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Nonlinear Mass Transfer at the Electrodes with Reversible Homogeneous; Reactions:Taylor'sSeries and Hyperbolic Function Method

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The mathematical model for mass transfer with reversible homogeneous reactions is discussed. Estimation of mass transfer to and from electrodes for this reaction needs the analytical solution of nonlinear reaction-diffusion equations. Taylor's series method and hyperbolic function method are used to solve the system of nonlinear reaction-diffusion equations. Approximate closed-form of analytical expression of the concentration of substrate, reactant and product are derived for all values parameters. The empirical results are compared with the simulation results, and there is noticeable agreement. The effect of various parameter on aqueous carbonate-species concentration are also discussed. The current density and homogeneous equilibrium constant are also obtained.

Keywords: Mathematical Modeling; Non-linear equations; Taylor's Series Method; Hyperbolic Function Method; Steady-state.

1. INTRODUCTION

Many electrode processes include homogeneous reactions (reactions between gases and between liquids or substances dissolved in liquids) that also occur in the boundary layer of mass transfer [1]. Descriptive analyzes of electrode-kinetics experiments as well as mathematical modelling need the evaluation of the concentrations of species on the electrode surface. The measurement of concentration profiles in the boundary layer of the solution near the electrodes is based on the mass balance equations of species.

$$\frac{\partial c_i}{\partial t} = -\nabla \bullet N_i + R_i \qquad (1)$$

Where c_i and R_i are the molar concentration and the net production rate of species *i*. In general, the molar flux N_i is defined by

$$N_i = -D_i \nabla c_i - z_i c_i D_i \frac{F}{RT} \nabla \phi + c_i v \quad (2)$$

This represents the transport of species by diffusion and convection along with ion migration in an electric field[2].The rate of production can be written as

$$R_i = v_i \left[k_r \prod_j c_j^{v_j} - k_f \prod_i c_i^{v_i} \right] \quad (3)$$

Each species in solution is combined with the condition of electroneutrality $\sum_i z_i c_i = 0$. Problems such as cyclic voltammetry, chronopotentiometry, chronoamperometry, square wave voltammetry, and differential pulse voltammetry, rotating electrodes, biosensor, biofuel-cell, and several boundary-layer problems have been solved for several important situations [3-6].Recently some of the nonlinear problems in rotating disk electrode [7-10], cyclic voltammetry [11], electroactive polymer film [12,13],biofuel cell[14] and biosensor [15] are solved using various analytical techniques.

Recently Chapman et al.[1] discuss the mass transfer at the electrodes for the homogeneous reactions for the fast and reversible reaction. In this paper, we propose a simple and efficient methods (Taylor's series and hyperbolic function)to solve the differential equations that arises in the context of mass transfer at the electrodes with reversible homogeneous reactions.The analytical expressions of the concentration of species and current are provided using Taylor's series method and hyperbolic function method.

2. MATHEMATICAL FORMULATION OF THE PROBLEM

Consider the followingreversible *reaction*

$$A + B \underset{k_r}{\overset{k_f}{\leftrightarrow}} C \quad (4)$$

Where A is formed at the known rate N_{Ao} at an electrode, and B is found outside a stationary diffusion layer of uniform thickness δ in the bulk solution. The homogeneous reaction forms the species C and diffuses into the bulk.The general scheme for second-order irreversible homogeneous reaction is represented in Figure.1.

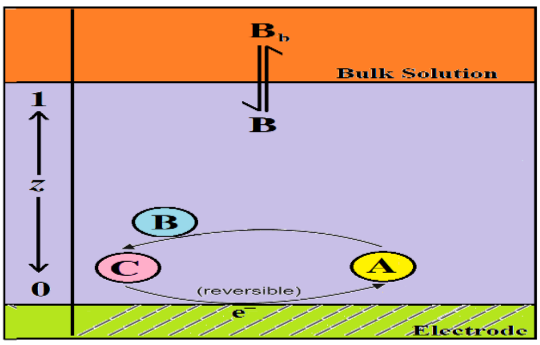


Figure 1. General scheme for second- order irreversible homogeneous reaction.

By neglecting ionic migration, it is possible to write the boundary value problem that must be solved asfollows[1]:

$$D\frac{d^2A(x)}{dx^2}=k_fA(x)B(x)-k_rC(x) \tag{5}$$

$$D\frac{d^2B(x)}{dx^2}=k_fA(x)B(x)-k_rC(x) \tag{6}$$

$$D\frac{d^2C(x)}{dx^2}=-k_fA(x)B(x)+k_rC(x) \tag{7}$$

where*A*, *B*, and *C*arethe concentration of species and $k_r$istheforward reaction-rate constant. For convenience, all coefficients of diffusion are assumed to be equal to a constant D. In the bulk solution, the concentrations of A and C are zero, and at the electrode, the fluxes of B and C are zero.This can be represented by the following boundary conditions.

$$D\frac{dA(x)}{dx}=-N_{Ao};\ \frac{dB(x)}{dx}=\frac{dC(x)}{dx}=0 \text{ at } x=0 \tag{8}$$

$$B(x)=B_b;\ A(x)=C(x)=0 \text{ at } x=\delta \tag{9}$$

The appropriate dimensionless variables are introduced.

$$a=\frac{A(x)}{B_b}, b=\frac{B(x)}{B_b},\ S=\frac{C(x)}{B_b}, z=\frac{x}{\delta},$$

$$\varepsilon=\left[\frac{D}{\delta^2k_fB_b}\right]^{\frac{1}{2}}, K^*=\left[\frac{k_fB_b}{k_r}\right], \mu=\left[\frac{N_{Ao}\delta}{DB_b}\right] \tag{10}$$

where *a*, *b* and *S* are dimensionless concentration of species *A, B* and *C*. ε represent the relative rates of diffusion and reaction , K^* denotes the homogeneous equilibrium constant.The rate of injection of A corresponding to the limiting flux of B toward the electrode was described by μ.Eqs.(5)-(7) becomes in dimensionless form as follows:

$$\varepsilon^2\frac{d^2a(z)}{dz^2}=a(z)b(z)-\frac{S(z)}{K^*} \tag{11}$$

$$\varepsilon^2\frac{d^2b(z)}{dz^2}=a(z)b(z)-\frac{S(z)}{K^*} \tag{12}$$

$$\varepsilon^2\frac{d^2S(z)}{dz^2}=\frac{S(z)}{K^*}-a(z)b(z) \tag{13}$$

The dimensionless boundary conditions are,

$$a'(z=0)=\mu,\ b'(z=0)=0,\ S'(z=0)=0 \tag{14}$$

$$a(z=1)=0,\ b(z=1)=1,\ S(z=1)=0 \tag{15}$$

The relation between the concentration of species is given in Appendix-A.

3. APPROXIMATE ANALYTICAL EXPRESSION OF CONCENTRATION OF SPECIES USING TAYLOR'S SERIES METHOD (TSM)

In this section, Taylor's series method is applied to solve the system ofnon-linear differential Eqs. This method[12,16-18] provides an analytical solution with quickly computable terms for rapidly convergent infinite power series. Taylor's series is an infinite sum of terms expressed on a single point in terms of the functional derivatives. We regard the solution to Eqs. (13)-(15) is sufficiently smooth so that it can be obtained using Taylors series **(**Appendix B) as follows:

$$a(z) = b(z) + \mu z - \mu - 1 \tag{16}$$

$$b(z) = m + \frac{\alpha z^2}{2\varepsilon^2} + \frac{(m\mu)z^3}{\varepsilon^2 3!} + \frac{\alpha\beta z^4}{\varepsilon^4 4!} + \frac{1}{\varepsilon^4}[\beta\mu m + 3\alpha\mu]\frac{z^5}{5!} + \frac{1}{\varepsilon^6}\left[\alpha\beta^2 + 6\alpha^2 + 4\varepsilon^2 m\mu^2\right]\frac{z^6}{6!} \tag{17}$$

$$S(z) = 1 - b(z) \tag{18}$$

where

$$\alpha = m(m - \mu - 1) + \frac{m-1}{K^*} \quad \beta = 2m - \mu - 1 + \frac{1}{K^*} \tag{19}$$

Here *m* is obtained from the following Eq.

$$m + \frac{\alpha}{2\varepsilon^2} + \frac{m\mu}{\varepsilon^2 3!} + \frac{\alpha\beta}{\varepsilon^4 4!} + \frac{1}{\varepsilon^4}[\mu\beta m + 3\mu\alpha]\frac{1}{5!} + \frac{1}{\varepsilon^6}\left[\alpha\beta^2 + 6\alpha^2 + 4\varepsilon^2 m\mu^2\right]\frac{1}{6!} - 1 = 0 \tag{20}$$

4. APPROXIMATEANALYTICAL EXPRESSION OF CONCENTRATIONUSING HYPERBOLIC FUNCTION METHOD (HFM)

Recently some the analytical methods are used to solve the nonlinear problems in physical chemistry [19-21]. In this paper, the hyperbolic function method is also used to solve non-linear differential equations. The HFM [21] yields without linearization, perturbation or transformation, a closed-form of analytical solution. The concentration of the species by using HFM(Appendix C**)** may be obtained as follows:

$$a(z) = \mu z - \mu - 1 + m\cosh\left(\cosh^{-1}\left(\frac{1}{m}\right)\right)z \tag{21}$$

$$b(z) = m\cosh\left(\cosh^{-1}\left(\frac{1}{m}\right)\right)z \tag{22}$$

$$S(z) = 1 - m\cosh\left(\cosh^{-1}\left(\frac{1}{m}\right)\right)z \tag{23}$$

Here *m*is obtained from the Eq. (20).

5. ESTIMATION CURRENT DENSITY i AND HOMOGENEOUS EQUILIBRIUM CONSTANT K^*.

The currentdensity becomes[1]

$$2N_{H_2CO_3} + N_{HCO_3} - N_{OH} = i/nF \text{ at } x = 0 \tag{24}$$

$$\frac{i}{nF} = 2a(0) - b(0) + c(0) = 2m - 2\mu - 3 \tag{25}$$

For the fast-irreversible homogeneous reaction, from the Eq.(5) we get

$$\frac{K^*}{B_b} = \frac{k_f}{k_r} = \frac{C(x)}{A(x)B(x)} \tag{26}$$

For all value of *x*, In terms of dimensionless variables this becomes

$$K^* = \frac{s(z)}{a(z)b(z)} \tag{27}$$

For all values of *z*. At z=0, this becomes

$$K^* = \frac{s(0)}{a(0)b(z0)} = \frac{1-m}{m(m-\mu-1)} \tag{28}$$

6. PREVIOUS WORKOF CHAMPAN ET AL.[1]

Using the relation between the concentration of species, Champan et al.[1]obtained the differential Eq.of second-order for the concentration of species $S(z)$ as follows:

$$\varepsilon^2 \frac{d^2S(z)}{dz^2} = -S^2 + \left[\mu(1-z)+1+\frac{1}{K*}\right]S - \mu(1-z) \tag{29}$$

Since the above equation is still nonlinear, Champan et al.[1] obtain the solution of the Eq.(29)when the homogeneous rate constant k_f is large or $\varepsilon = 0$. In this case a quadratic algebraic Eq. for *S* becomes

$$\overline{S} = \frac{1}{2}\left\{\left[\mu(1-z)+1+\frac{1}{K*}\right] - \left[\left(\mu(1-z)+1+\frac{1}{K*}\right)^2 - 4\mu(1-z)\right]^{1/2}\right\} \tag{30}$$

Champan et al.[1]also obtain the solution of the equation for large values of $K*$

$$S = \overline{S} + \varepsilon\left[\left.\left(\frac{d\overline{S}}{dz}\right)\right|_0\right]\frac{\exp[-(1-\mu)^{1/2}\eta]}{\sqrt{(1-\mu)}} \tag{31}$$

7. VALIDATION OF ANALYTICAL METHODS

Method of validation has received considerable attention in the literature. The nonlinear differential equations (11)-(13) with the boundary conditions (14) and (15) are solved numerically by using the function pdex4 in Scilab/Matlab, numerical software. The concentration of species derived by Taylor' s series method (equation (16), (17) and (18)) Hyperbolic function method (equation (21),(22) and (23)) are compared with a numerical solution in Figures 1-3 and Tables 1-3. Also, the average relative errors are given in the respective tables. From Tables 1-3, it is confirmed that the Taylor series method is the efficient tool for providing analytical expressions of concentrations of species for reversible homogeneous reactions. Also from the Eqs. (16) to (18) weget

$$a(z)+b(z)+2c(z) = \mu z - \mu + 1 \tag{32}$$

The derived analytical results also satisfy the above result.

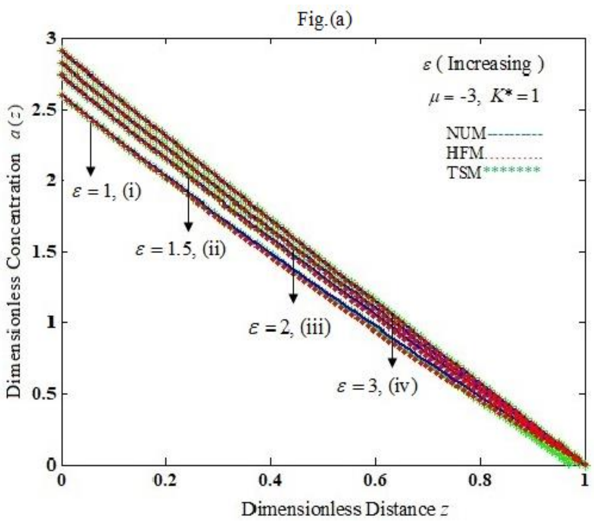
8. RESULT AND DISCUSSION

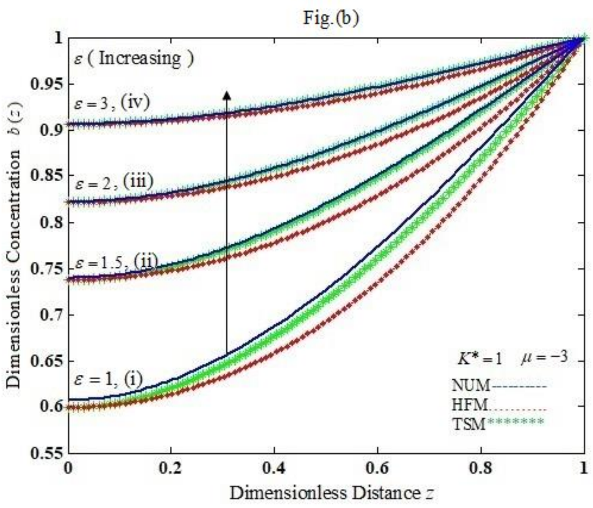
Eqs. (16)-(18) and (21)-(23)are the new analytical expressions of the concentration species *A*,*B*and *C*in reversible homogeneous reactionfor the steady-state conditions. The species concentration depends upon the variable relative rates of diffusion and reaction(ε), rate of injection of *A* relative to the limiting flux of *B* toward the electrode (μ) and homogeneous equilibrium constant (K^*).Figures1-3 shows the dimensionless steady-state concentration for various species $a(z)$, $b(z)$ and $S(z)$ involved in the reversible homogeneous reaction with respect to the distance from the electrode surface z for different values of parameters ε, μ and K^*.

From the Figure1 it is inferred that the concentration of the species $a(z)$ and $b(z)$ increases when ε increases. But the concentration of the species $S(z)$ increases when relative rates of diffusion decreases. The effect of different values of the parameter on the concentration profile is shown in Figure.2.From this Figure2, it is observed that an increase inequilibrium constant leads to increase in $a(z)$ and $b(z)$ and decreases in $S(z)$.Figure.3 illustrates the species concentration versus distance from the surface of the electrode for various values of a parameter.As the rate of injection of A relative to the limiting flux of B toward the electrode (μ) decreases,the concentration of species $a(z)$ and $S(z)$ increases and $b(z)$ increases.

9. CONCLUSIONS

This paper discusses the modeling of mass transfer at electrodes with homogeneous reversible reaction. The systems of non-linear second-order differential equations are solved using Taylor's series and hyperbolic function method. The approximate analytical expression for the concentration of the species is obtained. We have successfully used Taylor's series method and Hyperbolic function method to construct solutions for non-linear differential equations. With numerical results, the analytical results are compared, and adequate agreement is noted.The theoretical study of a simplified model system explores the nature of these problems.This method can be extended to non-steady-state problems in physical and chemical sciences.





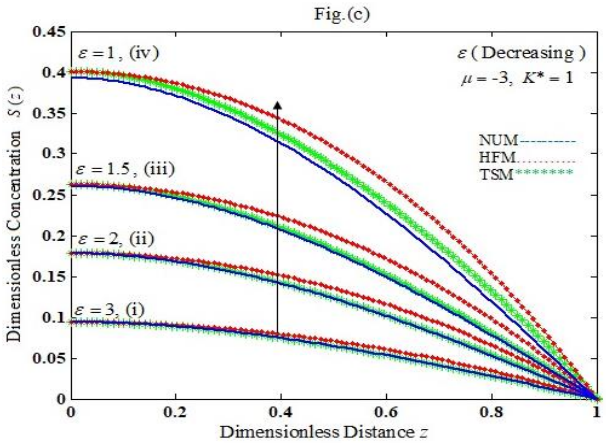


Figure 1. The plot of dimensionless concentrations $a(z)$,$b(z)$ and $S(z)$ versus dimensionless distance z. For various values of the parameter ε , for some fixed values of other parameters and Fig (a) and (b)).for the different values of (i).*m*= 0.59919,(ii). *m*= 0.737434, (iii). *m*= 0.82132, (iv). *m*= 0.90596 using Eqs. (16, 21)and(17, 22) and (c) for the different values of (i).*m*= 0.90596,(ii). *m*= 0.82132, (iii). *m*= 0.737434, (iv). *m*= 0.59919 using Eqs.(18, 23)

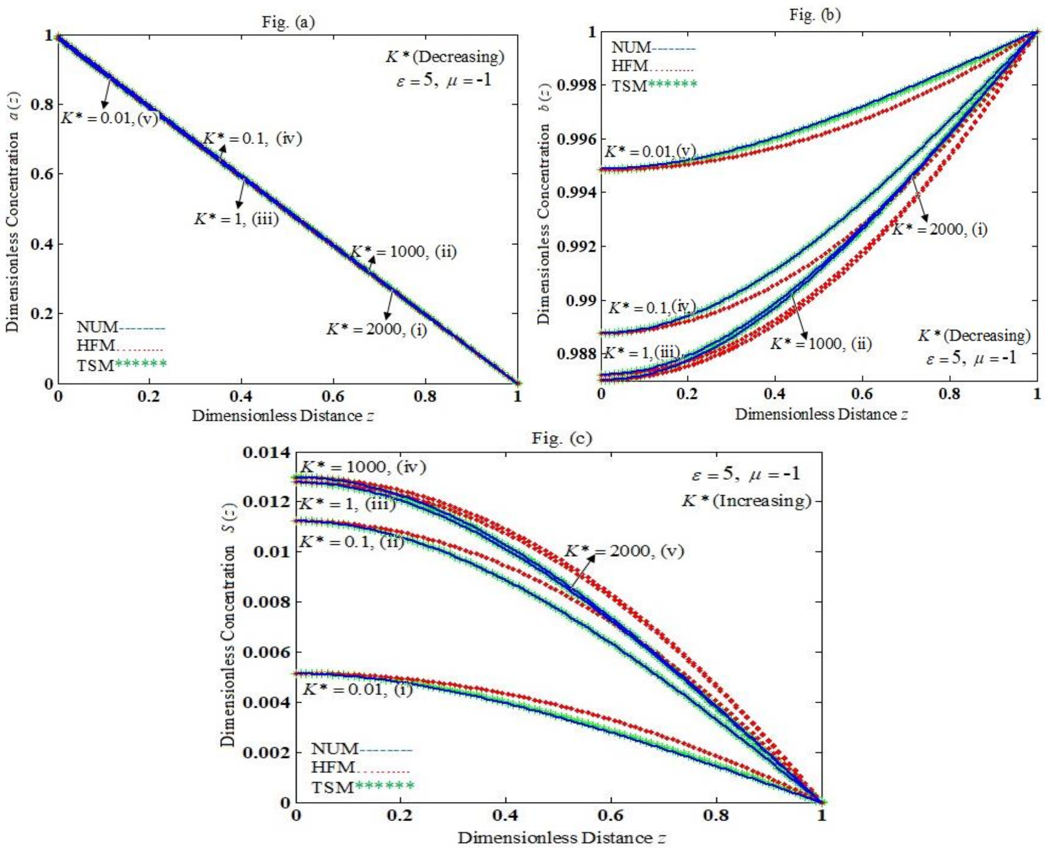


Figure 2. The plot of dimensionless concentrations $a(z)$,$b(z)$ and $S(z)$ versus dimensionless distance z .For various values of the parameter ε , for some fixed values of other parameters and Fig (a) and (b)), for the different values of (i). *m*= 0.98702, (ii).*m*= 0.98702, (iii). *m*= 0.98722, (iv). *m*= 0.988767, (v). *m*=0.994846using Eqs.(16, 21)and (17, 22)and (c) for the different values of (i). *m*= 0.994846, (ii). *m*= 0.988767, (iii).*m*= 0.98722, (iv). *m*= 0.98702, *m*=0.98702,usingEqs.(18, 23)

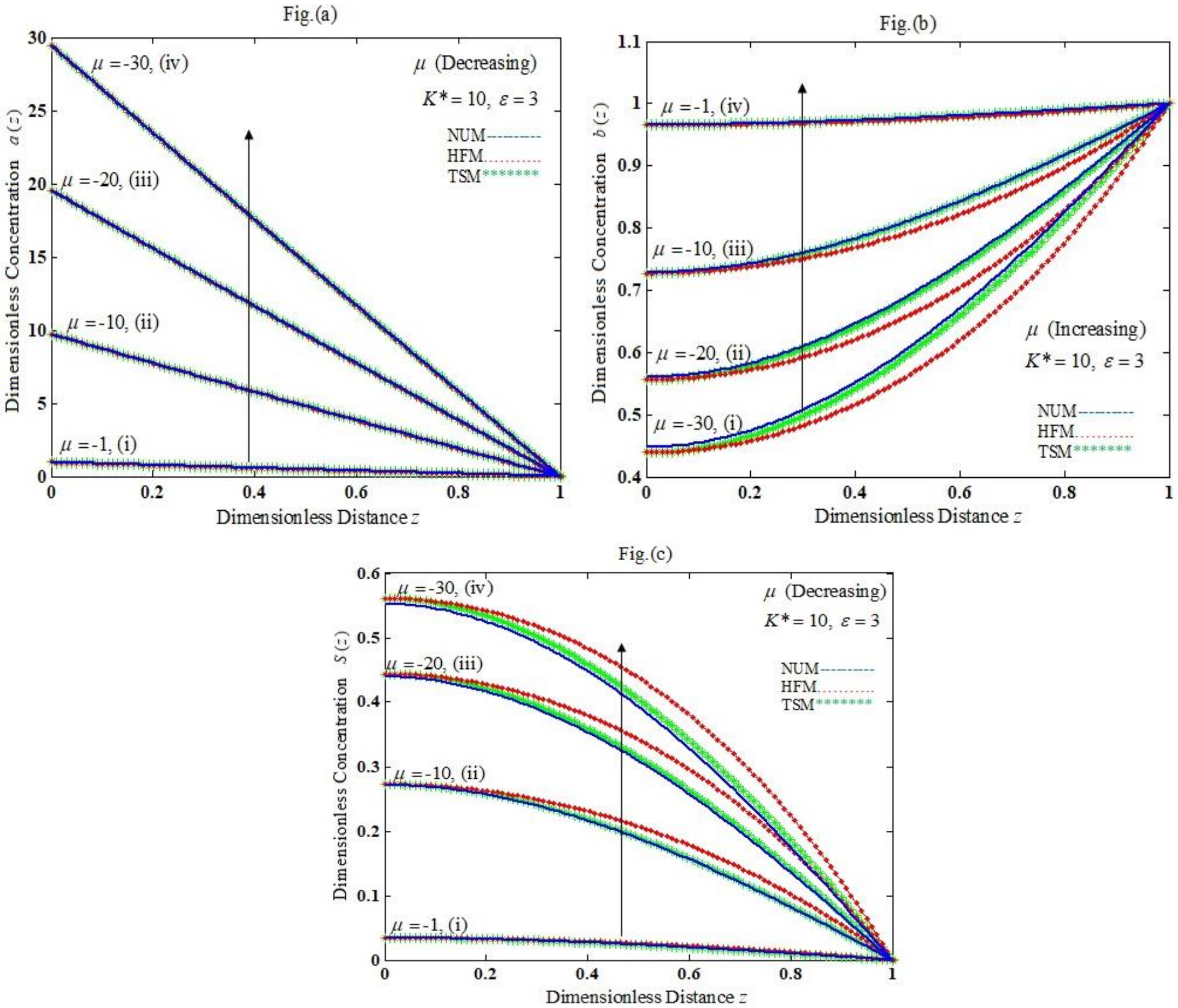


Figure 3. The plot of dimensionless concentrations $a(z), b(z)$ and $S(z)$ versus dimensionless distance z .For various values of the parameter ε , for some fixed values of other parameters and Fig (a) and (c)), for the different values of (i). m= 0.96570, (ii). m= 0.72744, (iii).m= 0.55637, (iv). m= 0.43914, using Eqs. (16, 21)and (17, 22)and (b) for the different values of (i). m= 0.43914,(ii). m= 0.55637, (iii). m= 0.72744, (iv). m= 0.96570using Eqs. (18, 23)

Table 1. Comparison of numerical solution of concentration of species $a(z)$ with the analytical solutions by Taylor series method and Hyperbolic function method for $\mu=-3, K^*=1$ and for different values of ε

ε =0.7, m = 0.482460 (TSM)						ε =0.8, m = 0.523922 (TSM)					ε =0.9, m = 0.562987 (TSM)					ε =1, m = 0.599190 (TSM)				
x	**Num**	**TSM Eq. (16)**	**Err% of TSM**	**HFM Eq. (21)**	**Err% of HFM**	**Num**	**TSM Eq. (16)**	**Err% of TSM**	**HFM Eq. (21)**	**Err% of HFM**	**Num**	**TSM Eq. (16)**	**Err% of TSM**	**HFM Eq. (21)**	**Err% of HFM**	**Num**	**TSM Eq. (16)**	**Err% of TSM**	**HFM Eq. (21)**	**Err% of HFM**
0.0	2.5	2.4825	0.7	2.4825	0.70	2.538	2.5239	0.56	2.5239	0.56	2.573	2.563	0.40	2.563	0.40	2.607	2.5992	0.30	2.5992	0.30
0.2	1.922	1.9069	0.79	1.9004	1.12	1.957	1.9476	0.48	1.9407	0.83	1.991	1.9854	0.28	1.9787	0.62	2.023	2.0202	0.14	2.0138	0.45
0.4	1.39	1.3708	1.38	1.3554	2.49	1.42	1.4102	0.69	1.3922	1.96	1.449	1.4452	0.26	1.4265	1.55	1.463	1.4765	0.92	1.4582	0.33
0.6	0.8942	0.8667	3.08	0.8517	4.75	0.9169	0.904	1.41	0.8816	3.85	0.9383	0.9346	0.39	0.9093	3.09	0.9531	0.9605	0.78	0.9346	1.94
0.8	0.4273	0.3994	6.53	0.3963	7.25	0.4395	0.429	2.39	0.4147	5.64	0.4507	0.4509	0.04	0.4315	4.26	0.4734	0.4679	1.16	0.4467	5.64
1.0	0	0	0	0	0.00	0	0	0.00	0	0.00	0	0	0.00	0	0.00	0	0	0.00	0	0.00
Average			**2.08**		**2.72**			**0.92**		**2.14**			**0.23**		**1.65**			**0.55**		**1.44**

Table 2. Comparison of numerical solution of concentration of substrate $b(z)$ with the analytical solutions by Taylor series method and Hyperbolic function method for $\mu = -3, K^* = 1$ and for different values of ε

	ε =1, *m*= 0.599190 (TSM)					ε =1.5, *m*= 0.737434 (TSM)					ε =2, *m*= 0.821320 (TSM)					ε =3, *m*= 0.905960 (TSM)				
x	**Num**	**TSM Eq. (17)**	**Err% of TSM**	**HFM Eq. (22)**	**Err% of HFM**	**Num**	**TSM Eq. (17)**	**Err% of TSM**	**HFM Eq. (22)**	**Err% of HFM**	**Num**	**TSM Eq. (17)**	**Err% of TSM**	**HFM Eq. (22)**	**Err% of HFM**	**Num**	**TSM Eq. (17)**	**Err% of TSM**	**HFM Eq. (22)**	**Err% of HFM**
0	0.6071	0.5992	1.3	0.5992	1.30	0.7395	0.7374	0.35	0.7374	0.35	0.8219	0.8213	0.10	0.8213	0.10	0.906	0.906	0.00	0.906	0.00
0.2	0.6291	0.6202	1.41	0.6138	2.43	0.7542	0.7518	0.32	0.7474	0.90	0.832	0.8312	0.10	0.8282	0.46	0.9114	0.9112	0.02	0.9097	0.19
0.4	0.6902	0.6765	1.98	0.6582	4.64	0.794	0.7907	0.42	0.7775	2.08	0.8594	0.858	0.16	0.8491	1.20	0.9259	0.9254	0.05	0.9208	0.55
0.6	0.7763	0.7605	2.04	0.7346	5.37	0.8528	0.8483	0.53	0.8286	2.84	0.8997	0.8977	0.22	0.8842	1.72	0.9472	0.9464	0.08	0.9394	0.82
0.8	0.8825	0.8679	1.65	0.8467	4.06	0.9249	0.9195	0.58	0.9021	2.47	0.949	0.9463	0.28	0.9342	1.56	0.9732	0.972	0.12	0.9658	0.76
1.0	1	1	0	1	0.00	1	1	0.00	0	0.00	1	1	0.00	1	0.00	1	1	0.00	1	0.00
Average			**1.40**		**2.97**			**0.37**		**1.44**			**0.14**		**0.84**			**0.05**		**0.39**

Table 3. Comparison of numerical solution of concentration of substrate $S(z)$ with the analytical solutions by Taylor series method and Hyperbolic function method for $\varepsilon = 2,\ \mu = -1$ and for different values of K^*

	K^* =0.1, *m*= 0.961202 (TSM)					K^* =0.2, *m*= 0.949830 (TSM)					K^* =0.5, *m*= 0.938947 (TSM)					K^* =100, *m*= 0.928570 (TSM)				
x	**Num**	**TSM Eq. (18)**	**Err% of TSM**	**HFM Eq. (23)**	**Err% of HFM**	**Num**	**TSM Eq. (18)**	**Err% of TSM**	**HFM Eq. (23)**	**Err% of HFM**	**Num**	**TSM Eq. (18)**	**Err% of TSM**	**HFM Eq. (23)**	**Err% of HFM**	**Num**	**TSM Eq. (18)**	**Err% of TSM**	**HFM Eq. (23)**	**Err% of HFM**
0	0.0386	0.0388	0.52	0.0388	0.52	0.0501	0.0502	0.26	0.0502	0.26	0.061	0.0611	0.26	0.0611	0.26	0.0714	0.0714	0.00	0.0714	0.00
0.2	0.0362	0.0364	0.55	0.0373	3.04	0.047	0.0472	0.43	0.0482	2.55	0.0574	0.0576	0.35	0.0586	2.09	0.0673	0.0674	0.15	0.0686	1.93
0.4	0.0297	0.0303	2.02	0.0326	9.76	0.0391	0.0394	0.77	0.0422	7.93	0.0479	0.0482	0.63	0.0514	7.31	0.0562	0.0566	0.71	0.0601	6.94
0.6	0.0211	0.0216	2.37	0.0249	18.01	0.0277	0.0282	1.81	0.0322	16.25	0.034	0.0345	1.47	0.0392	15.29	0.04	0.0406	1.50	0.0459	14.75
0.8	0.0109	0.0113	3.67	0.014	28.44	0.014	0.0147	5.00	0.0182	30.00	0.0172	0.018	4.65	0.0221	28.49	0.0203	0.0212	4.43	0.0259	27.59
1.0	0	0	0	0	0.00	0	0	0.00	0	0.00	0	0	0.00	0	0.00	0	0	0.00	0	0.00
Average			**1.52**		**9.96**			**1.38**		**9.50**			**1.23**		**8.91**			**1.13**		**8.53**

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NOMENCLATURE

Symbols	**Name**	**Unit**
A	Concentration of species A	mol/cm^3
B	Concentration of species B	mol/cm^3
C	Concentration of species C	mol/cm^3
D	Diffusion coefficient	cm^2/s

k_r, k_f	Reaction-rate constants	s^{-1}
N_{Ao}	Known rate constant	s^{-1}
B_b	Bulk concentration of species B	mol/cm^3
x	Distance from the electrode surface (Eqn.(2))	cm
δ	Diffusion layer of uniform thickness	cm^2/s
$a=\frac{A}{B_b}, b=\frac{B}{B_b}, S=\frac{C}{B_b}$	Dimensionless concentration of the species A, B and C	*None*
z	Dimensionless distance from the electrode surface	*None*
ε	Relative rates of diffusion and reaction	*None*
K^*	Homogeneous equilibrium constant	s^{-1}
μ	Rate of injection of A relative to the limiting flux of B toward the electrode	*None*

APPENDIX A:

Relation between *a*(*z*), *b*(*z*) and *S*(*z*)

Subtract of the Eq. (11) from (12) gives

$$\frac{d^2a}{dz^2}-\frac{d^2b}{dz^2}=0 \tag{A1}$$

Integrating we get,

$$\frac{da}{dz}-\frac{db}{dz}=c \tag{A2}$$

Using the boundary condition (14), we obtain

$$\frac{da}{dz}-\frac{db}{dz}=\mu \tag{A3}$$

Again integrating the above Eq. and using the boundary conditions (15),yields

$$a(z)-b(z)=\mu z-\mu-1 \tag{A4}$$

Similarly

Adding the Eqs. (12) and (13) we get

$$\frac{d^2b}{dz^2}+\frac{d^2S}{dz^2}=0$$

(A5)

Integrating the above Eq. and using the boundary condition(14), we obtain

$$\frac{db}{dz}+\frac{dS}{dz}=\mu \tag{A6}$$

The above Eq. is again integrated and the boundary condition (15) is used.

$$b(z)+S(z)=1 \tag{A7}$$

APPENDIX B:

The solution of eqs. (11)-(13) is using Taylor's series method

The solution of Eqs. (11)-(13) in the form of Taylor series can be written as follows:

$$a(z) = a_0 + za'(0) + \frac{z^2}{2}a''(0) + \frac{z^3}{3!}a'''(0) + \frac{z^4}{4!}a^{iv}(0) + \ldots, \tag{B1}$$

$$b(z) = b_0 + zb'(0) + \frac{z^2}{2}b''(0) + \frac{z^3}{3!}b'''(0) + \frac{z^4}{4!}b^{iv}(0) + \ldots, \tag{B2}$$

$$S(z) = S_0 + zS'(0) + \frac{z^2}{2}S''(0) + \frac{z^3}{3!}S'''(0) + \frac{z^4}{4!}S^{iv}(0) + \ldots \tag{B3}$$

Assume that

$$b(0) = m \tag{B4}$$

Using the relation (A4) we get

$$a(0) = m - \mu - 1, \tag{B5}$$

Using the relation (A7) we obtain

$$S(0) = 1 - m \tag{B6}$$

$$a'(z = 0) = \mu \tag{B7}$$

$$b'(z = 0) = 0 \tag{B8}$$

$$S'(z = 0) = 0 \tag{B9}$$

Using the Eqs. (11)-(13)andsubstitute $a(0), b(0)$ and $S(0)$ we get

$$b''(0) = \frac{1}{\varepsilon^2}\left(m(m - \mu - 1) + \frac{m-1}{k^*}\right), \tag{B10}$$

Using the relations (A1)and (A5), the following results are obtained.

$$a''(0) = b''(0), \tag{B11}$$

$$S''(0) = -b''(0) \tag{B12}$$

Differentiating the Eqs. (11)-(13) and $a'(0), b'(0)$ and $S'(0)$ yields

$$b'''(0) = \frac{1}{\varepsilon^2}(m\mu) \tag{B13}$$

Using the relations (A4) and (A7), we get

$$a'''(0) = b'''(0), \tag{B14}$$

$$S'''(0) = -b'''(0) \tag{B15}$$

Double differentiating the Eq. (11)-(13)and $a''(0), b''(0)$ and $S''(0)$ we obtain

$$b^{iv}(0) = \frac{1}{\varepsilon^4}\left(m(m - \mu - 1) + \frac{m-1}{k^*}\right)\left(2m - \mu - 1 + \frac{1}{k^*}\right) \tag{B16}$$

The following results are obtained using the Eq. (A1) and (A5).

$$b^{iv}(0) = a^{iv}(0), \tag{B17}$$

$$S^{iv}(0) = -b^{iv}(0) \tag{B18}$$

Again differentiating the Eq. we get

$$b^{v}(0) = \frac{1}{\varepsilon^4}\left\{(\mu m)\left(2m - \mu - 1 + \frac{1}{k^*}\right) + 3\mu\left(m(m - \mu - 1) + \frac{m-1}{k^*}\right)\right\} \tag{B19}$$

Again differentiating the Eq. we obtain

$$b^{vi}(0)=\frac{1}{\varepsilon^6}\left\{\left(m(m-\mu-1+\frac{m-1}{K^*}\right)\left(2m-\mu-1+\frac{1}{K^*}\right)^2+6\left(m(m-\mu-1)+\frac{m-1}{K^*}\right)^2+4\varepsilon^2 m\mu^2\right\}\frac{x^6}{6!}+$$

(B20)

We get

$$b(z)=m+\frac{z^2}{2\varepsilon^2}\left(m(m-\mu-1)+\frac{m-1}{k^*}\right)+\frac{z^3}{\varepsilon^2 3!}(m\mu)+\frac{z^4}{\varepsilon^4 4!}\left(2m-\mu-1+\frac{1}{k^*}\right)\left(m(m-\mu-1)+\frac{m-1}{k^*}\right)$$
$$+\frac{1}{\varepsilon^4}\left\{(\mu m)\left(2m-\mu-1+\frac{1}{k^*}\right)+3\mu\left(m(m-\mu-1)+\frac{m-1}{k^*}\right)\right\}\frac{x^5}{5!}$$
$$+\frac{1}{\varepsilon^6}\left\{\left(m(m-\mu-1+\frac{m-1}{K^*}\right)\left(2m-\mu-1+\frac{1}{K^*}\right)^2+6\left(m(m-\mu-1)+\frac{m-1}{K^*}\right)^2+4\varepsilon^2 m\mu^2\right\}\frac{x^6}{6!}+....$$

(B21)

Where m obtained as follows:

$$1=m+\frac{1}{2\varepsilon^2}\left(m(m-\mu-1)+\frac{m-1}{k^*}\right)+\frac{1}{\varepsilon^2 3!}(m\mu)+\frac{1}{\varepsilon^4 4!}\left(2m-\mu-1+\frac{1}{k^*}\right)\left(m(m-\mu-1)+\frac{m-1}{k^*}\right)$$
$$+\frac{1}{\varepsilon^4}\left\{(\mu m)\left(2m-\mu-1+\frac{1}{k^*}\right)+3\mu\left(m(m-\mu-1)+\frac{m-1}{k^*}\right)\right\}\frac{1}{5!} \quad \text{(B22)}$$
$$+\frac{1}{\varepsilon^6}\left\{\left(m(m-\mu-1+\frac{m-1}{K^*}\right)\left(2m-\mu-1+\frac{1}{K^*}\right)^2+6\left(m(m-\mu-1)+\frac{m-1}{K^*}\right)^2+4\varepsilon^2 m\mu^2\right\}\frac{x^6}{6!}+....$$

The concentration of species B (Eq. (17) in the text) can be obtained by simplifying the Eq.(B21).The concentration of species A (Eq.(16) and species S (Eq.(18)) can be computed using the Eq.(A4) and Eq. (A7).

APPENDIX C:

Solution of equations (11)-(13) is using Hyperbolic function method

The trail solution of Eq. (12) is assumed in the following form:

$$b(z)=A\cosh(nz)+B\sinh(nz) \quad \text{(C1)}$$

Using the boundary conditions Eqs. (14) and (15), we can obtain the constant

$$A=\frac{1}{\cosh m},\ B=0 \quad \text{(C2)}$$

The function$b(z)$ becomes

$$b(z)=\frac{\cosh(nz)}{\cosh n} \quad \text{(C3)}$$

Where n is a constant. Using (A4) we get

$$a(z)=\mu z-\mu-1+\frac{\cosh(nz)}{\cosh n} \quad \text{(C4)}$$

Using (A7) we obtain

$$S(z)=1-\frac{\cosh(nz)}{\cosh n} \quad \text{(C5)}$$

At z= 0 the equation (C3)becomes

$$b(0) = \frac{1}{\cosh n} = m \qquad \text{i.e., } n = \cosh^{-1}\left(\frac{1}{m}\right) \tag{C6}$$

Now the concentrations of species *A* and *S*can be obtained as follows:

$$a(z) = \mu z - \mu - 1 + m\cosh\left(\cosh^{-1}\left(\frac{1}{m}\right)\right)z \tag{C7}$$

$$S(z) = 1 - m\cosh\left(\cosh^{-1}\left(\frac{1}{m}\right)\right)z \tag{C8}$$

APPENDIX D.

Matlab Program For The Numerical Solution of Nonlinear Differential Eqs. (11)-(13)

```
function sol=ex6
ex6init=bvpinit(linspace(0,1),[0 1 1 0 0 0]);
sol = bvp4c(@ex6ode,@ex6bc,ex6init)
end
functiondydx=ex6ode(x,y)
dydx=[y(2)
(1/(2)^2)*(y(1)*y(3)-((y(5))/(3)))
y(4)
(1/(2)^2)*(y(1)*y(3)-((y(5))/(3)))
y(6)
(1/(2)^2)*(((y(5))/(3)))-y(1)*y(3)];
end
function res=ex6bc(ya,yb)
res=[ya(1)-0
yb(2)-1
ya(3)-1
yb(4)-0
ya(5)-0
yb(6)-0];
end
```

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