

CONDUCTOMETRIC DETERMINATION OF A FEW PHYSICO-CHEMICAL CONSTANTS OF MUREXIDE

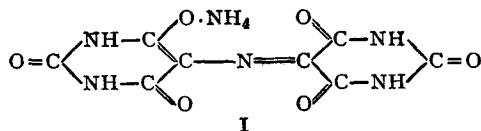
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MUREXIDE (I) or the ammonium salt of purpuric acid (NH_4P) was discovered by Prout (1818)¹ during the development of test for detection of uric acid. Hantzsch and Robinson² made elaborate attempts to prepare murexide in



a pure state. Davidson³ described in detail the method of preparation of murexide from alloxantin. Murexide is a reddish-brown shining crystalline substance.

In recent years, attention of a number of research workers has been drawn towards the use of murexide as metal ion indicator and as an analytical reagent. Swarzenbach and co-workers⁴ were the first to describe the use of murexide as an indicator for the titration of Ca^{++} with commercial chelating agents such as ethylene-diamine-tetra-acetic acid (EDTA). This marked the advent of development of series of analytical methods for estimation of Ca^{++} in various technical products such as pharmaceutical preparations, textile and sugar-house products. Flaschka⁵ gave a review with 23 references on the use of EDTA and murexide in titrations of both cations and anions. Specific directions are given for estimation of Ca^{++} in presence of Mg^{++} , Zn^{++} , Bi^{+++} , Hg^{++} , Al^{+++} and PO_4^{--} in pharmaceutical preparations. Engel⁶ described the method for estimation of combined quantities of Ca^{++} and Mg^{++} . Brunisholz⁷ used murexide, in presence of magnesium chloride, as an indicator in determination of fluoride with cerium chloride. A method for the estimation of Ca^{++} in sugar-house products has been recently reported from this laboratory.⁸

Williams and Moser⁹ have developed a spectrophotometric method for estimation of Ca^{++} . Murexide exhibits absorption maximum at $\lambda = 522 \text{ m}\mu$ in the visible region. When added to a solution containing Ca^{++} murexide

combines with Ca^{++} to form a complex with characteristic absorption maximum at $\lambda = 505 \text{ m}\mu$. The magnitude of extinction coefficient at this wavelength gives a measure of the amount of Ca^{++} .

No data exist in literature on physico-chemical constants such as ionic mobility, diffusion coefficient and ionic radius of purpurate ion and dissociation constant of murexide. The present paper reports conductometric studies on determination of these constants.

EXPERIMENTAL

Murexide of B.D.H. quality was used; this was purified by the method described by Davidson¹⁰ to obtain a sample of 99.9% purity. Solutions of murexide of desired strength were prepared in double distilled water (specific conductance 1.0×10^{-6}). The conductance measurements were made with Serfass conductivity bridge S. No. 3638 using a cell with the corresponding constant of 0.218; conductivity measurements were made at $30 \pm 0.05^\circ \text{C}$.

SYMBOLS USED

S	= Specific conductance
A	= Equivalent conductance
A₀	= Equivalent conductance at infinite dilution
A'	= Equivalent conductance of free ions
C	= Concentration in formalities
α	= Degree of dissociation
A and B	= Onsager constants
A'	= Debye-Huckel constant
η	= The viscosity of the medium
ϵ	= Dielectric constant
T	= Absolute temperature
e	= Electronic charge
a°	= Ionic parameter in angstrom units
N	= Avogadro Number
B₁	= Constant of the Robinson and Stokes' equation
k	= Boltzman constant
K	= Thermodynamic dissociation constant
K'	= $(A + BA_0)$

- κ = Debye-Huckel parameter
- k_0 = Classical dissociation constant from Ostwald's dilution law
- f = Activity coefficient
- Z = Charge of the ion
- μ = Ionic strength
- λ_0 = Limiting ionic mobility
- F = Faraday
- r_s = Ionic radius from Stokes' law
- r = Real ionic radius
- R = Gas constant
- D = Diffusion coefficient

RESULTS

Table I gives a typical set of results on the conductivity of murexide solutions at different concentrations. It may be pointed out that the conductivity measurements were made immediately after the preparation of

TABLE I
Conductance of murexide solutions at 30.0° C.

Concentration $\times 10^3$ M	Specific conductance	Equivalent conductance	Dissociation constant from Ostwald's law
3.28	16.11	107.40	2.06
3.19	15.73	107.66	2.05
2.85	14.13	108.15	1.91
2.80	13.93	108.64	1.96
2.36	11.83	108.61	1.81
1.58	8.17	112.74	1.70

the solutions for the following reasons: Murexide in aqueous solution undergoes decomposition^{11, 12} in the pH range of 1-3 and 9-12. This is accompanied by a change in the conductivity of the solution. The decomposition and the corresponding change in the conductivity were, however, inappreciable at pH-6 which corresponds to the pH of the murexide solutions.

Nevertheless, conductometric studies made immediately after the preparation of the solutions gave data of reproducible and reliable nature.

Figure 1 represents the variation of Λ with square-root of concentration (see below). Extrapolation of the straight line to y -axis gave a value of

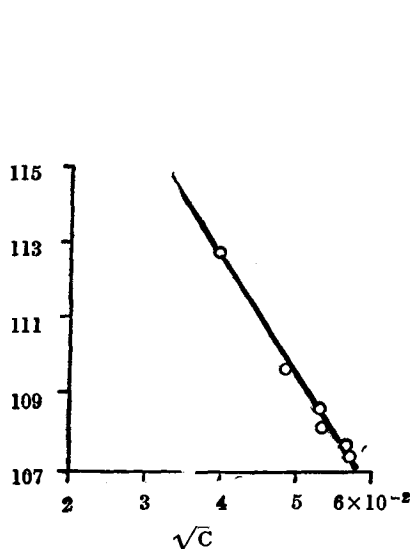


FIG. 1

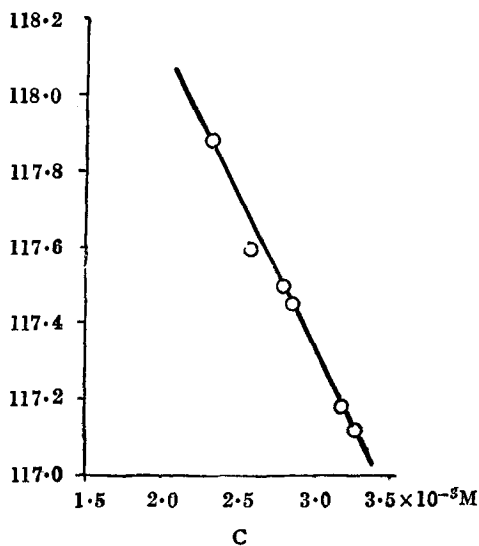


FIG. 2

122.37 mhos. cm^2 for Λ_0 . This was employed for the computation of α to give k_0 by the familiar equation.

$$k_0 = \frac{\alpha^2 C}{(1 - \alpha)} \quad (1)$$

These data are given in column 4 of Table I. It is seen that k_0 does not remain constant indicating the inapplicability of Ostwald's dilution law to the solution of murexide which behaves presumably as a strong electrolyte.

For strong electrolytes Onsager derived the following equation:

$$\Lambda = \Lambda_0 - (A + B\Lambda_0) \sqrt{C} \quad (2)$$

It is of interest to note from Fig. 1 that as required by equation 2, Λ is linearly variant with \sqrt{C} . The slope of the line gives $(A + B\Lambda_0)$. Here

$$A = \frac{82.5}{\eta (\epsilon T)^{1/2}} \quad \text{and} \quad B = \frac{8.2 \times 10^5}{(\epsilon T)^{3/2}} \quad (3)$$

For computation of Λ_0 from the slope, the following were used:—

Dielectric constant ¹³ (ϵ)	76.77
Viscosity ¹⁴ (η)	0.80
Temperature (T)	303.0° A
'A'	67.55
'B'	0.231

The value of Λ_0 obtained from the slope of the plot in Fig. 1 differed widely from the value of 122.37 mhos. cm.²/mole⁻¹ for Λ_0 obtained as the intercept of the plot (see Equation 2). Similar observations have been recorded with number of salts in mixed solvents.^{15, 16} These studies suggest that the number of ions contributing to conductivity of the solution is less than the total number obtainable by the dissociation process, which is due presumably to the existence in the system of associated ion-pairs.

5. ION-ASSOCIATION AND DISSOCIATION CONSTANT

For computation of the dissociation constant of a system in which ion-association is marked, the following methods have been found useful:—

- (i) Davies Method,¹⁷
- (ii) Robinson and Stokes' Method,¹⁸
- (iii) Brock's method.¹⁹

The applicability of these methods for the calculation of the dissociation constant of ammonium purpurate was examined in the following:—

5.1. Davies Method

According to this method α at a particular concentration is given by the ratio of the equivalent conductance of a system to the corresponding equivalent conductance with no association (A'). Here

$$A' = \Lambda_0 - (A + B\Lambda_0) \sqrt{\alpha C}. \quad (4)$$

The values of A' at different concentrations were calculated by the method of successive approximation. These are given in column 3 (Table II). The degree of dissociation and pK values computed from these results are given in columns 4 and 5 (Table II).

TABLE II

Calculation of classical dissociation constant by Davies method

Concentration $\times 10^3$ M	Equivalent conductance of free ions	Degree of dissociation	Classical dissocia- tion constant	pk
3.28	117.12	0.9170	3.32	1.479
3.19	117.18	0.9187	3.31	1.480
2.85	117.47	0.9208	2.99	1.520
2.80	117.49	0.9246	3.25	1.500
2.36	117.88	0.9298	2.90	1.537
1.58	118.65	0.9503	2.87	1.540
pk				1.51 ± 0.03

5.2. *Robinson and Stokes' Method*

Onsager and Fuoss²⁰ observe that

$$A = A_0 - (A + BA_0) \sqrt{C} + EC \log C + FC. \quad (5)$$

Equation 5 was found to give satisfactory results only up to concentrations ≥ 0.01 N. The constants E and F are to be empirically determined. It may be pointed that the influence of time of relaxation²¹ and of electrophoretic effect on the dissociation of a salt are to be considered:—

The relaxation effect²² can be represented as

$$\frac{\Delta X}{X} = \frac{-e^2}{3k\epsilon T} \cdot \frac{0.2929}{1 + a\kappa} \cdot \frac{e^{0.2929a\kappa} - 1}{0.2929a\kappa}. \quad (6)$$

The last term $e^{0.2929a\kappa} - 1/0.2929a\kappa$ in Equation 6 can be neglected for the values of $a\kappa < 0.3$. Further, in the above equation, κ is given by

$$\kappa = \frac{(8\pi N e^2)^{1/2} C^{1/2}}{(1000 \epsilon k T)^{1/2}} \left\{ 1 - \frac{1}{2} \frac{n_1}{N_1} - \frac{1}{2} \frac{n_2}{N_2} \right\} \quad (7)$$

where n_1 and n_2 denote the concentration of cations and anions per c.c. and N_1 and N_2 are the number of "sites" per c.c. available to these ions. κ is also given by

$$\kappa = \frac{(8\pi N e^2)^{1/2} C^{1/2}}{(1000 \epsilon k T)^{1/2}} \quad (8)$$

The difference between the values of κ from Equation 7 and from Equation 8 arises from the fact that in the derivation of Equation 7 distribution function²³ other than the Boltzman function has been employed. As pointed out by Wishaw and Stokes,²⁴ the derivation of the correction factor in Equation 7 (cf. Equation 8) by Falkenhagen *et al.*²² using Eigen-Wicke distribution function²³ instead of the usual Boltzman distribution, is of doubtful validity. The value of κ as given by Equation 8 is therefore used for estimating the relaxation (and electrophoretic) effect (*see* below).

The influence of electrophoretic effect is given by the expression²⁴

$$- \left(\frac{82 \cdot 5 C^{1/2}}{\eta (\epsilon T)^{1/2}} \right) (1 + a\kappa). \quad (9)$$

Combining the electrophoretic effect (Equation 9) and the relaxation effect (Equation 6) using the value of κ from Equation 8, the following equation for A of univalent electrolytes of non-associated type, is obtained

$$A = \left(A_0 - \frac{A\sqrt{C}}{1 + B_1 a^\circ \sqrt{C}} \right) \left(1 - \frac{B\sqrt{C}}{1 + B_1 a^\circ \sqrt{C}} \right). \quad (10)$$

The constant B_1 is given by

$$B_1 = \frac{50 \cdot 29}{(\epsilon T)^{1/2}}. \quad (11)$$

For systems involving ion-association, the concentration of free ions will be aC instead of C . Substituting in place of C in Equation 10 we get

$$A' = \left(A_0 - \frac{A\sqrt{aC}}{1 + B_1 a^\circ \sqrt{aC}} \right) \left(1 - \frac{B\sqrt{aC}}{1 + B_1 a^\circ \sqrt{aC}} \right) \quad (12)$$

where

$$aA' = \frac{A\eta}{\eta_0}. \quad (13)$$

The term η/η_0 gives the viscosity correction which is insignificant at low concentrations investigated and therefore omitted.

In order to calculate Λ' a suitable value is to be assigned to a° . It may be added that ion-pair formation will take place only when the sum of the effective radii of the ions is less than Bjerrum's critical distance of 3.57 Å. For free ions, a° can therefore, be assumed to be equivalent to or greater than 3.57 Å. Employing the minimum value of a° , viz., 3.57 Å, the equivalent conductance due to free ions (Λ') at different concentrations was calculated by using Equation 12. These are returned in column 3 of Table III. The value of α and pk are given in columns 4 and 5.

TABLE III
Calculation of classical dissociation constant by Robinson and Stokes' method

Concentration $\times 10^3$ M	Equivalent conductance of free ions	Degree of dissociation	Dissociation constant	pk
3.28	117.50	0.9135	3.16	1.501
3.19	117.54	0.9159	3.18	1.497
2.85	117.78	0.9182	2.94	1.532
2.80	117.81	0.9221	3.06	1.515
2.36	118.14	0.9278	2.81	1.552
1.58	118.84	0.9486	2.77	1.557
pk				1.525 \pm 0.03

5.3. Brock's Method

An extension of Davies method for evaluation of Λ' (5.1) has been recently developed. For this purpose Equation 4 is rearranged as

$$\Lambda = \alpha [\Lambda_0 - (A + B\Lambda_0) \sqrt{\alpha C}] \quad (14)$$

Equation 14 can be represented as a function of the degree of dissociation in the form

$$f(\alpha) = \alpha^{3/2} C^{1/2} \kappa' - \alpha \Lambda_0 + \Lambda = 0. \quad (15)$$

Let α_1' be the first approximation of α so that $\alpha_1 = \alpha + h$, where h is a constant. Expanding $f(\alpha)$ in Taylor's series we obtain

$$f(a) = f(a_1) + hf'(a_1) + \frac{h^2}{2} f''(a_1) + \dots \quad (16)$$

Assuming that the third and higher terms are small and negligible, we get

$$h = -\frac{f(a_1)}{f'(a_1)} \quad (17)$$

so that the second approximation of a_2 becomes

$$a_2 = a_1 - \frac{f(a_1)}{f'(a_1)} \quad (18)$$

Substituting Equation 15 in Equation 18 and putting $a_1 = A/A_0$ we get

$$a_2 = \frac{A}{A_0} - \frac{\left(\frac{A}{A_0}\right)^{3/2} C^{1/2} \kappa'}{\frac{3}{2} \left(\frac{A}{A_0}\right)^{1/2} C^{1/2} \kappa' - A_0} \quad (19)$$

The values of a_2 obtained from Equation 19 are given in column 2 of Table IV. Column 3 gives the pk values computed from data in columns 1 and 2.

Reference to data in Tables II to IV indicates that different values of pk obtained by varied methods agree with each other; the average values of these are given in column 2 of Table V.

TABLE IV

Calculation of classical dissociation constant by Brock's method

Concentration $\times 10^3$ M	Degree of dissociation	Classical dissocia- tion constant	pk
3.28	0.9122	3.10	1.508
3.19	0.9187	3.31	1.480
2.85	0.9208	3.07	1.513
2.80	0.9242	3.15	1.501
2.36	0.9298	2.90	1.537
1.58	0.9498	2.85	1.546
			$pk \ 1.512 \pm 0.03$

TABLE V

Classical k and thermodynamic K dissociation constant of murexide

		<i>pk</i>	<i>pK</i>
1. Davies Method	..	1.506 ± 0.03	1.555 ± 0.03
2. Robinson and Stokes' Method	..	1.523 ± 0.03	1.572 ± 0.03
3. Brock's method	..	1.512 ± 0.03	1.556 ± 0.03
Mean value	..	1.514 ± 0.03	1.561 ± 0.03

6. THERMODYNAMIC DISSOCIATION CONSTANT

The thermodynamic dissociation constant of murexide or ammonium purpurate (NH_4P) is given by

$$K = \frac{[\text{NH}_4^+][\text{P}^-]}{[\text{NH}_4\text{P}]} \cdot \frac{f_{\text{NH}_4^+} \cdot f_{\text{P}^-}}{f_{\text{NH}_4\text{P}}} \quad (20)$$

and is computed employing the following modified Debye-Huckel equation²⁵ for

$$-\log f_i = \frac{AZ_i^2\sqrt{\mu}}{1 + \sqrt{\mu}} \quad (21)$$

The values of *pK* obtained are given in column 3, Table V. The data suggest that the dissociation constant of murexide can be considered to be 2.75×10^{-2} (*pK* = 1.56) which indicates the strongly ionizable nature of ammonium purpurate. It is instructive to compare the dissociation constant of purpuric acid²⁶: $k = 1.58 \times 10^{-2}$ (*pk* = 1.80).

7. COMPUTATION OF IONIC MOBILITY AND IONIC RADIUS

The linear variation of *A'* with *C* is shown in Fig. 2. The extrapolation of the straight line to zero concentration gives the value of the equivalent conductance of the free ions at infinite dilution which corresponded to 119.7; λ_0 values of NH_4^+ was computed from the data²² on the conductivity of NH_4Cl and Cl^- . Simple application of Kohlrausch law gives 38.12 mhos. cm^2 for the limiting ionic mobility of purpurate ion.

Assuming that Stokes' law is applicable to the movement of ions under electric field, we have

$$r_s = \frac{0.82 Z}{\lambda_0 \eta} \quad (22)$$

Equation 22 gives a value of 2.68 Å for r_s . Stokes' law, however, requires the movement of a particle of macroscopic dimensions in an ideal medium. For the ions with radii less than 5 Å, the values of ionic radius obtained by Equation 5 are reported to be very low and are therefore to be corrected. A factor has been worked out²⁸ for ions of various sizes. For a value of 2.68 for r , this appeared to be approximately 1.44, leading to an approximate value of 3.88 Å as the real ionic radius of purpurate ion, in close agreement with the corresponding value of 3.4 Å computed from the data on conductivity of purpuric acid²⁶ obtained at 0° C.

8. DIFFUSION COEFFICIENT OF PURPURATE ION

The conductivity data presented in the previous articles are employed for determining the diffusion coefficient (D) of the purpurate ion on which no data exist in the literature. D is related to the limiting ionic mobility (λ_0) by the following equation due to Nernst²⁹

$$D = \frac{RT\lambda_0}{F^2Z} \quad (23)$$

λ_0 for the purpurate ion (see §7) corresponded to a value of 38.12 mhos.cm.² Substitution of this value in Equation 22 gives a value of 1.03×10^{-5} cm.²sec.⁻¹ for the diffusion coefficient of the purpurate ion.

SUMMARY

Conductance measurements of murexide or ammonium purpurate solutions were made at 30° + 0.05° C. using a Serfass conductivity bridge. Ostwald's dilution law was found to be inapplicable; equivalent conductance at infinite dilution and the classical and thermodynamic dissociation constants were computed by various methods applicable for systems involving ion association. The following physico-chemical constants of murexide were calculated:—

- (a) Thermodynamic dissociation constant.
- (b) Ionic mobility of purpurate ion.
- (c) Ionic radius,
- (d) Diffusion coefficient.

9. ACKNOWLEDGEMENT

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