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Diffusion in Multicomponent Electrolyte Systems

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ABSTRACT

The generalized Maxwell–Stefan diffusion equations have been used to model mass diffusion in multicomponent electrolyte systems. The Nernst–Planck equation, often used in practice, is shown to be a special limiting case of the generalized model. A simplified general procedure is suggested for the estimation of the diffusion fluxes. This simplified procedure is obtained by casting the diffusion equations in n-dimensional matrix notation where n represents the number of species present in the system (including solvent). The interesting effects obtained with mixed electrolyte systems are adequately reflected by the developed model. Comparison of the predictions of the simplified model with some experimental data shows that the suggested procedure is of acceptable engineering accuracy.

1. INTRODUCTION

There are many applications in chemical engineering where diffusion of charged ionic species is encountered. Examples are ion exchange, metals extraction, electrochemical reactors and membrane separations. The mass transfer process in such systems is usually described by the use of the Nernst–Planck relationship; see, for example, the excellent text by Newman [1]. The Nernst–Planck relationship is valid for *dilute* electrolyte systems, and for concentrated systems it is well recognized that the generalized Maxwell–Stefan equations provide the most convenient starting point [2, 3]. Though the formalism for dealing with concentrated electrolyte systems is available, no general procedure for the calculation of the mass fluxes, valid for multicomponent electrolyte systems, appears to have been presented. This is the objective of the present communication. A convenient *general* procedure for the calculation of the fluxes is developed by casting the diffusion equations in compact matrix notation.

2. DIFFUSION IN ELECTROLYTE SYSTEMS

The appropriate starting point for a general description of mass transport in electrolyte systems is afforded by the generalized Maxwell–Stefan (GMS) equations which can be written in the following form [2, 3]

$$\begin{aligned} \boldsymbol{d}_i \equiv{} & \frac{x_i}{RT}\nabla_{T,p}\mu_i + \frac{(c_i\bar{V}_i - \omega_i)}{c_t RT}\nabla p \\ & - \frac{1}{c_t RT}\left(c_i\boldsymbol{F}_i - \omega_i\sum_j^n c_j\boldsymbol{F}_j\right) \\ ={} & \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_i\boldsymbol{N}_j - x_j\boldsymbol{N}_i}{c_t\text{Đ}_{ij}} \qquad i = 1, 2, \ldots, n \end{aligned} \tag{1}$$

where $\boldsymbol{d}_i$ is the generalized driving force for transfer of species i.

Now, in many cases of practical interest the pressure gradients are negligibly small and this term may therefore be neglected in eqn. (1). For diffusion of charged species the external body force $\boldsymbol{F}_i$ is given by

$$\boldsymbol{F}_i = -z_i\mathcal{F}\nabla\phi \tag{2}$$

Except in regions close to electrode surfaces where there will be charge separation (double layer phenomena), the condition of electroneutrality

$$\sum_{i=1}^{n-1} z_ic_i = 0 \tag{3}$$

is met and therefore the expression for the driving force $\boldsymbol{d}_i$ simplifies to

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$$d_i = \frac{x_i}{RT} \nabla_{T,p}\mu_i + x_i z_i \frac{\mathcal{F}}{RT} \nabla\phi \quad (4)$$

In many cases of practical interest the nth species (solvent) is stationary, *i.e.* $N_n = 0$. It is convenient to work in terms of diffusion fluxes with respect to the solvent

$$\mathbf{J}_i^n \equiv N_i - x_i N_n = c_i(u_i - u_n) \quad (5)$$

Using the diffusion fluxes $\mathbf{J}_i^n$ in place of N_i in the GMS eqns. (1) we obtain

$$d_i = \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_i \mathbf{J}_j^n - x_j \mathbf{J}_i^n}{c_t Ð_{ij}} \qquad i = 1, 2, \ldots, n-1 \quad (6)$$

where we write only $n-1$ independent equations in view of the fact that $\mathbf{J}_n^n = 0$ and the n driving forces are not all independent ($\Sigma d_i = 0$). The set of eqns. (6), $n-1$ in number, may be conveniently cast into $n-1$ dimensional matrix notation

$$c_t(\mathrm{d}) = -[\mathbf{B}](\mathbf{J}^n) \quad (7)$$

where the elements of the matrix of inverted diffusion coefficients [**B**] are given by

$$\mathrm{B}_{ii} = \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j}{Ð_{ij}} \qquad i = 1, 2, \ldots, n-1 \quad (8)$$

$$\mathrm{B}_{ij} = -x_i/Ð_{ij} \qquad i,j = 1, 2, \ldots, n-1 \quad (i \neq j) \quad (9)$$

A convenient procedure for estimation of the diffusion fluxes $\mathbf{J}_i^n$ follows from eqns. (7) - (9) by assuming that the matrix [**B**] is constant along the diffusion path. Further, the driving forces d_i are approximated by linear composition and electrostatic potential profiles over the range of interest

$$-(\mathrm{d}) = [\mathbf{\Gamma}] \frac{(\Delta \mathrm{x})}{\delta} + (\mathrm{xz}) \frac{\mathcal{F}}{RT} \frac{\Delta\phi}{\delta} \quad (10)$$

where the matrix of thermodynamic correction factors [**Γ**] is

$$\Gamma_{ij} = \delta_{ij} + x_i \frac{\partial \ln \gamma_i}{\partial x_j} \qquad i,j = 1, 2, \ldots, n-1 \quad (11)$$

and can be estimated (at an averaged composition) provided data on the activity coefficients in the electrolyte system are available.

With the above simplifications the fluxes $\mathbf{J}_i^n$ are calculated from

$$(\mathbf{J}^n) = -c_t[\mathbf{B}]^{-1}(\mathrm{d}) \quad (12)$$

Information on the velocity of the solvent u_n is required before the fluxes N_i can be calculated from

$$N_i = \mathbf{J}_i^n + x_i N_n = \mathbf{J}_i^n + c_i u_n \quad (13)$$
$$i = 1, 2, \ldots, n-1$$

The procedure outlined above is not restricted to dilute systems. For such dilute electrolyte systems the treatment is very much simplified because we have

$$\frac{x_i}{RT} \nabla_{T,p}\mu_i = \nabla x_i \qquad \text{(dilute electrolyte)} \quad (14)$$

$$\Gamma_{ij} = \delta_{ij} \quad \text{or} \quad [\mathbf{\Gamma}] = [\mathbf{I}] \qquad \text{(dilute electrolyte)} \quad (15)$$

$$\mathrm{B}_{ii} = 1/Ð_{in}^0 \qquad i = 1, 2, \ldots, n-1 \qquad \text{(dilute electrolyte)} \quad (16)$$

$$\mathrm{B}_{ij} = 0 \qquad i,j = 1, 2, \ldots, n-1 \quad (i \neq j) \qquad \text{(dilute electrolyte)} \quad (17)$$

With the above simplifications the GMS diffusion equations collapse to the form

$$N_i = -c_t Ð_{in}^0 \nabla x_i - c_i z_i Ð_{in}^0 \frac{\mathcal{F}}{RT} \nabla\phi + c_i u_n$$
$$i = 1, 2, \ldots, n-1 \quad (18)$$

which are the Nernst–Planck equations commonly used to describe mass transport in electrolyte systems [1]. For concentrated electrolyte systems the matrix [**B**] has significant non-diagonal elements. Further, the matrix of thermodynamic correction factors also has significant non-diagonal elements for concentrated systems. The general approach to the estimation of the fluxes is by use of eqn. (12).

Now, eqn. (12) can be used, provided the $n-1$ independent driving forces d_i can be calculated (say, by use of eqn. (10)). In many practical chemical engineering applications such as in ion exchange etc, *no* external potential is *applied* to the system and there is no flow of current, *i.e.*

$$\sum_{i=1}^{n-1} z_i N_i = \sum_{i=1}^{n-1} z_i \mathrm{J}_i^n = 0 \tag{19}$$

In this situation there is a finite electrostatic potential gradient *created* due to the motion of the charged species. The $\nabla\phi$ term is not known *a priori* and the formal procedure given above cannot be applied as such. For such cases we proceed somewhat differently.

Equations (6) are written in the form

$$-c_t \frac{x_i}{RT} \nabla_{T,p}\mu_i = \sum_{j=1}^{n-1} \mathrm{B}_{ij}\mathrm{J}_j^n + c_i z_i \frac{\mathcal{F}}{RT}\nabla\phi$$
$$i = 1, 2, \ldots, n-1 \tag{20}$$

There are n unknowns ($\mathrm{J}_1^n, \mathrm{J}_2^n, \ldots, \mathrm{J}_{n-1}^n$ and $\nabla\phi$). Equation (19), when used in conjunction with the $n-1$ eqns. (20) is sufficient for the calculation of the n unknowns.

A convenient method of solution of the set of n eqns. (19) and (20) is to cast these into n-dimensional matrix notation. This is done by defining the following matrices:

(i) an augmented matrix of inverted diffusion coefficients $[B]$ with elements given by

$$B_{ij} = \mathrm{B}_{ij} \qquad i, j = 1, 2, \ldots, n-1 \tag{21}$$

$$B_{in} = c_i z_i \qquad i = 1, 2, \ldots, n-1 \tag{22}$$

$$B_{nj} = z_j \qquad j = 1, 2, \ldots, n-1 \tag{23}$$

$$B_{nn} = 0 \tag{24}$$

(ii) an augmented vector of driving forces $(\nabla\mathrm{Y})$

$$\nabla Y_i = \frac{x_i}{RT}\nabla_{T,p}\mu_i, \quad i = 1, 2, \ldots, n-1 \tag{25}$$

$$\nabla Y_n = 0 \tag{26}$$

(iii) an augmented vector of "unknowns" (J)

$$J_i = \mathrm{J}_i^n \qquad i = 1, 2, \ldots, n-1 \tag{27}$$

$$J_n = \frac{\mathcal{F}}{RT}\nabla\phi \tag{28}$$

With the above definitions, the "unknowns" can be determined by

$$(J) = -c_t[B]^{-1}(\nabla\mathrm{Y}) \tag{29}$$

The assumption of constant matrix $[B]$ and linear composition profiles allows the explicit evaluation of the fluxes J_i^n and the "diffusion potential" $\Delta\phi$.

For dilute systems the approximations given by eqns. (14) - (17) are valid. It is interesting to note that even in dilute systems of electrolytes the rates of diffusion of ionic species are "coupled" to one another. This coupling arises because of the constraints (3) and (19), the latter valid for "pure" diffusion. To illustrate this we have presented some calculations of the diffusion coefficients for the system $Na^+(1)$–$Cl^-(2)$–$H_2O(3)$; the data on the GMS diffusivities Đ_{ij} were obtained from Laity [4]. The "effective" diffusivities of the ionic species, $D_{i,\mathrm{eff}}$, were calculated from

$$D_{i,\mathrm{eff}} = -\frac{\mathrm{J}_i^n}{c_t\nabla x_i} \qquad i = 1, 2 \tag{30}$$

using eqn. (29); these values are also given in Table 1. It is to be noted that the effective ionic diffusivities for the binary electrolyte system are equal to each other. This is despite the fact that the diffusivities of Na^+ and Cl^- in H_2O (*i.e.* Đ_{13} and Đ_{23}) are different from

TABLE 1

Diffusion coefficients in the system $Na^+(1)$–$Cl^-(2)$–$H_2O(3)$ at 25 °C. The data on the generalized Maxwell–Stefan diffusion coefficients D_{ij} have been recalculated from the paper of Laity [4].

c_{NaCl} (kmol m^{-3})	*Generalized Maxwell–Stefan* D_{ij} (10^{-9} m^2 s^{-1})			*Elements of* $[\mathrm{B}]^{-1}$ (10^{-9} m^2 s^{-1})				*Effective ion diffusivity* (10^{-9} m^2 s^{-1})
	D_{13}	D_{23}	D_{12}	B_{11}^{-1}	B_{12}^{-1}	B_{21}^{-1}	B_{22}^{-1}	$D_{1,eff} = D_{2,eff}$
0.01	1.333	2.065	0.0078	1.295	0.059	0.059	1.974	1.621
0.02	1.333	2.083	0.0113	1.283	0.080	0.080	1.960	1.627
0.05	1.325	2.083	0.0197	1.258	0.109	0.109	1.915	1.623
0.10	1.312	2.083	0.0302	1.231	0.136	0.136	1.875	1.615
0.20	1.298	2.101	0.0468	1.204	0.167	0.167	1.845	1.616

each other. The electrostatic potential acts in a manner to slow down the Cl^- ion and speed up the Na^+ ion such that the requirement of electroneutrality is maintained and there is no net current flowing through the system (*cf.* eqn. (19)). Examination of the values of the elements of $[B]^{-1}$ in Table 1 shows that as the concentration of the electrolyte increases the value of the cross-coefficients B_{ij}^{-1} $(i \neq j)$ increases and for salt concentrations above about 0.2 kmol m^{-3} it will be necessary to use the generalized Maxwell–Stefan formulation in place of the commonly used Nernst–Planck relationship (16). Put another way, the Nernst–Planck relationship can be used for salt concentrations below about 0.1 kmol m^{-3}.

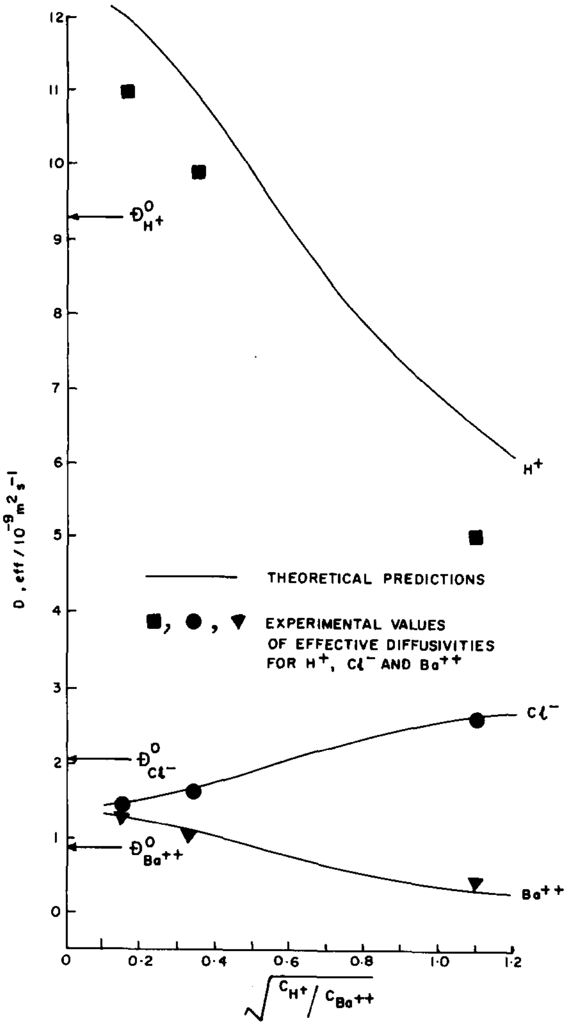

Fig. 1. Effective diffusivities in the mixed electrolyte system HCl–$BaCl_2$–H_2O. The experimental data are taken from Vinograd and McBain [3]. The theoretical predictions are based on eqns. (29) and (30).

For an electrolyte system containing three or more ions there is no requirement that the effective diffusivities of the individual ionic species $D_{i,\text{eff}}$ be equal to one another. In fact it is possible to accelerate, or decelerate, a particular ion to a significant extent above its "intrinsic" mobility, *i.e.* mobility unhindered by the other ionic species. Figure 1 shows the calculations for the effective diffusivities for the system $H^+(1)$–$Cl^-(2)$–$Ba^{++}(3)$–$H_2O(4)$ using eqns. (29) and (30). The intrinsic mobility values $Đ_{in}{}^0$ were obtained from Newman [1]. The theoretical calculations are compared with the experimentally determined effective diffusivity values reported in Vinograd and McBain [5]. The agreement for Cl^- and Ba^{++} ions is extremely good, while there is a systematic deviation for the diffusivity values for H^+ ion. This systematic deviation could be due to experimental inaccuracies inherent in measuring extremely high diffusivity values. For all three ions the correct experimental trends with ion concentrations are predicted by the linearized GMS approach.

Figure 2 presents a similar comparison between theoretical predictions and experimentally measured effective diffusivities for the system $H^+(1)$–$Cl^-(2)$–$K^+(3)$–$H_2O(4)$. Again the agreement between linearized theory and experiment is good for Cl^- and K^+, while there is a larger deviation for H^+ effective diffusivity, especially at higher diffusivity values. The deviation is significantly reduced for low values of H^+ diffusivity. The correct experimental trends are reproduced by the theoretical model based on a linearized GMS approach.

3. CONCLUDING REMARKS

The generalized Maxwell–Stefan equations have been used as a basis for modelling the mass transport process in electrolyte systems. The set of equations describing the mass transfer process is conveniently cast into matrix notation and a simplified solution procedure has been suggested for the calculation of the diffusion fluxes and "effective" diffusivities. The linearized procedure has been shown to be of acceptable engineering accuracy by comparisons of theoretical predictions with experimental effective dif-

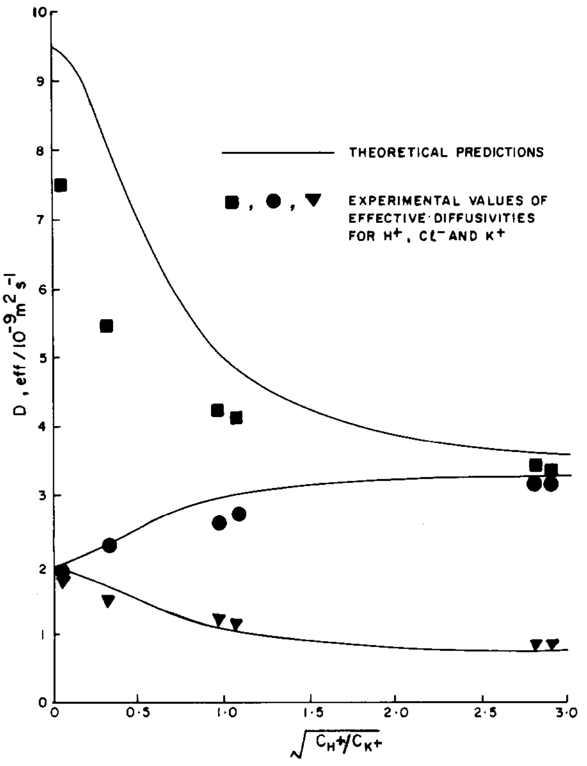

Fig. 2. Effective diffusivities in the mixed electrolyte systems HCl–KCl–H_2O. The experimental data are taken from Vinograd and McBain [3]. The theoretical predictions are based on eqns. (29) and (30).

fusivity values. Some of the interesting features of multicomponent electrolyte — *i.e.* mixed ion — systems have been pointed out in the discussions.

There are many applications in chemical engineering where mixed ion diffusion effects can have significant consequences; some examples are ion exchange [6, 7], metals extraction [8, 9] and neutralization reactions [10]. The model formulation developed in this paper could be profitably used to calculate the fluxes in these cases.

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APPENDIX A: NOMENCLATURE

[B]	matrix of inverted diffusion coefficients with elements defined by eqns. (8) and (9) (m^{-2} s)
$[B]$	n dimensional augmented matrix with elements given by eqns. (21) - (24)
c_i	molar concentration of species i (kmol m^{-3})
c_t	mixture molar concentration (kmol m^{-3})
d_i	generalized driving force defined by eqn. (1) (m^{-1})
$Ð_{ij}$	generalized Maxwell–Stefan diffusivities for the pair i–j in multicomponent mixture (m^2 s^{-1})
$D_{i,\text{eff}}$	effective diffusivity of ionic species i in mixture (m^2 s^{-1})
$\mathcal{F}$	Faraday's constant (9.65×10^7 C kg-equiv^{-1})
F_i	external body force acting on species i (N $kmol^{-1}$)
j_i	mass diffusion flux of component i with respect to mass average reference velocity of mixture (kg m^{-2} s^{-1})
J_i^n	molar diffusion flux of species i with respect to nth component (solvent) velocity (kmol m^{-2} s^{-1})
(J)	augmented column matrix of dimension n with elements given by eqns. (27) and (28)
n	number of species in system
N_i	molar diffusion flux of species i in fixed coordinate reference frame (kmol m^{-2} s^{-1})
p	pressure (N m^{-2})
R	gas constant (8314.4 J $kmol^{-1}$ K^{-1})
T	absolute temperature (K)
u_i	velocity of diffusing species i in fixed coordinate reference frame (m s^{-1})
u_n	nth component velocity (m s^{-1})
$\overline{V}_i$	partial molar volume of species i (m^3 $kmol^{-1}$)
x_i	mole fraction of species i

(∇Y)	n dimensional augmented column matrix of driving forces defined by eqns. (25) and (26)
z_i	charge on species i

Greek symbols

γ_i	activity coefficient of species i in solution
$[\Gamma]$	matrix of thermodynamic factors defined by eqn. (11)
δ	length of diffusion path (m)
δ_{ij}	Kronecker delta
μ_i	molar chemical potential of species i (J kmol^{-1})
ϕ	electrostatic potential (V)
ω_i	mass fraction of species i

Subscripts

i, j	reffering to species i, j in multicomponent mixture
n	referring to species n (solvent)
T	at constant temperature conditions
T, p	at constant temperature and pressure conditions
	conditions
eff	"effective" parameter

Superscripts

0	infinite dilution value
n	referred to solvent
$-$	overbar denotes partial molar quantity
$\sim$	tilde denotes specific quantity

Matrix notation

[ ]	square matrix of dimension $n-1 \times n-1$ or $n \times n$
$[\ ]^{-1}$	inverted matrix
( )	column matrix

Vector notation

∇	gradient operator (m^{-1})
$\cdot$	dot product between vectors

Operators

Δ	difference operator
Σ	summation
$\mathrm{d}/\mathrm{d}t$	substantial time derivative