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CONDITIONAL DIFFUSION COEFFICIENTS OF IONS AND MOLECULES IN SOLUTION AN APPRAISAL OF THE CONDITIONS AND METHODS OF MEASUREMENT

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AN APPRAISAL OF THE CONDITIONS AND METHODS OF MEASUREMENT

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STATEMENT

In electroanalytical chemistry, many techniques involve the transport of electroactive species, charged or neutral, and among the migration processes, diffusion is the most widely encountered. A quantitative description of the processes and data on the relevant rate constants are necessary for the proper understanding and application of the technique. Many diffusion coefficients can be calculated from conductance data, but such values have only academic value in that they relate to ideal conditions not normally accessible in analytical practice.[1-4] This problem has been treated in detail from the experimental point of view by Turnham.[5] Tabulations of such values may, therefore, be more misleading than helpful, unless they be of conditional values,[6] the conditions being completely defined as below.

A conditional diffusion coefficient is of immediate use if the conditions under which it was determined are fully detailed and can be replicated. By the term conditional diffusion coefficient is meant the mass transfer rate under thermal diffusion conditions, i.e. correction has been made for electromigration where necessary, and is the proportionality constant between the flux and concentration gradient of the diffusing species. A thermodynamic diffusion coefficient is not of use unless the effects of all the matrix factors are fully and unambiguously correctable, and this is seldom possible in the complex matrices of high ionic strength encountered in typical analytical samples.

It appeared, therefore, that a critical compilation of such conditional values together with specifications of the conditions would be of use to electro-chemists. A brief examination of the requirements for such a compilation and a classification and brief appraisal of the principal methods of measurement are made in order to define the perspective and context.

CONDITIONS

Many factors affect the value of the conditional diffusion coefficient and would require specification. The value is know to vary, _inter alia_, with the solvent, the concentration of the diffusing species, the nature and concentration of other ionic and non-ionic species in the solution, the temperature, viscosity and density of the solution. Although the diffusion process is independent of the charge transfer kinetic parameters of an electrode process, it enters directly into the charge transfer overpotential, which is logarithmically dependent on the ratio of mass to charge transfer rate constants. The mass transfer rate is further dependent on current density and the potential of the working electrode, and, in many methods, on other transport processes such as convection, thermal and density gradients, electromigration, etc.

Diffusion coefficients in isolation can be determined by a variety of electrochemical methods wherein the whole system - electrodes and solution - is at perfect rest, free from convection arising from thermal effects at the electrode and from density gradients produced by mass transfer. They can likewise be determined when the solution and/or the electrode is moving and the hydrodynamic conditions are well-defined. When such conditions are not fulfilled, as with turbulently stirred solutions, the isolated diffusion coefficient ceases to be of individual value, and it is recommended that a conditional overall mass transfer rate constant be substituted in its stead. Non-electrical methods of both classical and recent origin may also be used, but values so obtained should be examined for their applicability in electrochemical contexts.

THE DETERMINATION OF CONDITIONAL DIFFUSION COEFFICIENTS

Certain general and cautionary points must be made before listing the methods individually.

1. The reliability and reproducibility of the selected method must be assessed by determination of the value of a diffusion coefficient for which good literature values are available, for example hexacyanoferrate(III)/(II) and dianisidine, and also by statistical evaluation of an adequate number of replicate determinations. A standard deviation of 2.5% of the quantity being determined is considered to be reasonable. Precisions of a few tenths of a per cent have been claimed for the trace-ion methods[7], and a highly sophisticated rotating electrode (disc, ring-disc, etc.) is also capable of attaining a relative standard deviation better than 1%.

2. Agreement between values obtained by different methods should be examined; more than one method should be used whenever possible. Again a standard deviation of 2-5% is considered acceptable.

3. The question, "can a value obtained by one method, e.g., chronoamperometry, be applied with confidence in a different technique, e.g., cyclic voltammetry?" must be considered with a good deal of care. Although fundamentally the diffusion coefficient should be independent of the method of measurement, provided that solution conditions are held constant, much depends on the care and insight with which the experiment is performed.

A further question of interest concerns the relationship between values of diffusion coefficients determined by non-electrochemical methods and those determined by electrochemical methods. Of value in this respect is the work of Bearman[8] concerning the theoretical relationship between values of diffusion coefficients of the electroactive species determined polarographically and by tracer methods. These diffusion coefficients, strictly speaking, are not equal, the polarographic value being the greater. The difference, however, is of a sufficiently small magnitude to permit its being regarded as insignificant within the limit of the validity of the limiting current equations. Mills has reviewed the various theoretical approaches to the interpretation of diffusion process, including cross-term coefficients,[9] and has made a critical compilation of tracer diffusion coefficients.[10] The difference between polarographic and tracer coefficients can be summarized in the equations[9]

$$D_A^P = \frac{RT}{c_B \zeta_{AB} + c_R \zeta_{AR} + c_S \zeta_{AS} - c_A \zeta_{RA}} \tag{1}$$

$$D_A = \frac{RT}{c_B \zeta_{AB} + c_R \zeta_{AR} + c_S \zeta_{AS}} \tag{2}$$

As the concentration c_A becomes very small, the two coefficients tend to equality, the difference depending on the frictional factor, ζ_{RA}. Other theoretical treatments of diffusion in an electric field may be noted.[11,12] Comparison of the polarographic diffusion current with that calculated using tracer diffusion coefficients gave good agreement for monovalent thallium, but not for divalent ions such as lead and zinc.[13]

4. The question, "do values for a certain geometry, e.g., spherical diffusion, apply, with or without some conversion factor, to a different geometry, e.g., cylindrical diffusion?" must also be scrutinized in detail.[14]

5. The conditions of the determination must be fully spelt out in complete detail. This calls for a specification of which conditions must be so detailed, and the first paragraph under the heading "conditions" is no more than a partial listing of the more important factors.

Tamamushi of Commission I-3 has prepared a standard layout for presentation of results for later collation. Useful as this is, it does not include such important matters as the pretreatment of electrodes, potential scan rates, kinematic viscosity, angular velocity of rotating electrodes, extrapolation of Levich plots to determine the intercept, rate of deactivation of electrodes, established purity of solvent and dissolved substances, or ranges of conditions on which measurements have been made.

There now follows an annotated listing of a selection of the more useful methods.

I ELECTROCHEMICAL METHODS[14-18]

A. Stationary solution and electrodes

1. Conductance measurements, and ionic mobilities. Only when medium effects can be completely and specifically evaluated are results calculated from such measurements of value.[1-4,9]

2. Linear sweep voltammetry and polarography[6,14,19] offer excellent values when the limiting current region is well defined, but otherwise become approximate. Cyclic voltammetry, though used, is regarded as an unreliable technique for this particular application. There is a difference of opinion about the quality of values obtained by polarography: compilers of polarographic data in the Clarkson Project aver that the values are of little worth, probably because conditions are inadequately defined or the experimental techniques are not of the best. Critical compilation of electrode kinetic data by Tamamushi of Commission I-3 claim to contain a number of reliable values of diffusion coefficients.

3. Chronoamperometry affords a useful source of good values. Under defined conditions, chronoamperometry gives both reliable and precise results; it has been particularly successful in the determination of diffusion coefficients of metals in amalgams.[20,21]

4. Chronopotentiometry is also used, but gives less precise results because adequate precision in the measurement of transition times is not always attainable, and density gradients arise to disturb the mass transfer control.

5. Large perturbation methods, again provided that the limiting current regions, are well-defined, can give both individual values for D_{ox} and D_{red} and the useful ratio thereof, which in many cases is all that is required.

B. Moving electrodes or solutions under conditions of well-defined hydrodynamics

1. Spinning disc [14,15,17,18,22] electrode methods are frequently used and are capable of producing results of high accuracy and reliability, provided that the apparatus is soundly constructed. The strictest attention must be paid to avoidance of vibration, constancy of rotation speed, electrode centring, adequate ratio of vessel to electrode assembly and electrode assembly to disc radii, adequate depth of a vessel, the design and disposition of counter and reference electrode and so on.

2. Spinning cylinder [14] electrode methods are considerably less precise than spinning disc methods, but have been used. The mass transfer pattern is ill-defined and the method is not at present considered to be reliable.

3. Tubular flowing systems, when the equipment is very carefully constructed so as to ensure near laminar flow, have virtues of their own which give them a useful flexibility, but in general the spinning disc method is best.

C. Undefined hydrodynamic conditions

Although Levich has shown, and many others have confirmed, that in turbulently stirred solutions mass transfer is proportional to the concentration of the active species, specific hydrodynamic equations cannot be derived for such a situation, and diffusion coefficients are neither measurable nor usable.

These conditions are, however, of considerable practical application, as in coulometry, and it is then convenient to replace the flux proportionality constant by a conditional overall mass transfer rate constant which incorporates all the factors which are difficult or impossible to evaluate separately.[23]

II NON-ELECTRICAL METHODS

Classical methods[1-4] need not be further elaborated here. Different vessels filled with solutions of the diffusing species, and diverse methods of determination of the concentration distribution of the test species, have been applied. The capillary method finds continuing use.[24,25] The tracer technique of more recent origin affords a considerable simplification, although it must be applied with caution to light elements. The method is particularly valuable for organic compounds labelled with tritium.[10,26,27] Gosting[28] has made use of the Gouy interferometric method, and the diaphragm cell has also been employed,[29,30] with considerable success, [31-5] and confirmed by radiotracer methods

using ^{15} N.[34]

Conclusions

Isolated values of thermal diffusion coefficients are of merit only when the conditions, both hydrodynamic and experimental, are fully interpretable and fully detailed. On the other hand, in situations of well-defined hydrodynamics, a conditional diffusion coefficient in terms of a flux divided by a pulsatance can have a well recognized meaning and applications.

Fast perturbation methods are considered to be too limited by charge transfer phenomena to be of much assistance in the determination of diffusion coefficients. It is considered that linear sweep voltammetry and polarography, and especially chronoamperometry and spinning disc electrode methods, are the most reliable sources of electrochemical measurements. Non-electrical methods, particularly the capillary, diaphragm and tracer methods, offer useful alternatives.

In turbulently stirred solutions, a situation having special reference to coulometric analysis in stirred solutions with both solid and liquid electrodes and therefore of considerable practical importance, it is recommended that an overall conditional mass transfer rate constant be substituted for the diffusion coefficients.

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