

Analytical Solution of Non Linear Problems in Homogeneous Reactions Occur in the Mass-Transfer Boundary Layer: Homotopy Perturbation Method

Rajagopal Swaminathan¹, R. Saravanakumar³, Kothandapani Venugopal², L. Rajendran^{4,*}

¹ Department of Mathematics, VidhyaaGiri College of Arts and Science, Sivaganga - 630108, India

² PG, Research & Department of Mathematics, Govt Arts College (Affiliated to Bharathidasan University), Kulithalai - 639120, India

³ Department of Mathematics, Anna University, University college of Engineering, Dindigul, India

⁴ Department of Mathematics, AMET (Deemed to be university), Kanathur, Chennai, India

*E-mail: raj_sms@rediffmail.com

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Mathematical models for mass transfer accompanied by a reversible homogeneous chemical reaction are discussed. This model is based on a system of nonlinear equations containing a nonlinear term related to reversible homogeneous reactions. When reactions arise in the mass-transfer boundary layer, the measurement of mass transfer to and from electrodes frequently needs the species concentrations. We can obtain the concentration of species by solving the nonlinear equations using the homotopy perturbation method. Our approximate analytical results are also compared with the simulation result. A satisfactory agreement is observed between our analytical and simulation results. The approximate analytical expression obtained here can be used to estimate the system's dynamical behaviour. The influence of the parameters on concentration is discussed and presented graphically.

Keywords: Mathematical modeling, Nonlinear equations, Homotopy perturbation method, Reversible homogeneous reactions.

1. INTRODUCTION

Many electrode processes with homogeneous reactions that occur continuously in the mass-transfer boundary layer. These reactions involve splitting or forming in the process of deposition or degradation of metal-linking complexes, the interaction and dissociation of ions and redox soluble mediators. Quantitative studies of electrode-kinetics experiments as well as simulation of electrochemical reactor processes require the description of species concentrations at the electrode surface. Homogeneous reactions can strongly affect the concentration of species.

The computation of concentration profiles near electrodes in the solution is based on the species conservation equation.

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i + R_i \tag{1}$$

where c_i is the molar concentration of species i , and R_i is the net rate of production of i locally by homogeneous reactions. The molar flux N_i and the rate of production of $M_i^{z_i}$ usually represented by

$$N_i = -D_i \nabla c_i - z_i c_i D_i \frac{F}{RT} \nabla \phi + c_i v \text{ and } R_i = v_i \left[k_r \prod_j c_j^{v_j} - k_f \prod_i c_i^{v_i} \right] \tag{2}$$

This describes species transport through diffusion and convection and ion migration in an electric field [1]. When charged species are involved, equations 1-2 must be written for each species in solution and combined with the electroneutrality state $\sum_i z_i c_i = 0$, and ϕ must be determined. Implementation of appropriate boundary conditions on the electrode surface and in the bulk solution is needed for their solution. This kind of nonlinear problems occurs in many relevant situations, such as cyclic voltammetry, chronopotentiometry, rotating disk and ring-disk electrodes, and various boundary-layer flows with multiple geometries, system chemistries, flow and boundary conditions [2]-[6].

Recently Chapman et al [7] discuss the mass transfer at the electrodes for the homogeneous and fast reversible reaction. More recently the empirical expression of species concentration using the Taylor series method and hyperbolic function method was obtained by Mary et al. [8]. In this communication, we present a simple and effective homotopy perturbation approach for solving the nonlinear differential equation in the sense of mass transfer at the electrodes with reversible homogeneous reactions. An approximate analytical expression for the concentration of species in the homogeneous electrochemical reaction is obtained for various parameter values.

2. MATHEMATICAL FORMULATION OF THE PROBLEM

Consider the reversible homogeneous reaction



A is formed at a known rate N_{A0} at an electrode surface, and B is present in the bulk solution. The concentrations of A and C in the bulk solution are negligible, and the fluxes of B and C at the electrode surface are also zero. The homogeneous reaction forms the species C and diffuses into the bulk. For measuring concentration profiles, Eqs. (1) and (2) may be combined for each component. We assume the steady-state and ignore migration and convection in the diffusion layer [7]. In this case, the system of nonlinear one-dimensional reaction-diffusion equations becomes as follows [7]:

$$D \frac{d^2 A(x)}{dx^2} = -k_r C(x) + k_f A(x)B(x) \tag{4}$$

$$D \frac{d^2 B(x)}{dx^2} = -k_r C(x) + k_f A(x) B(x) \tag{5}$$

$$D \frac{d^2 C(x)}{dx^2} = k_r C(x) - k_f A(x) B(x) \tag{6}$$

The k coefficients denote the forward and reverse reaction rate constants, and A , B , and C represent the species concentrations. Both diffusion coefficients are assumed to be equal to a constant D for the sake of consistency. The boundary conditions are

$$D \frac{dA}{dx} = -N_{Ao}; \quad \frac{dB}{dx} = \frac{dC}{dx} = 0 \text{ at } x = 0 \tag{7}$$

$$A = 0; \quad B = B_b; \quad C = 0 \text{ at } x = \delta \tag{8}$$

By introducing the following dimensionless variables

$$a = \left[\frac{A}{B_b} \right], \quad b = \left[\frac{B}{B_b} \right], \quad S = \left[\frac{C}{B_b} \right], \quad z = \left[\frac{x}{\delta} \right], \tag{9}$$

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

Eqns. (4)-(6) becomes in dimensionless form as follows:

$$\varepsilon^2 \frac{d^2 a(z)}{dz^2} = a(z)b(z) - \frac{S(z)}{K^*} \tag{10}$$

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

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

The corresponding dimensionless boundary conditions are,

$$a'(z=0) = \mu, \quad b'(z=0) = 0, \quad S'(z=0) = 0 \tag{13}$$

$$a(z=1) = 0, \quad b(z=1) = 1, \quad S(z=1) = 0 \tag{14}$$

where ε is the relative rates of diffusion and reaction. K^* is the homogeneous equilibrium constant. μ is the rate of injection of A relative to the limiting flux of B toward the electrode

3. ANALYTICAL EXPRESSION OF THE CONCENTRATION USING HOMOTOPY PERTURBATION METHOD

The nonlinear equations (10)-(12), in recent years, numerous methods have been developed to derive analytical or semi-analytical solutions regardless of how strong the nonlinearity maybe. Homotopy analysis method [9,10], variational iteration method[11,12], Adomian decomposition method[13] and Green's function iterative method[14,15] are used to solve the nonlinear equations. Due to its simple implementation and high accuracy, the homotopy perturbation method(HPM)[16-20], Residual method[21], Padé approximants method[22], Akbari-I Ganji's method (AGM)[23] and Taylor series method[24], the new approach of homotopy perturbation method(NHPM)[25,26] has received great deal of attention.

By solving equations (10)-(12) using the homotopy perturbation approach (details in Appendix A), the following approximate analytical representation of ionic concentration is obtained .

$$a(z) = \mu(z-1) + \frac{\mu}{120K^* \varepsilon^4} \left[(z-1)(z^2 - 2z - 4)^2 + 20K^* \varepsilon^2 (z^3 - 3z^2 + 2) \right] \quad (15)$$

$$b(z) = 1 + \frac{\mu}{120K^* \varepsilon^4} \left[(z-1)(z^2 - 2z - 4)^2 + 20K^* \varepsilon^2 (z^3 - 3z^2 + 2) \right] \quad (16)$$

$$S(z) = 1 - b(z) \quad (17)$$

4. PREVIOUS ANALYTICAL RESULTS

Chapman [7] derived approximate distributions of concentration. Consider the case of small ε , that is, the case where the homogeneous rate constant k_f is large enough to make ε small. If the first term ε is neglected, the following solutions are obtained from a quadratic algebraic equation for S.

$$S(z) = \frac{1}{2} \left[\left(\mu(1-z) + 1 + \frac{1}{K^*} \right) - \left(\left(\mu(1-z) + 1 + \frac{1}{K^*} \right)^2 - 4\mu(1-z) \right)^{1/2} \right] \quad (18)$$

$$a(z) = \mu(1-z) - S(z) \quad (19)$$

$$b(z) = 1 - S(z) \quad (20)$$

Recently, Mary et al. [8] used Taylor's series method (TSM) to obtain the analytical representation of species concentration as follows:

$$a(z) = b(z) + \mu z - \mu - 1 \quad (21)$$

$$b(z) = m + \frac{\alpha z^2}{2\varepsilon^2} + \frac{(m\mu)z^3}{\varepsilon^2 3!} + \frac{\alpha \beta z^4}{\varepsilon^4 4!} + \frac{1}{\varepsilon^4} [\beta \mu m + 3\alpha \mu] \frac{z^5}{5!} + \frac{1}{\varepsilon^6} [\alpha \beta^2 + 6 \alpha^2 + 4\varepsilon^2 m \mu^2] \frac{z^6}{6!} \quad (22)$$

$$S(z) = 1 - b(z) \quad (23)$$

$$\text{where } \alpha = m(m - \mu - 1) + \frac{m-1}{K^*} \quad \beta = 2m - \mu - 1 + \frac{1}{K^*} \quad (24)$$

The value of m is obtained by solving the following equation.

$$m + \frac{\alpha}{2\varepsilon^2} + \frac{m\mu}{\varepsilon^2 3!} + \frac{\alpha\beta}{\varepsilon^4 4!} + \frac{1}{\varepsilon^4} [\mu \beta m + 3\mu\alpha] \frac{1}{5!} + \frac{1}{\varepsilon^6} [\alpha \beta^2 + 6 \alpha^2 + 4\varepsilon^2 m \mu^2] \frac{1}{6!} - 1 = 0 \quad (25)$$

But in this method, it is very difficult to find the constant m. Our analytical results (Eqs. (15)-(17)) are easily computable when compared with Taylor's series solution (Eqs. (21)-(23)).

5. NUMERICAL SIMULATION AND DISCUSSION

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

z	$\varepsilon = 0.7$					$\varepsilon = 0.8$					$\varepsilon = 0.9$				
	Num	Our HPM Eq.(15)	Error % of HPM	TSM Eq.(21)	Error % of TSM	Num	Our HPM Eq.(15)	Error % of HPM	TSM Eq.(21)	Error % of TSM	Num	Our HPM Eq.(15)	Error % of HPM	TSM Eq.(21)	Error % of TSM
0	2.500	2.494	0.24	2.483	0.70	2.538	2.527	0.44	2.483	0.56	2.573	2.568	0.21	2.563	0.40
0.2	1.922	1.920	0.11	1.907	0.79	1.957	1.949	0.42	1.907	0.48	1.991	1.997	0.31	1.985	0.28
0.4	1.390	1.380	0.70	1.371	1.38	1.420	1.415	0.37	1.371	0.69	1.449	1.436	0.90	1.445	0.26
0.6	0.894	0.889	0.53	0.867	3.08	0.917	0.909	0.82	0.867	1.41	0.938	0.929	0.95	0.935	0.39
0.8	0.427	0.424	0.88	0.399	6.53	0.440	0.436	0.84	0.399	2.39	0.451	0.444	1.51	0.451	0.04
1	0.000	0.000	0.00	0.000	0.00	0.000	0.000	0.00	0.000	0.00	0.000	0.000	0.00	0.000	0.00
Average % error			0.41		2.08			0.48		0.92			0.65		0.23

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

z	$\varepsilon = 1$					$\varepsilon = 1.5$					$\varepsilon = 2$				
	Num	Our HPM Eq.(16)	Error % of HPM	TSM Eq.(22)	Error % of TSM	Num	Our HPM Eq.(16)	Error % of HPM	TSM Eq.(22)	Error % of TSM	Num	Our HPM Eq.(16)	Error % of HPM	TSM Eq.(22)	Error % of TSM
0	0.607	0.603	0.68	0.599	1.30	0.740	0.737	0.34	0.737	0.35	0.821	0.816	0.62	0.822	0.10
0.2	0.629	0.624	0.80	0.614	1.41	0.754	0.747	0.91	0.752	0.32	0.832	0.827	0.64	0.832	0.10
0.4	0.690	0.687	0.42	0.658	1.98	0.794	0.789	0.68	0.791	0.42	0.859	0.855	0.54	0.858	0.16
0.6	0.776	0.778	0.15	0.735	2.04	0.853	0.849	0.47	0.848	0.53	0.900	0.896	0.41	0.898	0.22
0.8	0.883	0.885	0.25	0.847	1.65	0.925	0.921	0.39	0.919	0.58	0.949	0.946	0.33	0.947	0.28
1	1.000	1.000	0.00	1.000	0.00	1.000	1.000	0.00	1.000	0.00	1.000	1.000	0.00	1.000	0.00
Average % error			0.38		1.40			0.46		0.37			0.43		0.14

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

z	$K^* = 0.1$					$K^* = 0.2$					$K^* = 0.5$				
	Num	Our HPM Eq.(17)	Error % of HPM	TSM Eq.(23)	Error % of TSM	Num	Our HPM Eq.(17)	Error % of HPM	TSM Eq.(23)	Error % of TSM	Num	Our HPM Eq.(17)	Error % of HPM	TSM Eq.(23)	Error % of TSM
0	0.039	0.038	0.78	0.039	0.52	0.050	0.050	0.20	0.050	0.26	0.061	0.061	0.49	0.061	0.26
0.2	0.036	0.036	0.84	0.036	0.55	0.047	0.047	0.04	0.047	0.43	0.057	0.058	0.35	0.058	0.35
0.4	0.030	0.030	0.34	0.030	2.02	0.039	0.039	0.93	0.039	0.77	0.048	0.048	0.42	0.048	0.63
0.6	0.021	0.021	0.42	0.022	2.37	0.028	0.027	0.91	0.028	1.81	0.034	0.034	0.58	0.035	1.47
0.8	0.011	0.011	0.46	0.011	3.67	0.014	0.014	0.14	0.015	5.00	0.017	0.017	0.58	0.018	4.65
1	0.000	0.000	0.00	0.000	0.00	0.000	0.000	0.00	0.000	0.00	0.000	0.000	0.00	0.000	0.00
Average % error			0.47		1.52			0.37		1.38			0.40		1.23

The differential Eqns. (10)-(12) with the corresponding boundary conditions has also been solved numerically using SCILAB/MATLAB program (Appendix-B). The numerical solution is compared with our analytical results (HPM method) and previously available results(Taylors series method) in Tables 1–3. There is no much difference in average error percentage between HPM and TSM. But we can easily calculate the concentration for all values of the parameter in HPM.

Also, a comparison between the analytical and numerical results are shown in Figures 1.The maximum error between analytical (HPM) and the numerical result is 1.35%. It is evident from Tables 1-12 and Fig. 1 that our results are very close to the exact simulation results.

Table 4. Comparison of our analytical expression of concentration of species *a* with the numerical result for various values of the parameter μ and some fixed values parameter $\varepsilon = 2, \mu = -1$ using Eqn. (15).

<i>z</i>	$K^* = 1$			$K^* = 10$			$K^* = 1000$		
	Numerical Result	Our Eq.(15)	% of deviation	Numerical Result	Our Eq.(15)	% of deviation	Numerical Result	Our Eq.(15)	% of deviation
0	0.934	0.925	0.98	0.929	0.918	1.26	0.929	0.917	1.28
0.2	0.736	0.729	0.92	0.731	0.722	1.24	0.731	0.721	1.28
0.4	0.544	0.541	0.64	0.540	0.535	1.03	0.540	0.534	1.06
0.6	0.357	0.358	0.09	0.354	0.353	0.29	0.354	0.353	0.35
0.8	0.173	0.178	2.66	0.172	0.176	2.21	0.172	0.175	2.18
1	0.000	0.000	0.00	0.000	0.000	0.00	0.000	0.000	0.00
Average percentage error: 0.88			Average percentage error: 1.00			Average percentage error: 1.02			

Table 5. Comparison of our analytical expression of concentration of species *b* with the numerical result for various values of the parameter μ and some fixed values parameter $\varepsilon = 2, \mu = -1$ using Eqn. (16).

<i>z</i>	$K^* = 1$			$K^* = 10$			$K^* = 1000$		
	Numerical Result	Our Eq.(16)	% of deviation	Numerical Result	Our Eq.(16)	% of deviation	Numerical Result	Our eq.(16)	% of deviation
0	0.934	0.925	0.99	0.929	0.918	1.26	0.929	0.917	1.28
0.2	0.938	0.929	0.93	0.933	0.922	1.19	0.933	0.921	1.22
0.4	0.948	0.941	0.79	0.944	0.935	1.01	0.944	0.934	1.03
0.6	0.963	0.958	0.59	0.960	0.953	0.75	0.960	0.953	0.76
0.8	0.981	0.978	0.35	0.980	0.976	0.43	0.980	0.975	0.45
1	1.000	1.000	0.00	1.000	1.000	0.00	1.000	1.000	0.00
Average percentage error: 0.61			Average percentage error: 0.77			Average percentage error: 0.79			

Table 6. Comparison of our analytical expression of concentration of species S with the numerical result for various values of the parameter μ and some fixed values parameter $\varepsilon = 4, \mu = -1$ using Eqn. (17).

z	$K^* = 1$			$K^* = 10$			$K^* = 1000$		
	Numerical Result	Our Eq.(17)	% of deviation	Numerical Result	Our Eq.(17)	% of deviation	Numerical Result	Our Eq.(17)	% of deviation
0	0.020	0.019	0.89	0.020	0.020	0.73	0.020	0.020	0.23
0.2	0.018	0.018	0.79	0.019	0.019	0.64	0.019	0.019	0.65
0.4	0.015	0.015	0.51	0.015	0.016	3.19	0.016	0.016	0.29
0.6	0.011	0.011	0.25	0.011	0.011	0.45	0.011	0.011	0.44
0.8	0.006	0.006	2.91	0.006	0.006	3.09	0.006	0.006	3.11
1	0.000	0.000	0.00	0.000	0.000	0.00	0.000	0.000	0.00
Average percentage error : 0.89			Average percentage error : 1.35			Average percentage error : 0.79			

Table 7. Comparison of our analytical expression of concentration of species a with the numerical result for various values of the parameter μ and some fixed values parameter $\varepsilon = 2, K^* = 1$ using Eqn. (15).

z	$\mu = -1$			$\mu = -1.5$			$\mu = -2$		
	Numerical Result	Our Eq.(15)	% of deviation	Numerical Result	Our Eq.(15)	% of deviation	Numerical Result	Our Eq.(15)	% of deviation
0	0.934	0.925	0.98	1.388	1.404	1.18	1.875	1.850	1.33
0.2	0.736	0.729	0.92	1.094	1.106	1.10	1.478	1.459	1.32
0.4	0.544	0.541	0.64	0.811	0.818	0.88	1.094	1.082	1.15
0.6	0.357	0.358	0.10	0.536	0.537	0.15	0.718	0.715	0.38
0.8	0.173	0.178	2.65	0.267	0.261	2.40	0.348	0.356	2.18
1	0.000	0.000	0.00	0.000	0.000	0.00	0.000	0.000	0.00
Average percentage error : 0.88			Average percentage error : 0.95			Average percentage error : 1.06			

Table 8. Comparison of our analytical expression of concentration of species a with the numerical result for various values of the parameter ε and some fixed values parameter $\mu = -1, K^* = 4$ using Eqn. (15).

z	$\varepsilon = 2$			$\varepsilon = 5$			$\varepsilon = 8$		
	Numerical Result	Our Eq.(15)	% of deviation	Numerical Result	Our Eq.(15)	% of deviation	Numerical Result	Our Eq.(15)	% of deviation
0	0.930	0.919	1.22	0.987	0.987	0.04	0.995	0.995	0.01
0.2	0.732	0.723	1.20	0.786	0.788	0.21	0.793	0.795	0.25
0.4	0.541	0.536	0.96	0.586	0.590	0.63	0.592	0.596	0.67
0.6	0.355	0.354	0.26	0.387	0.393	1.49	0.391	0.397	1.52
0.8	0.172	0.176	2.31	0.188	0.196	4.18	0.191	0.199	4.18
1	0.000	0.000	0.00	0.000	0.000	0.00	0.000	0.000	0.00
Average percentage error: 0.99			Average percentage error: 1.09			Average percentage error : 1.11			

Table 9. Comparison of our analytical expression of concentration of species *b* with the numerical result for various values of the parameter μ and some fixed values parameter $\varepsilon = 2, K^* = 10$ using Eqn. (16).

<i>z</i>	$\mu = -1$			$\mu = -1.5$			$\mu = -2$		
	Numerical Result	Our Eq.(16)	% of deviation	Numerical Result	Our Eq.(16)	% of deviation	Numerical Result	Our Eq.(16)	% of deviation
0	0.9272	0.9173	1.07	0.8967	0.8873	1.05	0.8661	0.8497	1.92
0.2	0.9329	0.9219	1.17	0.9021	0.8936	0.94	0.8737	0.8582	1.81
0.4	0.9435	0.9345	0.95	0.9186	0.9108	0.85	0.8943	0.8810	1.51
0.6	0.9594	0.9530	0.66	0.9420	0.9360	0.64	0.9212	0.9147	0.71
0.8	0.9798	0.9755	0.44	0.9705	0.9667	0.40	0.9617	0.9555	0.65
1	1.0000	1.0000	0.00	1.000	1.000	0.00	1.0000	1.0000	0.00
Average percentage error : 0.72			Average percentage error : 0.65			Average percentage error : 1.10			

Table 10. Comparison of our analytical expression of concentration of species *b* with the numerical result for various values of the parameter ε and some fixed values parameter $\mu = -2, K^* = 50$ using Eqn. (16).

<i>z</i>	$\varepsilon = 1$			$\varepsilon = 4$			$\varepsilon = 7$		
	Numerical Result	Our Eq.(16)	% of deviation	Numerical Result	Our Eq.(16)	% of deviation	Numerical Result	Our Eq.(16)	% of deviation
0	0.8652	0.8437	2.55	0.9607	0.9456	1.60	0.9867	0.9815	0.53
0.2	0.8729	0.8530	2.33	0.9630	0.9487	1.51	0.9874	0.9825	0.50
0.4	0.8936	0.8783	1.75	0.9690	0.9569	1.26	0.9895	0.9853	0.42
0.6	0.9242	0.9155	0.95	0.9780	0.9691	0.92	0.9925	0.9895	0.30
0.8	0.9614	0.9608	0.07	0.9888	0.9839	0.50	0.9960	0.9945	0.15
1	1.0000	1.0000	0.00	1.0000	1.0000	0.00	1.0000	1.0000	0.00
Average percentage error : 1.27			Average percentage error : 0.96			Average percentage error : 0.32			

Table 11. Comparison of our analytical expression of concentration of species *S* with the numerical result for various values of the parameter ε and some fixed values parameter $\varepsilon = 4, K^* = 100$ using Eqn. (17).

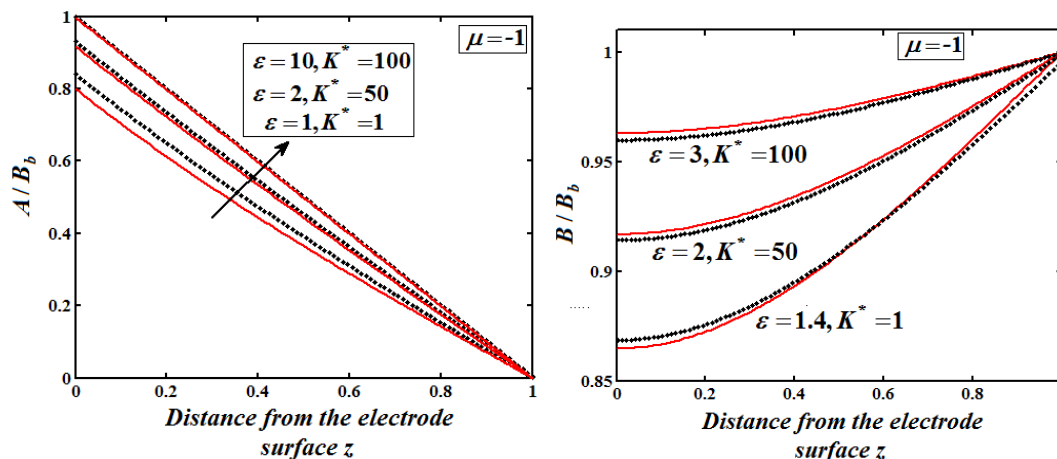
<i>z</i>	$\mu = -1$			$\mu = -1.5$			$\mu = -2$		
	Numerical Result	Our Eq.(17)	% of deviation	Numerical Result	Our Eq.(17)	% of deviation	Numerical Result	Our Eq.(17)	% of deviation
0	0.0200	0.0198	0.71	0.0297	0.0294	0.93	0.0393	0.0388	1.14
0.2	0.0189	0.0187	1.21	0.0280	0.0278	0.83	0.0370	0.0367	1.06
0.4	0.0157	0.0157	0.31	0.0234	0.0233	0.54	0.0310	0.0307	0.76
0.6	0.0115	0.0112	1.81	0.0167	0.0167	0.23	0.0220	0.0220	0.03
0.8	0.0057	0.0059	3.00	0.0085	0.0087	2.80	0.0112	0.0115	2.54
1	0.0000	0.0000	0.00	0.0000	0.0000	0.00	0.0000	0.0000	0.00
Average percentage error : 1.17			Average percentage error : 0.89			Average percentage error : 0.92			

Table 12. Comparison of our analytical expression of concentration of species S with the numerical result for various values of the parameter ε and some fixed values parameter $\mu = -2, K^* = 500$ using Eqn. (17).

z	$\varepsilon = 5$			$\varepsilon = 7$			$\varepsilon = 10$		
	Numerical Result	Our Eq.(17)	% of deviation	Numerical Result	Our Eq.(17)	% of deviation	Numerical Result	Our Eq.(17)	% of deviation
0	0.0257	0.0255	0.63	0.0133	0.0133	0.27	0.0066	0.0066	0.09
0.2	0.0242	0.0241	0.51	0.0126	0.0126	0.17	0.0062	0.0062	0.59
0.4	0.0202	0.0202	0.17	0.0105	0.0105	0.24	0.0051	0.0052	1.61
0.6	0.0144	0.0145	0.63	0.0075	0.0076	1.03	0.0037	0.0037	1.87
0.8	0.0073	0.0075	3.18	0.0038	0.0039	3.60	0.0019	0.0020	2.75
1	0.0000	0.0000	0.00	0.0000	0.0000	0.00	0.0000	0.0000	0.00
Average percentage error: 0.85			Average percentage error : 0.88			Average percentage error : 1.15			

The concentration of species depends upon the parameter 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^*). Figure 1, shows the concentration of species $a(z), b(z)$ and $S(z)$ for various values of relative rates of diffusion and reaction and the homogeneous equilibrium constant.

From this fig.1, it is observed that an increase in equilibrium constant leads to increase in $a(z)$ and $b(z)$ and decreases in $S(z)$. From this fig.2, it is noted that an increase in rate of injection leads to decrease in $a(z), b(z)$ and $S(z)$.



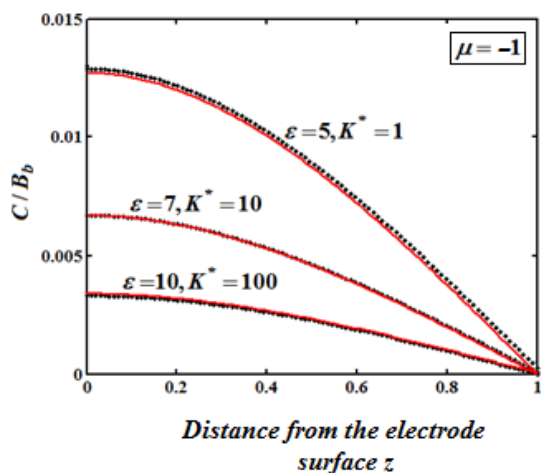


Figure 1. Comparison of concentrations $a(z), b(z)$ and $S(z)$ (Eqns. (15)-(17)) with simulation results for various values of parameters ε, K^* and μ .

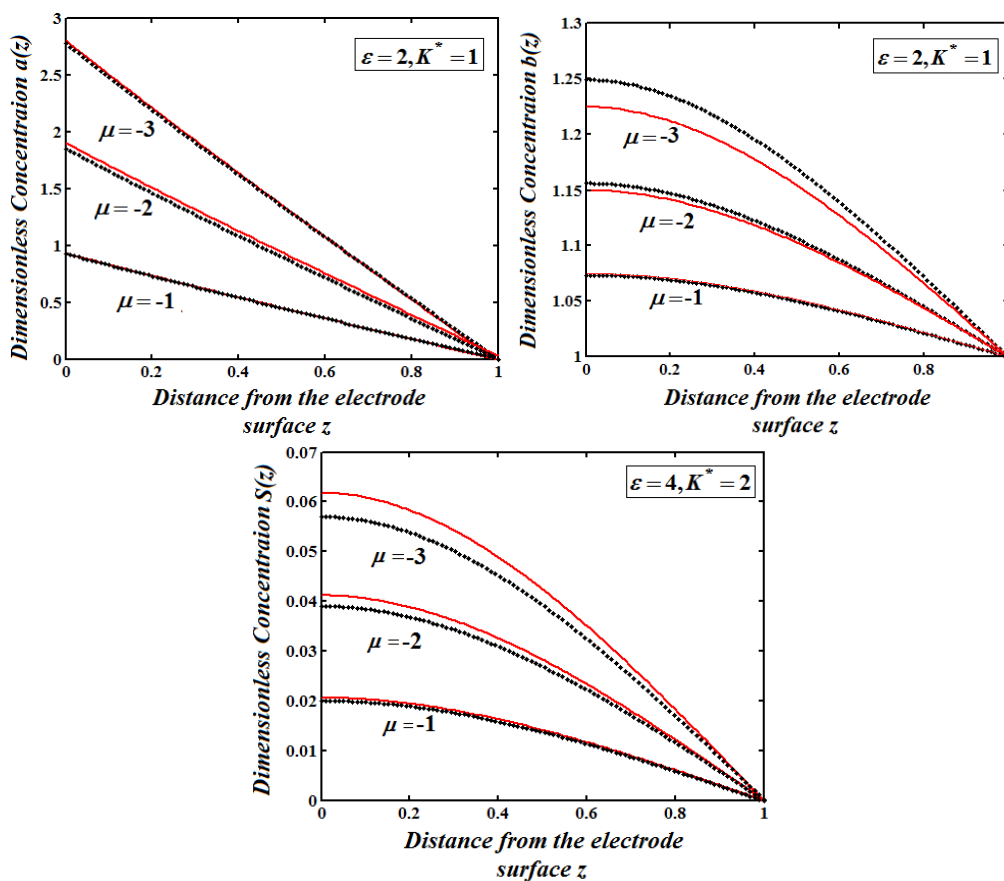


Figure 2. Comparison of concentrations $a(z), b(z)$ and $S(z)$ (Eqns. (15)-(17)) with simulation results for various values of parameters ε, K^* and μ .

6. CONCLUSION

An analytical expression has effectively derived the concentration in the rotating disc electrode controlled by migration and convection in the diffusion layer for all values of the reaction rate constants. In this analysis, the model is applied to a rotating disk electrode in a one-dimensional situation. The nonlinear reaction-diffusion equations at steady-state are solved analytically by a new approach to HPM. There is a very good agreement between the analytical and the numerical solutions for all values of rate constant.

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APPENDIX A: Analytical expression of the concentration using homotopy perturbation method

We construct the homotopy for the equations (10)-(12) as follows

$$(1-p) \left[\frac{d^2 a}{dz^2} \right] + p \left[\frac{d^2 a}{dz^2} - \frac{ab}{\epsilon^2} + \frac{S}{K^* \epsilon^2} \right] = 0 \tag{A1}$$

$$(1-p) \left[\frac{d^2 b}{dz^2} \right] + p \left[\frac{d^2 b}{dz^2} - \frac{ab}{\epsilon^2} + \frac{S}{K^* \epsilon^2} \right] = 0 \tag{A2}$$

$$(1-p) \left[\frac{d^2 S}{dz^2} + \frac{ab}{\epsilon^2} \right] + p \left[\frac{d^2 S}{dz^2} + \frac{ab}{\epsilon^2} - \frac{S}{K^* \epsilon^2} \right] = 0 \tag{A3}$$

where $p \in [0,1]$ is an embedding parameter. Using Maclaurin series

$$a(z) = a(0) + za'(0) + z^2 \frac{a''(0)}{2!} + \dots, \tag{A4}$$

Now, assume that the solutions of Eqs. (A1) - (A3) is

$$a = a_0 + pa_1 + p^2 a_2 + \dots, \quad b = b_0 + pb_1 + p^2 b_2 + \dots \text{ and } S = S_0 + pS_1 + p^2 S_2 + \dots \tag{A5}$$

Substituting Eq. (A5) into Eqs. (A1)-(A3) and equating the like coefficients of 'p' on both sides lead to the following linear differential equations:

$$p^0 : \frac{d^2 a_0}{dz^2} = 0 \tag{A6}$$

$$p^0 : \frac{d^2 b_0}{dz^2} = 0 \tag{A7}$$

$$p^0 : \frac{d^2 S_0}{dz^2} + \frac{a_0 b_0}{\epsilon^2} = 0 \tag{A8}$$

Solving Eqs. (A6)-(A8) Subject to boundary conditions:

$$a_0'(z=0) = \mu, \quad b_0'(z=0) = 0, \quad S_0'(z=0) = 0 \tag{A9}$$

$$a_0(z=1)=0, b_0(z=1)=1, S_0(z=1)=0 \tag{A10}$$

$$p^1 : \frac{d^2 a_1}{dz^2} - \frac{a_0 b_0}{\varepsilon^2} + \frac{S_0}{K^* \varepsilon^2} = 0. \tag{A11}$$

$$p^1 : \frac{d^2 b_1}{dz^2} - \frac{a_0 b_0}{\varepsilon^2} + \frac{S_0}{K^* \varepsilon^2} = 0. \tag{A12}$$

Solving Eqs. (A9) and (A10), subject to boundary conditions:

$$a_1'(z=0)=\mu, b_1'(z=0)=0 \tag{A13}$$

$$a_1(z=1)=0, b_1(z=1)=1 \tag{A14}$$

The solution of the Eqns. (A6) to (A8) are given by

$$a_0(z) = \mu(z-1) \tag{A15}$$

$$b_0(z) = 1 \tag{A16}$$

$$S_0(z) = \frac{\mu(2+z^3-3z^2)}{6\varepsilon^2} \tag{A17}$$

and the solution of the Eqns. (A11) to (A12) are given by

$$a_1(z) = \frac{\mu}{120K^* \varepsilon^4} \left((z-1)(z^2-2z-4)^2 + 20K^* \varepsilon^2 (z^3-3z^2+2) \right) \tag{A18}$$

$$b_1(z) = \frac{\mu}{120K^* \varepsilon^4} \left((z-1)(z^2-2z-4)^2 + 20K^* \varepsilon^2 (z^3-3z^2+2) \right) \tag{A19}$$

With the use of these two iterations only, we obtain an approximate solution for the ionic concentration given by:

$$a(z) = a_0(z) + a_1(z), \quad b(z) = b_0(z) + b_1(z) \tag{A20}$$

APPENDIX B: Matlab program for the numerical solution of nonlinear differential equations (10)-(12)

```
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

NOMENCLATURE AND UNITS

Symbols	Name	Unit
B_b	Bulk concentration of species B	mol/cm ³
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
x	Distance from the electrode surface (Eqn.(2))	cm
δ	Diffusion layer thickness	cm
k_r, k_f	Reaction-rate constants	cm/s
N_{Ao}	Known rate constant	cm/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
\mathcal{E}	Dimensionless relative rates of diffusion and reaction	None
K^*	Dimensionless homogeneous equilibrium constant	None
μ	Dimensionless rate of injection of A relative to the limiting flux of B toward the electrode	None

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