₂Cl₂/Hg. Electrodes with a microcapillary tube supplied by Tacussel Electronique, France, were found to be most suitable. The potential is independent of the activity of chloride ions as the cell reaction



involves only solid substances, and is found to be 0.0456 V (ref. 16). The electrodes were found to attain equilibrium potential faster than thermal or thermal electrolytic electrodes¹⁷. The zinc electrodes were specpure zinc rods supplied by Johnson Matthey, UK, sleeved by glass tube, fixed with epoxy with 1 cm length of rod exposed, which is amalgamated with distilled mercury. The procedure for preparation of zinc chloride solutions and the experimental set-up used is the same as described elsewhere¹⁵.

Solid AgCl was used to make solid ion transmitter because of its unique plasticity characteristics. For this purpose, pure AgCl was melted into a bridge in the form of a 'U' tube made from pyrex glass with a capillary of 2 mm bore diameter so that it is a uniform solid on par with rolled or cast AgCl sheet or rod. The tubes are put in the furnace maintained at 380°C and held at this temperature for 10 h and then allowed to cool slowly. This will eliminate porosity, cracks and fissure formation and maintain continuity of the solid chloride between the two tips of the bridge.

The bridges were subjected to:

1. *Pressure test.* On application of gas at a high pressure from a nitrogen cylinder, there was no pressure drop, thereby confirming that there are no crevices, leaks or cracks in the solid AgCl.

2. *Electrochemical test.* The measured potential of the cell Ag/AgCl, KCl(satd)/Bridge/KCl(satd), Hg₂Cl₂/Hg was 45.6 mV in accord with expected value.

3. *Creep test.* One arm of the bridge was placed in saturated KCl solution and the other in AgNO₃ solution. No turbidity or precipitate of AgCl was found even after 24 h. It was also found that the potential-measuring capability is not affected when we switch over from saturated KCl to ZnCl₂ (0.1 m) solution as shown in the experiment. These tests confirm that there is no creep of Cl⁻ ions from one cell to another.

A potential of 1000 V was applied across the two ends of the bridge by connecting to a DC power source and at a point 1 cm away from tips by fusing a Pt wire. The current was in the picoampere range and there was no precipitate of AgCl formed when the bridge was dipped in AgNO₃ solution; the potential was applied for several hours. No evolution of gas (chlorine or hydrogen) was observed, thus ruling out the possibility of corrosion reactions. The conductivity of AgCl is 3 × 10⁻⁸ mho/cm.

It is noteworthy that the potentials do not vary irrespective of whether a thin bent sheet of rolled AgCl or a glass tube filled with cooled molten AgCl is used. Therefore, the question of creep of KCl through capillary crack or glass tube will not arise. Solid AgCl cannot, therefore, be considered as an equitransferent bridge like KCl.

The activity of zinc chloride electrolyte was determined by measuring the potential of the cell without liquid junction between the Zn electrode and a Ag/AgCl electrode in ZnCl₂ solution, i.e. the cell Zn/ZnCl₂(m)/AgCl/Ag.

The activity of the chloride ion was obtained by measuring the potential of chloride-ion-responsive electrode in the respective zinc chloride solutions against the Ag/AgCl reference electrode of fixed potential of 0.199 V (ref. 18), i.e., the potential of the cell



AgCl has high ohmic resistance; and it is, therefore, necessary to use a voltage-measuring instrument of very high input impedance for handling signals from high-resistance sources, with negligible IR drop. The instrument used for this study was ORION expandable ion analyser, model no. EA 940, from ORION Research Inc., USA.

It is more convenient to measure the difference in potentials between the various ZnCl₂ solutions as the impedances of the two solutions are closer. The experiments carried out for this purpose involve measurement of potentials of the following cells:

1. Ag/AgCl, ZnCl₂ 0.1 m/bridge/ZnCl₂ 0.01 m, AgCl, Ag.
2. Ag/AgCl, ZnCl₂ 0.1 m/bridge/ZnCl₂ 0.001 m, AgCl, Ag.

The AgCl-based bridge is best described as a solid-state ion conductor. If the current in the picoampere range is carried entirely by Ag⁺ ions, the schematic will be as in Figure 1 a, which is in keeping with the normal assumption that Ag⁺ ion is the migrant ion in solid AgCl^{19,20}. If chloride is to be considered, the reaction schematic can be visualized as in Figure 1 b. In any case both the schemes are equivalent. The actual studies on the electromigration of ions is beyond the scope of this paper. But the fact remains that without liquid junction the bridge is able to establish contact between the reference and the test solutions. Further, the instrument used for

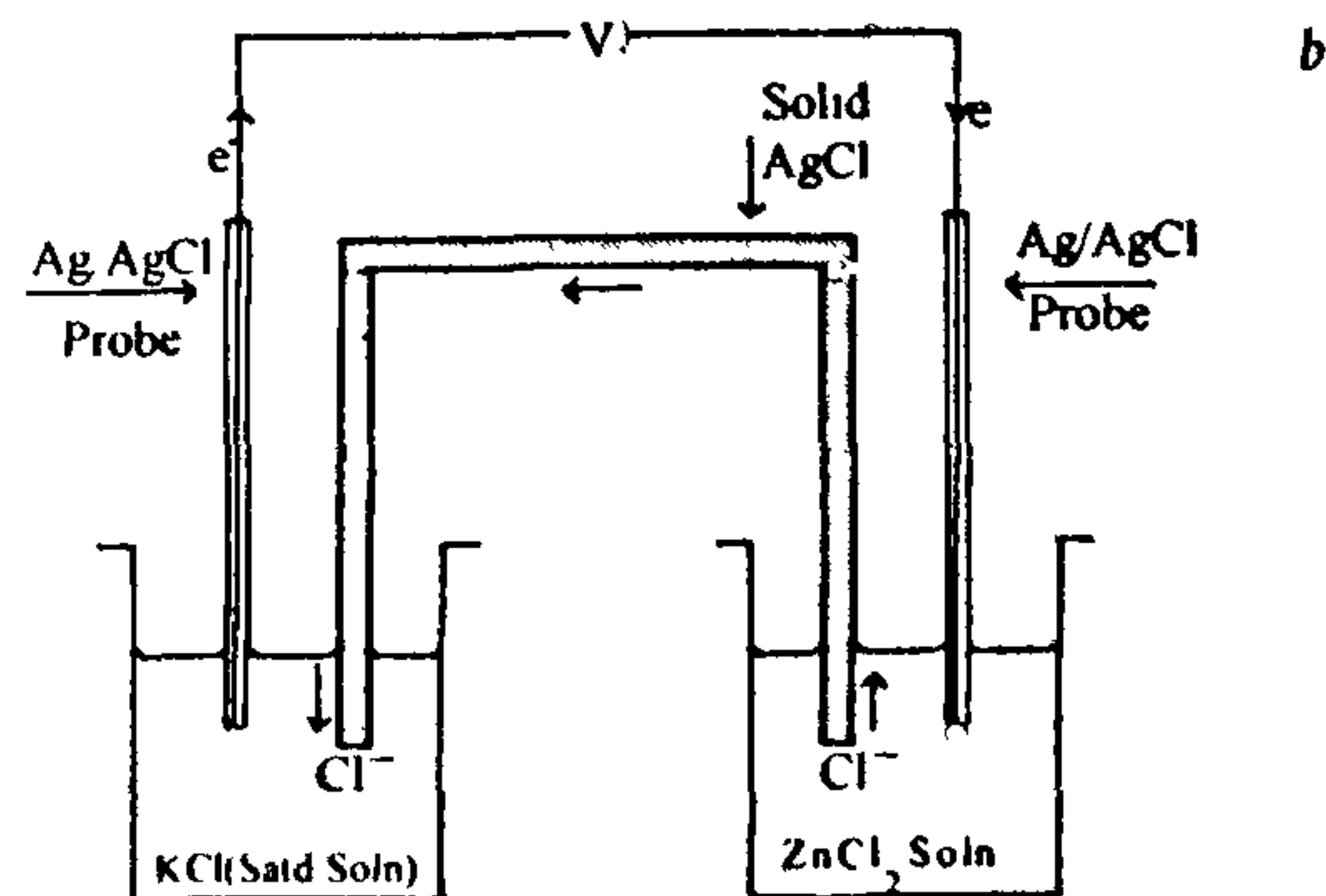
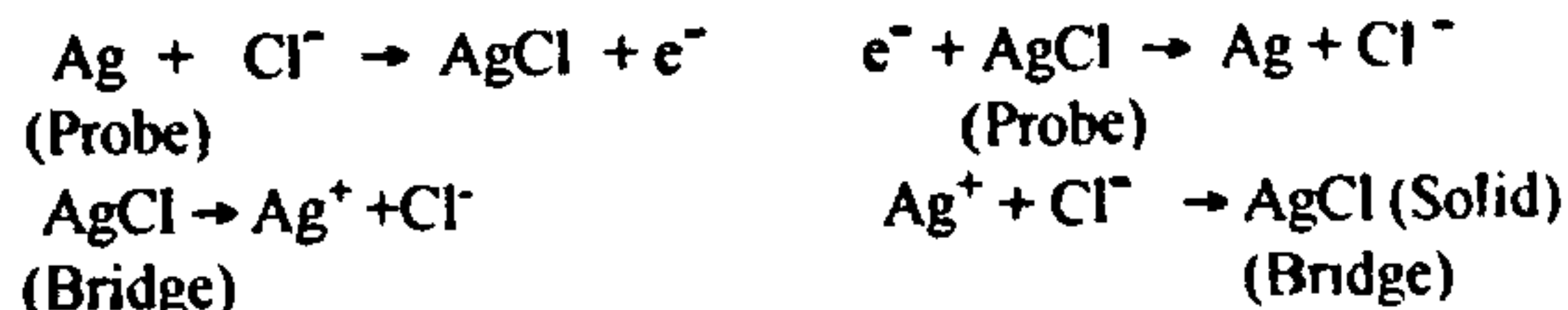
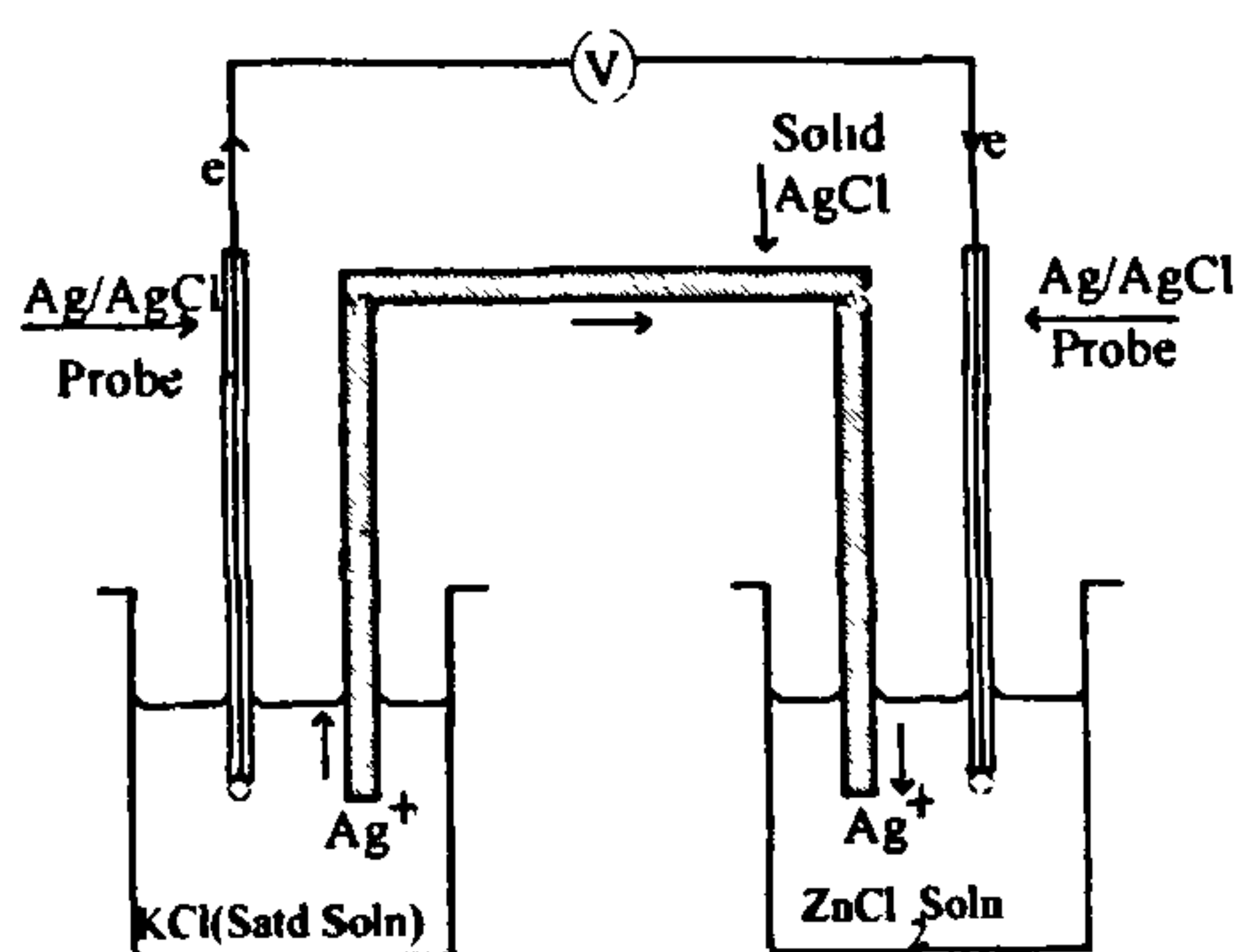


Figure 1. Schematic for a, silver ion transmission, b, chloride ion transmission.

Table 1. Activities of ions in ZnCl₂ solutions with related data at 25°C

Description	Symbol	Data			Remarks
Molality	<i>m</i>	0.1	0.01	0.001	
Activity coefficient					
Chloride ion	γ_{Cl^-}	0.709	0.841	0.938	
Potentials (V)					
Zn/ZnCl ₂ /AgCl/Ag	<i>e</i> ₁	1.082	1.157	1.237	Observed values
Ag/AgCl, KCl(satd)/ZnCl ₂ , AgCl/Ag	<i>e</i> ₂	0.0915	0.1463	0.2024	Observed values
Ag/AgCl, Cl ⁻ electrode	<i>e</i> ₃	0.2905	0.3453	0.4014	[<i>e</i> ₂ + 0.1990]
Activities					
Observed	<i>a</i> _{Cl⁻}	0.0706	0.00847	0.00096	antilog $\frac{(0.2224 - e_3)}{0.05916}$
Calculated	<i>a</i> _{Cl⁻}	0.0709	0.00841	0.00094	<i>m</i> γ_{Cl^-}
By textbook method	<i>a</i> _{Cl⁻}	0.1418	0.01682	0.00188	2 <i>m</i> γ_{Cl^-}
Calculated	<i>a</i> _{Zn²⁺}	0.0998	0.0207	0.0033	<i>a</i> _{ZnCl₂} / <i>a</i> _{Cl⁻} ²
Observed	<i>a</i> _{Zn²⁺}	0.0998	0.0212	0.0032	ref. 14
By textbook method	<i>a</i> _{Zn²⁺}	0.0252	0.005	0.00077	<i>a</i> _{ZnCl₂} / <i>a</i> _{Cl⁻} ²

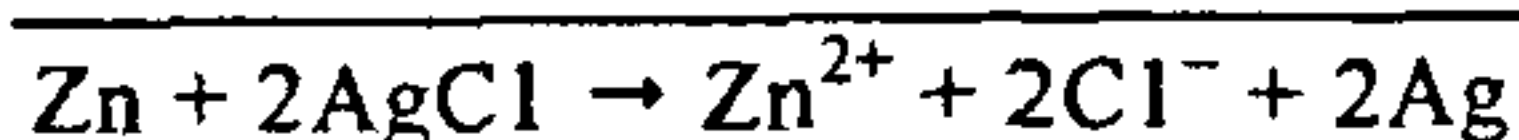
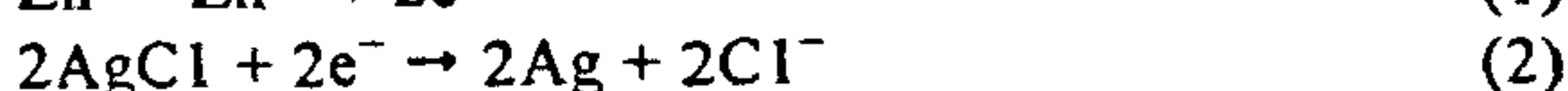
$E_{Ag/AgCl, KCl(satd)} = 0.199$ V; $E_{Ag/AgCl}^0 = 0.2224$ V.

measuring the potentials has an input impedance of 10¹² Ω. Being a solid-state device and the mechanism clearly a Grotthuss type of conduction of the ion inside the bridge, the requirement that the transference number of conducting ion should be unity will not arise.

A membrane potential cannot be associated with AgCl, as it can by no means function as a membrane. AgCl, being ionized in the solid state, will not permit absorption of either negative or positive ions.

Table 1 presents the potentials measured to calculate the activity of the electrolyte and the chloride ion.

For the cell Zn/ZnCl₂(*m*)/AgCl/Ag, the reactions are:



Following the IUPAC convention, the cell potential *e*₁ is given by

$$e_1 = E_{Ag/AgCl}^0 - E_{Zn/Zn^{2+}}^0 - (RT/2F) \ln [a_{ZnCl_2}]. \quad (3)$$

The electrolyte activity for different concentrations calculated from the *e*₁ values are given in Table 2. The activity values are in close agreement with those reported earlier²¹⁻²³.

For measuring the chloride ion activity, a liquid-junction free solid ion transmitter was used to bridge the reference half cell and the half cell comprising the test solutions. The cell set-up used was:



As the liquid junction potential is zero, following IUPAC convention, the potential *e*₂ of the cell is given by

$$e_2 = E_{Ag/AgCl}^0 + (RT/F) \ln (1/a_{Cl^-}) - E_{ref}.$$

If we denote, *E*₂ + *E*_{ref} as *e*₃,

$$a_{Cl^-} = \text{antilog} [(0.2224 - e_3)/0.05916].$$

Equation (3) can be split as

$$E_1 = E_{Ag/AgCl}^0 + (RT/2F) \ln 1/a_{Cl^-}^2, \quad (4)$$

$$E_1 = E_{Ag/AgCl}^0 - (RT/2F) \ln a_{Cl^-}, \quad (5)$$

$$E_2 = E_{Zn/Zn^{2+}}^0 + (RT/2F) \ln a_{Zn^{2+}}. \quad (6)$$

In a completely dissociated strong electrolyte system like MA₂, e.g. ZnCl₂, there is an inherent asymmetry arising out of the charge factor, the cation being doubly charged and the anion being singly charged. It is this asymmetry that is reflected in the Nernst equation appropriate to the anion, which can reflect only the activity of each dissociating fragment. In terms of the electrolyte molality *m*, the molality of cation is *m* and that of the anion will be 2*m*. Then the question arises as to whether which of these two factors 'charge' or 'total molality' is relevant to arrive at the ionic activity. If the charge factor is ignored in Cl⁻ ion, the activity of the chloride ion will be 2*m* γ_{Cl^-} and will contribute a (2*m* γ_{Cl^-})² term in the expression for the activity of the electrolyte. On the other hand, if charge is the factor to be reckoned with, the chloride ion will contribute only (*m* γ_{Cl^-})² term to the expression for the activity of the electrolyte.

Table 2. Activities of ZnCl₂ electrolyte

Concentration (m)	0.1	0.01	0.001
Activity	5.017 × 10 ⁻⁴	1.462 × 10 ⁻⁶	2.89 × 10 ⁻⁹

Table 3. Difference in potential measured against reference solutions at 25°C

Description	Symbol	Data	Remarks
Molality	m	0.01	0 001
Cell potential (V)			
Ag/AgCl, ZnCl ₂ , 0.1/ZnCl ₂ (m), AgCl/Ag	e_4	0 055	0 111
Ag/AgCl, Cl ⁻ electrode	e_5	0 3451	0 4011 $e_4 + 0 2901$

Table 4. Calculation of electrolyte activity

Currently used method	New method proposed
$a_{ZnCl_2} = a_{Zn^{2+}} \times a_{Cl^-} \times a_{Cl^-}$ $= m\gamma_+ \times 2m\gamma_- \times 2m\gamma_-$ $= 4m^3 \gamma_{\pm}^3$	$a_{ZnCl_2} = a_{Zn^{2+}} \times a_{Cl^-} \times a_{Cl^-}$ $= 4m\gamma_+ \times m\gamma_- \times m\gamma_-$ $= 4m^3 \gamma_{\pm}^3$

Clearly, the current definition of activity of an ion as a product of its concentration m and the activity coefficient needs to be revised as the experiments show that the activity is the same as the effective ionic strength defined as $(Z_1^2 m) \gamma_1$ (ref. 15), where Z_1 is the valency of the ion.

Table 3 represents the difference in potentials between the chloride-ion-responsive probes in different ZnCl₂ solutions. Ag/AgCl, ZnCl₂ (0.1) has been used as reference solution with an electrode potential of 0.2901 V (ref. 15). These results confirm the activity of the chloride ion obtained using Ag/AgCl electrode in saturated KCl as the reference electrode shown in Table 1.

The activity of the zinc ion in ZnCl₂ solution can be obtained from the activity of the electrolyte and activity of chloride ions, i.e.

$$a_{Zn^{2+}} = a_{ZnCl_2} / a_{Cl^-}^2$$

This is found to be in close agreement with our earlier measurement¹⁵ of activity of zinc ion using solid ion transmitter bridge. In the case of zinc ion in ZnCl₂ solutions, the charge factor assumes greater importance, and, if activity is treated as the product of the ionic strength of the zinc ion and its activity coefficient, the expected value for the zinc ion will be $4m\gamma_+$. The results of measurements of zinc ion activity using solid ion transmitter is in agreement with the value of $4m\gamma_+$.

The activity of the electrolyte calculated using the current definition to activity of ion and the new definition proposed leads to $a_{ZnCl_2} = 4m^3 \gamma_{\pm}^3$. This is just an accidental coincidence and would not be the case with all electrolytes.

Bates¹⁴ in his recent review on single-ion activities covering a period of 75 years has concluded that individual ion activities are not amenable to thermodynamic

measurements. However, in this paper we have shown that liquid junction potentials can be eliminated, thus paving the way for thermodynamic analysis of single-ion activity, overcoming the impasse highlighted by Harned⁶.

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