

TRANSFERENCE – NUMBER MEASUREMENT OF SILVER NITRATE IN TETRAMETHYL UREA + WATER MIXTURE USING ELECTROMOTIVE FORCE METHOD

قياس عدد الانتقال لنترات الفضة في مزيج رباعي مثيل اليوريا والماء باستعمال طريقة القوة الدافعة الكهربائية

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ABSTRACT:

An e.m.f. cell with transference similar in design to that developed by Rupert and recently by Braun Weingaertner has been fabricated. Using this cell, transference numbers of NO_3^- ($t_{\text{NO}_3^-}$) in AgNO_3 have been measured in the concentration range 3.922×10^{-4} to 11.2×10^{-3} mole dm^{-3} in 0.0606 mole fraction of tetra methyl urea (TMU) + water mixture at 298.15 K. The method is fast and reliable for transference number measurements of AgNO_3 in mixed solvents. The transference number of NO_3^- in the solvent mixture showed practically no change with a change in AgNO_3 concentrations. The limiting transference number of NO_3^- ($t_{\text{NO}_3^-}^{\circ}$) has been estimated by calculating the average of the transference number values of NO_3^- at different AgNO_3 concentrations.

Densities and specific conductivities of all solutions have been measured at 298.15 K. Values of Λ , the molar conductivity; have been used to derive the values of the molar conductivity at the infinite dilution (Λ°). The value of Λ° was then utilized to calculate the Walden product for the electrolyte in the solvent system at 298.15 K.

الخلاصة :

تم تصنيع خلية قياس القوة الدافعة الكهربائية على غرار الخلية التي قام بتصميمها لأول مرة الباحث روبيرت ومن ثم الباحث براون فينكارتر. استخدمت هذه الخلية في ايجاد اعداد الانتقال لايونات NO_3^- ($t_{\text{NO}_3^-}$) في نترات الفضة على مدى التراكيز من $3,922 \times 10^{-4}$ الى $11,2 \times 10^{-3}$ مول للدسيمتر المكعب في مذيب رباعي مثيل اليوريا في الماء الذي بلغ الكسر المولي لرباعي مثيل اليوريا فيه 0,0606 وذلك بدرجة 15, 298 كلفن. والطريقة المستخدمة هذه تعتبر سريعة وموثوقة لقياس اعداد الانتقال لنترات الفضة في مخاليط المذيبات وكان عدد انتقال أيون النترات في المحاليل ثابتاً تقريباً على مدى تراكيز نترات الفضة المستخدمة. واستخدم متوسط قيم اعداد الانتقال المستحصلة تجريبياً بمثابة عدد انتقال ايون النترات في المحاليل المخففة الى ما لانهاية ($t_{\text{NO}_3^-}^{\circ}$). وقد تم قياس الكثافة والتوصيل النوعي لكافة المحاليل بدرجة 15, 298 كلفن، واستخدمت قيم التوصيل المولاري (Λ) المحسوبة بعد ذلك في استخراج قيمة (Λ°) وهو التوصيل المولاري لنترات الفضة في المالا لانهاية من التخفيف. وتم استخدام قيمة (Λ°) بعد ذلك في حساب ثابت والدين لنترات الفضة في المذيب بدرجة 15, 298 كلفن

INTRODUCTION:

The solution behavior of ions in pure and mixed solvents can be studied if the limiting ion conductances (λ_{\pm}°) are available. Limiting ion conductances are usually obtained by combining limiting equivalent conductances of electrolytes (Λ°) with the limiting transference number (t_{\pm}°) of an ion and the relation:

$$\lambda^{\circ} = \Lambda^{\circ} t_{\pm}^{\circ} \dots \dots (1)$$

For this purpose the transference number measurements of at least one electrolyte in a solvent or a solvent mixture at a given temperature are required. During the last few years the conductances of a large number of electrolytes in mixed solvents have been measured.⁽¹⁻⁸⁾

Unfortunately transference number measurements are rare in mixed solvents. Wherever transference number measurements are available in the literature. Hittorf's method⁽⁹⁾ has been

commonly used in preference to moving boundary and e. m. f. methods. The transference number measurements are rare in mixed solvents⁽¹⁰⁻¹¹⁾. In the absence of transference number data, indirect methods have been used for the calculation of λ° values of the ions in pure and mixed solvents.

In this work the transference number measurements of silver nitrate in tetramethyl urea (TMU) + water (W) mixtures using e. m. f. method are reported. Since such measurements are completely lacking, the present study, therefore, provides such data for the first time in the literature.

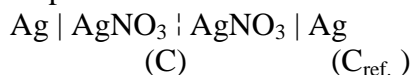
AgNO₃ appeared to be a good choice for the following reasons:

- 1- AgNO₃ solutions give a stable e. m. f. for a sufficiently long time;
- 2- It is appreciably soluble in many solvent mixtures;
- 3- Conductance measurements of AgNO₃ in the same solvent mixture (TMU + W) were performed in the mean time, so that association constant (K_A) values could be determined by more than one method; and;
- 4- Same transference- number data for AgNO₃ in H₂O and same solvent mixtures obtained by Hittorf method are available with which the present results may be compared. The choice of TMU + water mixture as a solvent for this work was made because of its relatively high dielectric constant and other good physical properties which could be derived directly from the available literature⁽¹²⁻¹³⁾.

EXPERAMENTAL

The e. m. f. cell used for the transference-number measurements is shown in fig.1. It is essentially an adaptation of the design developed by Rupert⁽¹⁴⁾ recently used by Braun and Weingaertner⁽¹⁵⁾ for transference number measurements of Na⁺ using sodium- selective glass electrodes. Pure (99.999) silver wires were used as reversible electrodes in the present measurements. The silver electrodes were thoroughly cleaned with dilute nitric acid, distilled water and finally with anhydrous acetone and then dried.

The e. m. f. measurements were performed with a cell of the type:



The cell compartments were filled with solutions and the cell was clamped into a thermostat bath maintained at 25 ± 0.01 °C .

After a constant temperature was attained, the three-way stopcock was turned to form the liquid junction. The e. m. f. of the cell became stable within 5-10 min. and remained constant for one hour.

The e. m. f. of the cell was measured with a precision potentiometer (PYE type) supplied by PYE UNICAM. The uncertainty of the e. m. f. measurements in all cases was ± 0.1 mV. Tetramethyl urea (TMU), obtained from FLUKA, was 99.5% pure and it was further purified before use; the utilized sample had a refractive index of 1.4512 . Doubly distilled water with electrolytic conductance $10^{-6} \Omega^{-1} \text{cm}^{-1}$ was used for the preparation of TMU + water mixture containing 0.0606 mole fraction TMU. Weighed samples of AgNO₃ were dissolved in this solvent mixture to obtain a stock solution of desired concentration. The stock solution was diluted, using the same solvent mixture, to give a number of concentrations which were used for the transference number measurements. An AgNO₃ solution ($3.922 \times 10^{-4} \text{ mol dm}^{-3}$) was used as a reference solution against which the e. m. f. of all other solutions was measured. Densities of all solutions were measured accurately using DMA 60 digital density meter manufactured by ANTON PAAR, K. G.

The conductance of all solutions were measured at 25 °C with the aid of a conductivity meter model CD810 supplied by SOLEA, TACUSSEL. Several possible values of frequencies according to the conductivity of the solution under investigation could be selected. A preliminary setting of the cell constant could be made before effecting measurements with the conductivity cell.

The precision of subsequent measurements on solution of unknown conductivity depended upon the care with which this setting was done.

Fig. 1. Cell design for transference number measurements A and B, electrode compartments; C, three way stopcock; D, glass tube; E, silver wire electrodes ; F, glass tubes with stopcock; G, position of the liquid junction.

RESULTS AND DISCUSSION

The measured e. m. f. values in Volt (E_t) using several concentrations of $AgNO_3$ in the concentration range ($1.538 - 11.2$) $\times 10^{-3}$ mol dm⁻³ against a reference concentration of 3.922×10^{-4} mol dm⁻⁴ in TMU + water solvent mixture containing 0.0606 mole fraction TMU are reported in table (1).

The E_t values from table 1 were fitted to a constant- order polynomial in the form:

$$E_t = P + q \log a_{\pm} + r (\log a_{\pm})^2 \dots\dots\dots(2)$$

And it was observed that r values were small. The fit of the data to a first-order polynomial in the form:

$$E_t = P' + q' \log a_{\pm} \dots\dots\dots(3)$$

was then tried and it was found a better fit of the experimental data to a first- order polynomial was obtained. The transference numbers of NO_3^- ($t_{NO_3}^-$) in all solutions studied were calculated using the equation⁽¹⁰⁾:

$$t_{NO_3^-} = \frac{Z_A Z_B}{Z_A + Z_B} \frac{F}{2.303RT} \left(\frac{dE_t}{d \log a_{\pm}} \right) \dots\dots\dots(4)$$

$$= 8.4522 \left(\frac{\Delta E_t}{\Delta \log a_{\pm}} \right) \dots\dots\dots(5)$$

Where $Z_A, Z_B = 1$, R is the gas constant, T is the absolute temperature, F is Faraday's constant and ($dE_t / d \log a_{\pm}$) = ($\Delta E_t / \Delta \log a_{\pm}$) is the variation of the e. m. f. of the cell from the reference value to a particular concentration with the variation of $\log a_{\pm}$ from the reference value to the corresponding concentration value. The mean – ion activity coefficients (f_{\pm}) for $AgNO_3$ in the present solvent system are not available in the literature, therefore a_{\pm} values could not be directly obtained. The (f_{\pm}) values have been calculated theoretically and combined with the corresponding C values to calculate a_{\pm} values using the relation

$$a_{\pm} = C \alpha f_{\pm} \dots\dots\dots \mathbf{195} \dots\dots(6)$$

where AgNO₃ is associated, α being the degree of dissociation of AgNO₃ . The numerical value of 2.303 RT / F at 25 °C was calculated as 0.059156.

The f± values at various concentrations of AgNO₃ were calculated from the extended Debye- Hückel equation ⁽¹⁶⁾ in the form:

$$-\log f_{\pm} = \frac{1.8246 \times 10^6 (C\alpha)^{1/2} / (\epsilon T)^{3/2}}{1 + 50.29 a^{\circ} \times 10^8 (C\alpha)^{1/2} / (\epsilon T)^{1/2}} \dots\dots\dots(7)$$

Equation (7) has been frequently used for calculating f± values of electrolytes in pure and mixed solvents, and its validity up to concentrations > 0.1 mol dm⁻³ for 1:1 electrolytes has been established in water and in other solvents of moderately high dielectric constant.

In the present solvent system where AgNO₃ was associated α was calculated from the association constant (K_A) using the relation:

$$K_A = \frac{1 - \alpha}{C\alpha^2 f_{\pm}^2} \dots\dots\dots(8)$$

The value of association constant (K_A) was estimated using the modified Bjerrum equation which may be expressed as :

$$K_A = \frac{4\pi N_A e^2}{1000} \frac{e^b}{b} \dots\dots\dots(9)$$

Where:

$$b = \frac{(Z_+)(Z_-)e^2}{\epsilon a^{\circ} kT} \dots\dots\dots(10)$$

Where:

a^o is the ion- size parameter, k the Boltzmann constant, e the electronic charge, Z₊ and Z₋ are the charges by the cation and anion respectively and N_A is the Avogadro number. Following a suggestion by Justice⁽¹⁷⁾, the a^o values in equations (5) and (8) were set equal to the corresponding Bjerrum critical distance⁽¹⁶⁾ q.

Where:

$$q = \frac{e^2}{2 \epsilon kT} \dots\dots\dots(11)$$

Using equations (9) and (10), a value of K_A of 1.3×10^4 has been determined for the association constant at 298.15 K. A computer program to estimate α and f_{\pm} simultaneously from equations (7) and (8) was made. As a first approximation α in equation (7) was set equal to 1 and the tentative values of f_{\pm} at different concentrations were calculated. Using these f_{\pm} values, α values were approximated from equation (8). These values were then used in equation (7) to calculate better values of f_{\pm} and hence better values of α . In this way constant values of α and f_{\pm} were calculated iteratively. The dielectric constant (ϵ) of the solvent system used in equation (7) was taken from references⁽¹²⁻¹³⁾.

Table (2) gives the values of α , f_{\pm} and a_{\pm} at various electrolyte concentrations which have been calculated by the method forwarded above.

A plot of E_t values against the corresponding a_{\pm} values is indicated in fig. (2) from which various values of $(dE_t / d \log a_{\pm})$ have been derived.

These values were then inserted in equation (5) to obtain the corresponding values of $t_{NO_3^-}$; these values did not alter significantly from 0.44.

THE CONCENTRATION DEPENDANCE OF t :

The dependence of transference numbers on the concentration of an electrolyte is usually small. From interionic attraction theory⁽¹⁴⁾, which only applies for dilute solutions, it is expected that $(\delta t / \delta C)_T > 0$ if $t > 0.5$, $(\delta t / \delta C)_T = 0$ if $t = 0.5$ and $(\delta t / \delta C)_T < 0$ if $t < 0.5$. Such predictions have been found true from transference number measurements of electrolytes in various pure solvents⁽¹¹⁾. Transference number of HCL in EtOH and a 50 mol % EtOH- H₂O mixture, however, have been found to vary in the opposite direction to that predicted by the theory⁽¹⁸⁾.

It has been found that $(\delta t_{NO_3^-} / \delta C)_T < 0$ was satisfied in the present work because $t_{NO_3^-} < 0.5$.

LIMITING TRANSFERENCE NUMBER:

The limiting transference number of an ion, like the Λ° value of an electrolyte, cannot be measured directly^(18,19). It can be extrapolated from the transference number data at different concentrations of an electrolyte. The transference number are far less sensitive than conductance to the change in concentration. The extrapolation of transference number data to obtain the limiting transference number (t°) is thus much less uncertain than the extrapolation of conductance data.

In the present work the values of $t_{NO_3^-}$ did not depend on the concentration of AgNO₃ solutions. The value of $t_{NO_3^-}$ was therefore taken to be equal to $t_{NO_3^-}^{\circ}$, the limiting transference number of NO₃. Hence :

$$t_{NO_3^-} = t_{NO_3^-}^{\circ} = 0.443$$

The cation Longworth function $t_{Ag^+}^{\circ}$ was calculated by the method reported by Kay and Day⁽²⁰⁾ using the equations:

$$\bar{t}_{Ag^+} = t_{Ag^+} + (0.5 - t_{Ag^+}) \frac{\Lambda_e}{\Lambda_o} \dots\dots\dots(12)$$

And

$$\Lambda_e = \frac{BC^{1/2}}{1 + Ka} \dots\dots\dots(13)$$

Where

$$B = \frac{82.487}{\eta_o (\epsilon T)^{1/2}} \dots\dots\dots(14)$$

And

$$K = \frac{50.2916 C^{1/2}}{(\epsilon T)^{1/2}} \dots\dots\dots(15)$$

And *a* was set equal to the Bjerrum critical distance *q*, as present in equation (11). The ϵ and η_o values for calculation of *B* and *K* values were taken from references (12) and (13). The value of Λ_o for $AgNO_3$ in TMU + water mixture estimated by making the conductance measurements in the range 3.922×10^{-4} to $11.2 \times 10^{-3} \text{ mol dm}^{-3}$ and by analyzing the conductance data using modified Onsager and Bjerrum equation⁽²¹⁾. Using the values of *K* and *B*, as estimated from equations (14) and (15), the corresponding values of Λ_e have been alculated. These values of Λ_e have been inserted in equation (12) to derive the values of \bar{t}_{Ag^+} , an average of which was 0.449 .

THE LIMITING CONDUCTANCE (Λ_o) OF $AgNO_3$:

The specific conductance (σ) of all solutions have been measured at 298.15 K from which the corresponding values of molar conductives (Λ) have been calculated. A plot of Λ values against the square root of the molar concentration ($C^{1/2}$) of $AgNO_3$ solution TMU-water mixtures at 298.15 K are shown in fig. (3); the value of Λ_o , derived from the intercept of the plot, was $143 \text{ mol}^{-1} \Omega^{-1} \text{cm}^2$. This is compared with 133.34 for Λ_o in water.

Walden product (k^-) for $AgNO_3$ in TMU + water mixture at 298.15 K has been calculated from the relation :

$$\lambda_{(Ag^+)}^o \eta_o = k^- \dots\dots\dots(16)$$

Where η_o is the viscosity of the solvent of 1.372×10^{-2} poise. Taking the value $\lambda_{(Ag^+)}^o = \bar{t}_{Ag^+} \Lambda_o = 79.508 \text{ mol}^{-1} \Omega^{-1} \text{cm}^2$ the value of k^- was 1.0912 at 298.15 K. data are available in the literature to be compared with these experimental results in TMU + water mixture at 298.15 K.

Table (1): Specific conductivity (σ), density (ρ) and electromotive force (E_t) of the cell at 298.15 K for various concentrations (*C*) of $AgNO_3$ in TMU + Water mixture.

C (Mol.dm^{-3}) $\times 10^{-3}$	σ (S.cm^{-1}) / 10^{-6}	ρ (g. cm^{-3})	E_t (v)	Remark
0.392	160.2	1.0068	0.0000	Reference Solution
1.538	167.4	1.0072	0.0500	Test sol.
3.334	195.7	1.0075	0.0590	=
6.667	375.4	1.0084	0.0620	=
8.450	457.2	1.0089	0.0720	=
11.200	603.0	1.0098	0.0920	=

Table (2): Values of α , f_{\pm} , and a_{\pm} at various concentrations (C) of AgNO_3 in TMU + Water mixture at 298.15 K.

$C \times 10^{-3}$	α	f_{\pm}	$a_{\pm} = (C \alpha f_{\pm}) \times 10^{-4}$
0.392	0.3576	0.9924	1.39
1.538	0.2018	0.9898	3.07
3.334	0.1423	0.9882	4.68
6.667	0.1030	0.9867	6.77
8.450	0.0921	0.9861	7.68
11.200	0.0806	0.9855	8.89

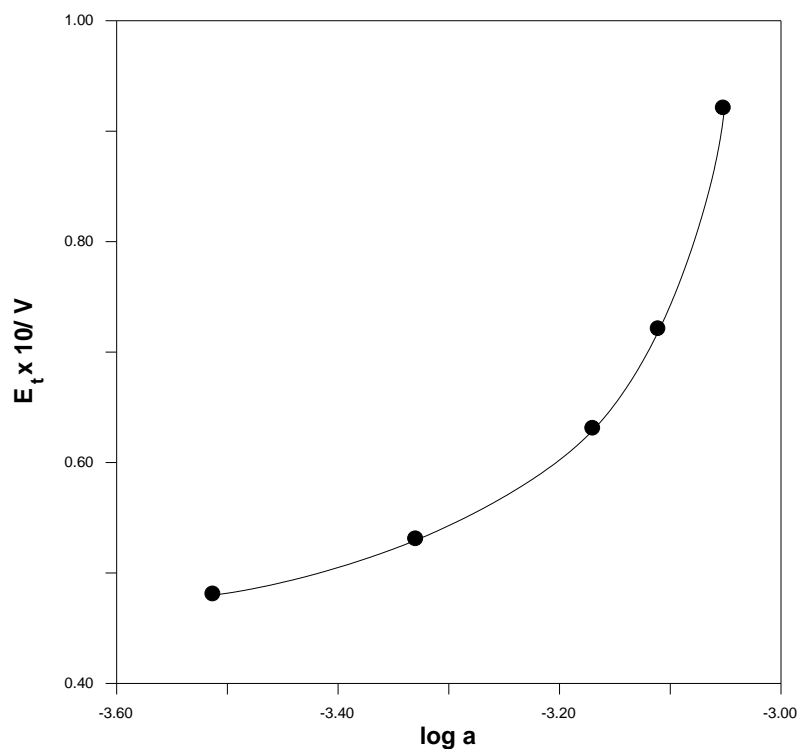


Fig. 2. Variation of the cell potential (E) with log a at various concentration Of $AgNO_3$ in tetramethyl urea + water mixture at 298.15 K.

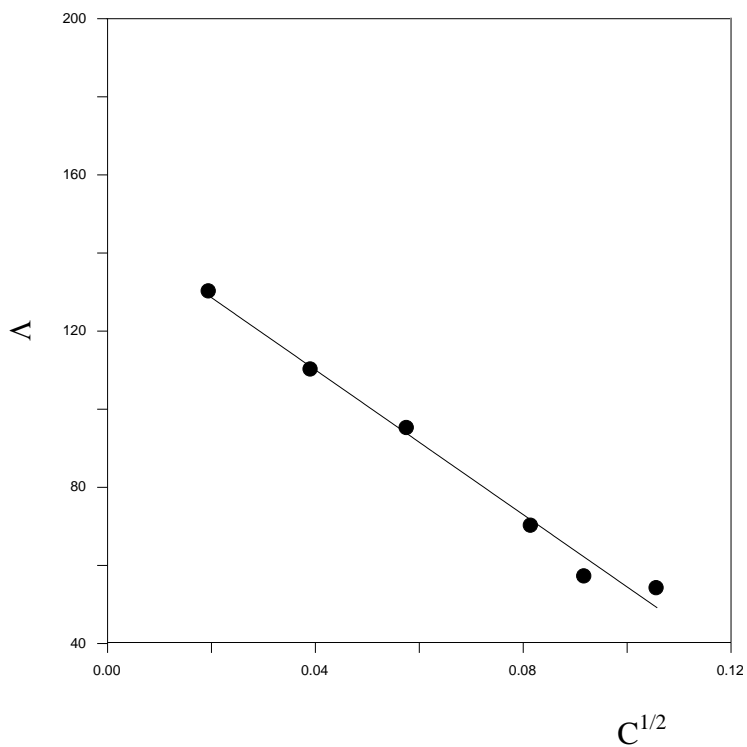


Fig. 3. Variation of molar conductivity (Λ) with molar concentration ($C^{1/2}$) Of $AgNO_3$ solutions at 298.15 K.

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