MISCIBLE FLOW THROUGH POROUS MEDIA WITH DISPERSION AND ADSORPTION

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RESUMEN

Se resuelve numéricamente por diferencias finitas la ecuación diferencial a derivadas parciales no lineal que describe el flujo unidimensional de fluidos miscibles a través de un medio poroso con dispersión y adsorción del tipo Langmuir.

Se determina el error local de truncamiento y se aplica el análisis de estabilidad de Von Neumann. A fin de eliminar la dispersión numérica o la inestabilidad, se ajustan convenientemente los parámetros ponderados y los incrementos de distancia y tiempo.

Las soluciones numéricas son verificadas con la solución exacta para el caso de adsorción lineal. Se presentan y discuten los resultados obtenidos para diferentes condiciones de borde.

Las soluciones numéricas son comparadas con los resultados experimentales de un barrido con polímeros publicados por Szabo[1]. Las diferencias entre resultados experimentales y numéricos son minimizadas aplicando técnicas de optimización para obtener los parámetros físicos más adecuados.

ABSTRACT

The partial differential nonlinear equation which describes the one-dimensional flow of miscible fluids through porous media with dispersion and Langmuir equilibrium adsorption is numerically solved by finite differences.

Local truncation error is determined and von Neumann stability analysis is applied. In order to eliminate either numerical dispersion or unstability, weighting parameters and distance and time increments are conveniently adjusted.

Finite differences results are verified with the exact solution for the linear adsorption case. They are obtained for different boundary conditions, whose influence is discussed.

Numerical solutions are matched with experimental results from Szabo's [1] polymer flooding tests. Differences between numerical and experimental results are minimized applying optimization techniques to obtain the most suitable physical parameters.

INTRODUCTION

Multicomponent single-phase flow through porous media is found in many technological problems of petroleum engineering, chemical engineering and hydrology, such as: oil recovery miscible displacement processes, ion exchange columns, fixed-bed chemical reactors, soil physics and ground-water flow. In these problems the mixture of solute and solvent is ruled by a diffusion type equation in which molecular diffusivity is replaced by an axial dispersion coefficient. When adsorption of solute onto porous media surface occurs, a source term must be added to this equation. The source term is considered here to be ruled by the Langmuir equilibrium isotherm.

Numerical solutions of the one-dimensional convection/dispersion/Langmuir equilibrium adsorption equation have been previously presented. Gupta and Greenkorn [2] and Ramirez et al [3] solved the equation using the Crank-Nicolson finite differences scheme. The first authors considered a semi-infinite porous media. Ramirez et al [3] assumed a finite-length model with a Neumann boundary condition at the outlet face. With the last boundary condition Satter et al [4] solved the same equation applying the Barakat-Clark [5] technique.

The convection/dispersion/Langmuir type adsorption equation is solved here with a more general finite differences method. The method, which is an extension of Peaceman's [6] proposal, employs distance-weighting and time-weighting parameters. Truncation error is determined and stability is analyzed by applying von Neumann criterion. The most appropiate numerical parameters are found, so as to avoid numerical dispersion and oscillations.

Numerical solutions are obtained for every possible combination of realistic boundary conditions. Consequently, the procedure followed in this paper is entirely general. Particular cases of this method are solutions [2,3,6] previously published.

The influence of numerical parameters in the solution (distance- and time-weighting parameters and distance and time increments) is analyzed. Furthermore, the dependence of the solution on the different boundary conditions is discussed.

In order to verify the numerical solutions, they are compared with the exact solution for the linear adsorption case and with experimental results.

Analytical solutions for linear adsorption have been presented by Lapidus and Amundson [7]. They have been reviewed by Coats and Smith [8] for different boundary conditions. Our numerical solutions agree satisfactorily with analytical solutions for linear adsorption.

Szabo [1] has presented experimental results of polymer adsorption obtained by static and dynamic tests. Static measurements are adequately simulated by Langmuir equilibrium isotherm. From them, Langmuir adsorption parameters can be determined.

The convection/dispersion/Langmuir equilibrium adsorption equation has three physical parameters: two adsorption parameters and the dispersion coefficient (or its equivalent, Péclet number). In order to compare numerical solutions with experimental results obtained from dynamic tests, the three parameters are used. The two adsorption parameters are estimated from static adsorption tests as it was mentioned above. The remaining parameter, Péclet number, is obtained by minimizing the differences between experimental and numerical results. This is accomplished by applying the Fibonacci [9] optimization technique.

Gupta and Greenkorn [10] have already determined dispersion coefficients from dynamic tests using nitrate and phosphate anions, with a similar procedure. However, they have applied a different optimization technique.

Numerical solutions obtained here have also been compared with results from other experimental data. They are: displacement tests done by Bae and Petrick [11] to estimate adsorption of petroleum sulfonates in Berea cores and our own process [12] which employs radio isotopes to measure concentration at several points inside a porous media. However, for space reasons, comparison with these experiments will be presented in a different paper.

MATHEMATICAL MODEL

The transport equation characterizing convection, dispersion and adsorption of a solute flowing through a porous medium can be written as,

$$\mathcal{D} \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} + \frac{\partial C_R}{\partial t} \qquad (1)$$

The most important assumptions in eq.(1) are:

1. The porous medium is homogeneous with constant cross section and porosity.
2. Flow is isothermal and one-dimensional.
3. Intersticial velocity, v -obtained dividing Darcy velocity by porosity-, is constant.
4. Dispersion of the solute occurs in the longitudinal direction. Diffusion is negligible compared with dispersion. Dispersion coefficient, $\mathcal{D}$, is independent of concentration and it is constant at a fixed velocity and porous media.
5. There is no chemical reaction between the injected solution and the rock or the fluid in-situ.

The last term in eq.(1) refers to the adsorption of solute onto the rock. It is considered to be ruled by Langmuir equilibrium adsorption:

$$C_R = \frac{a\, C}{1 + bC} \qquad (2)$$

$$a = \frac{(1-\phi)}{\phi}\, \rho_R\, a' \qquad (3)$$

where a is dimensionless, a' and b could be measured by static adsorption experiments.

By differentiating eq.(2) and introducing it into eq.(1),

$$D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = g(C) \frac{\partial C}{\partial t} \tag{4}$$

where $g(C)$ *is*,

$$g(C) = 1 + \frac{a}{(1 + bC)^2}$$

Considering a semi-infinite porous media, boundary conditions to solve eq.(4) are,

$$\begin{aligned} &C(0,t) = C_0 \,, \quad t>0 \\ &C(x,t) \longrightarrow 0 \quad as \quad x \longrightarrow \infty, \; t>0 \end{aligned} \tag{5}$$

where injection concentration C_0 is kept constant at inlet. A second set of boundary conditions arises by the requirement that there should be no loss of solute from the bed through the inlet plane,

$$\begin{aligned} &vC_0 = vC - D \frac{\partial C}{\partial x} \quad , at \; x=0, \; t>0 \\ &C(x,t) \longrightarrow 0 \quad as \quad x \longrightarrow \infty, \; t>0 \end{aligned} \tag{6}$$

Eqs.(5) and (6) are adequate as long as solutions are insensitive to the core length.

On the other hand, for a finite porous media, boundary conditions are imposed by the conservation of mass flux of solute at inlet and outlet,

$$\begin{aligned} &vC_0 = vC - D \frac{\partial C}{\partial x} \quad ,at \; x=0, \; t>0 \\ &vC - D \frac{\partial C}{\partial x} = vC_s \quad ,at \; x=L, \; t>0 \end{aligned} \tag{7}$$

where exit concentration C_s could vary with time, $C_s = C(t)$.

Several authors [4,13,14] consider that eq.(7) may be simplified as

$$\begin{aligned} &vC_0 = vC - D \frac{\partial C}{\partial x} \quad , at \; x=0, \; t>0 \\ &\frac{\partial C}{\partial x} = 0 \quad , at \; x=L, \; t>0 \end{aligned} \tag{7'}$$

A last possible combination of boundary conditions is,

$$\begin{aligned} &C(0,t) = C_0 \,, \quad t>0 \\ &\frac{\partial C}{\partial x} = 0 \,, \; at \; x=L, \; t>0 \end{aligned} \tag{8}$$

Initial condition is always,

$$C(x,0) = 0 \tag{9}$$

Defining dimensionless variables

$$y = \frac{x}{L} \qquad \tau = \frac{vt}{L} \tag{10}$$

where τ is the number of porous volumes injected, and Péclet number is

$$P_e = \frac{vL}{D} \tag{11}$$

eq.(2) is rewritten as,

$$\frac{1}{P_e}\frac{\partial^2 C}{\partial y^2} - \frac{\partial C}{\partial y} = g(C)\,\frac{\partial C}{\partial t} \tag{12}$$

The boundary conditions (5), (6), (7') and (8) are transformed into dimensionless form, by introducing eqs.(10) and (11).

ANALYTICAL SOLUTIONS

Transport equation (12), without adsorption $-g(C)=1-$, is called here the convection/dispersion equation. Its complete analytical solutions $-C(y,\tau)-$ for boundary conditions (5) and (6) have been reviewed by Coats and Smith [8]. The solution $C(\tau)$ at $y=1$ for boundary condition (7') appears in the same paper.

Analytical solutions can also be deduced for the convection/dispersion/adsorption equation, when adsorption is linear,

$$b = 0 \qquad g(C) = 1 + a$$

since, with the following replacement of variables,

$$y' = \frac{x(1 + a)}{L} \qquad P'_e = \frac{P_e}{(1 + a)} \tag{13}$$

eq.(12) is transformed into the convection/dispersion equation

$$\frac{1}{P'_e}\frac{\partial^2 C}{\partial y'^2} - \frac{\partial C}{\partial y'} = \frac{\partial C}{\partial \tau} \tag{14}$$

NUMERICAL SOLUTIONS

Transport equation (12) is numerically solved by finite differences using distance-weighting and time-weighting parameters. For the convection/dispersion equation (14), local truncation error is determined and stability is analyzed by applying von Neumann criterion. Peaceman's [6] guidelines have been followed with some modifications which will be mentioned below. The convection/dispersion/Langmuir type adsorption equation (12) is nonlinear. Therefore an iterative scheme has been applied.

Convection/dispersion equation

The difference form of first derivative with respect to dimensionless distance is

$$\frac{\partial C_i^n}{\partial y} \cong \frac{-w\, C_{i-1}^n + (2w-1)\, C_i^n + (1-w)\, C_{i+1}^n}{\Delta y} = \frac{\Delta_y C_i^n}{\Delta y} \qquad (15)$$

where distance-weighting parameter Θ=0., 0.5 or 1. corresponds to downstream, midpoint and upstream differences, respectively.

The second derivative is approximated by its second-difference quotient,

$$\frac{\partial^2 C_i^n}{\partial y^2} \cong \frac{C_{i-1}^n - 2\, C_i^n + C_{i+1}^n}{\Delta y^2} = \frac{\Delta_y^2\, C_i^n}{\Delta y} \qquad (16)$$

The first derivative with respect to dimensionless time is,

$$\frac{\partial C_i^m}{\partial \tau} \cong \frac{C_i^{n+1} - C_i^n}{\Delta \tau} = \frac{\Delta_y C_i^m}{\Delta \tau} \qquad (17)$$

with $m = (1-\Theta)n + \Theta(n+1)$. The dimensionless time-weighting parameter Θ=0, 0.5 or 1.0 corresponds to explicit, centered and implicit schemes respectively.

By introducing eqs.(15), (16) and (17) into the dimensionless convection/dispersion equation, and time-weighting parameters into the first and second differences with respect to distance, the convection/dispersion equation can be expressed as

$$\frac{1}{P_e}\, \frac{\varepsilon \Delta_y^2\, C_i^{n+1} + (1-\varepsilon)\, \Delta_y^2\, C_i^n}{\Delta y^2} - \frac{\Theta\, \Delta_y\, C_i^{n+1} + (1-\Theta)\, \Delta_y\, C_i^n}{\Delta y} = \frac{\Delta_\tau\, C_i^n}{\Delta \tau} \qquad (18)$$

where ε= 0, 0.5 or 1.0 is the time-weighting parameter for the second difference. The introduction of this parameter, ε, is a modification of Peaceman's [6] original proposal.

Local truncation error has been deduced in Appendix A. And it is

$$e_t = [\, \Delta y\, (w-\tfrac{1}{2}) - \Delta t\, (\Theta-\tfrac{1}{2})]\, \frac{\partial^2 C}{\partial y^2} + O(\Delta y^2) + O(\Delta t^2)\ , \qquad (19)$$

the factor which multiplies the second derivative is called numerical dispersion, [6]

$$D_{num} = \Delta y\, (w-\tfrac{1}{2}) + \Delta t\, (\Theta-\tfrac{1}{2}) \qquad (20)$$

In eq.(19) the parameter ε does not appear because the derivatives of order greater than two are neglected.

Unconditional stability has been deduced according to von Neumann criterion in Appendix B. It is obtained with every possible combination of w, Θ and ε taking values 0.5 or 1.0.

Convection/dispersion/Langmuir type adsorption equation

The complete eq.(12), which is nonlinear, can be approximated by a difference linear form similar to eq.(18). Iteratively it is solved as,

$$\frac{1}{P_e}\,\frac{\varepsilon\,\Delta_y^2\,C_i^{n+1,k+1} + (1-\varepsilon)\,\Delta_y^2\,C_i^{n}}{\Delta y^2} - \frac{\theta\,\Delta y\,C_i^{n+1,k+1} + (1-\theta)\,\Delta y\,C_i^{n}}{\Delta y} =$$

$$= g^{m,k}\,\frac{C_i^{n+1,k+1} - C_i^{n}}{\Delta t} \tag{21}$$

where,

$$g^{m,k} = g(\Theta C_i^{n+1,k} + (1-\Theta)C_i^{n}) \tag{22}$$

and k is the iteration parameter.

Numerical solutions for the various boundary conditions (5), (6), (7') and (8) are found with this method. They have also been obtained and analyzed for different combinations of weighting parameters, and time and space increments.

RESULTS AND DISCUSSION

Comparison between analytical and numerical solutions

For the convection/dispersion equation and boundary conditions given by eq.(5), comparison between numerical and analytical solutions has been analyzed by Peaceman [6].

For the convection/dispersion/adsorption equation considering linear adsorption, numerical solutions of eq.(21) for different sets of boundary conditions are compared with analytical solutions of eq.(14).

In order to have solutions without numerical dispersion, weighting parameters are chosen as: $w = \Theta = \varepsilon = 0.5$. These values minimize the truncation error. Distance and time increments $\Delta y = \Delta\tau = 0.01$ are selected to avoid oscillations of dimensionless concentration curves.

Results, $C(\tau)/C_0$, at different points inside the porous media, appear in Figs. 1A, 1b, 1C, for $P_e = 90.$, and different values of a. The case $a = 0.$ corresponds to the convection/dispersion equation.

$C(\tau)/C_0$ profiles are shown: in Fig.1A, at outlet $y = 1$ for boundary conditions given by eq.(8); in Fig.1b, at midpoint $y = 0.5$, for boundary conditions given by eq.(5); and in Fig.1C, at inlet $y = 0$, for boundary conditions given by eq.(6).

Numerical and analytical solutions agree satisfactorily.

Influence of boundary conditions

The influence of boundary conditions given by eqs.(5), (6), (7') and (8) can be seen in Fig.2. The parameters, P_e, a and b correspond to

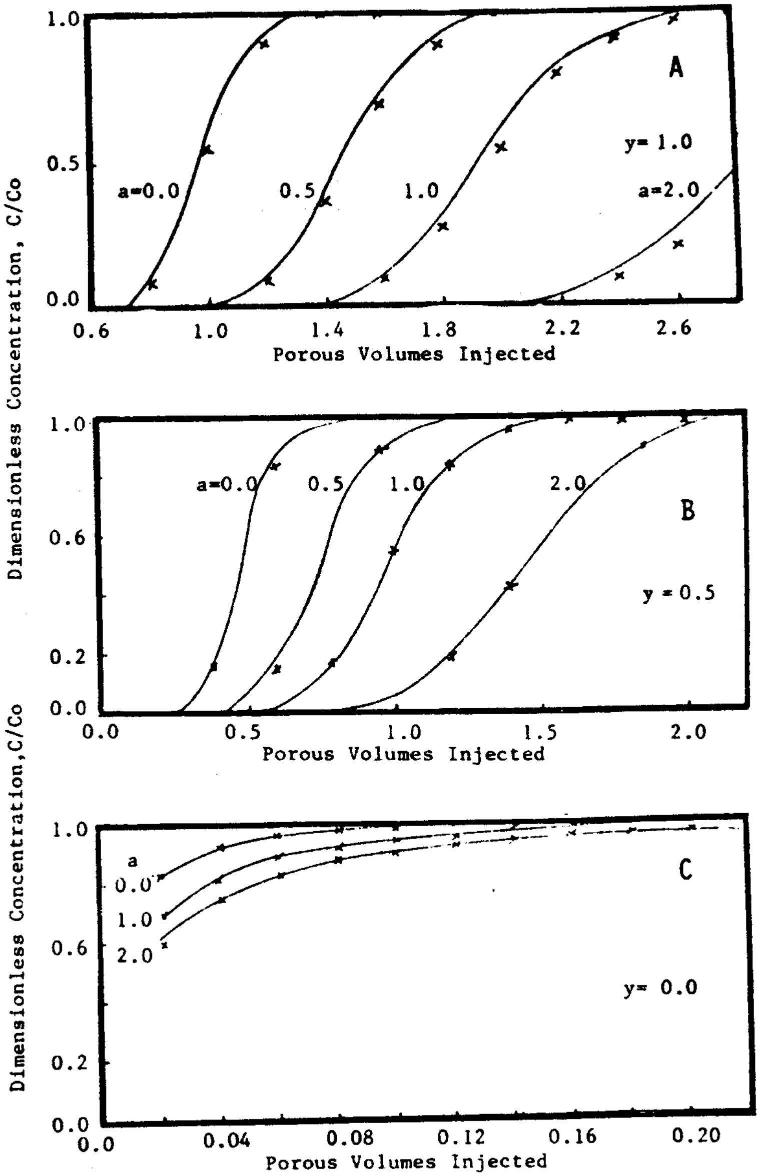

Fig.1: Comparison between analytical (—) and numerical (x x x) solutions, for different cases of linear adsorption. Dimensionless concentration profiles as a function of porous volumes injected. The different equations are space and time-centered, $\omega = \Theta = \varepsilon = 0.5$, with increments $\Delta y = \Delta\tau = 0.01$.

A- At outlet. BC: $C = Co$ at $y=0$, $\partial C/\partial y = 0$ at $y=1$.

B- At midpoint. BC: $C = Co$ at $y=0$, $C \rightarrow 0$ as $y \rightarrow \infty$.

C- At inlet. BC: $C - Co = \frac{1}{Pe} \frac{\partial C}{\partial y}$ at $y=0$, $C \rightarrow 0$ as $y \rightarrow \infty$

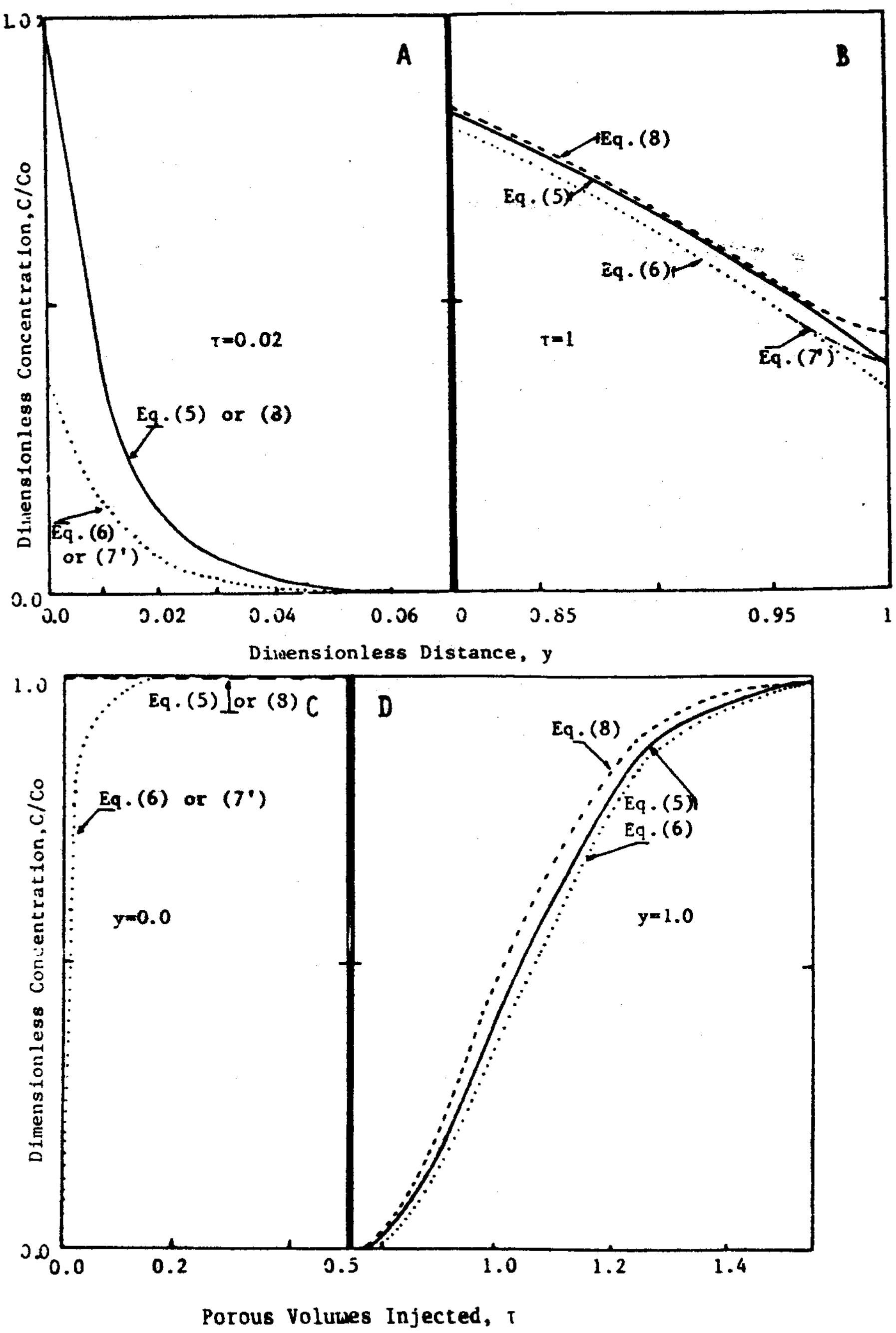

Fig.2: Effect of boundary conditions. Dimensionless concentration as a function of dimensionless distance: (A) and (B). Dimensionless concentration as a function of porous volumes injected: (C) and (D). At inlet and earlier times: (A) and (C). At outlet and later times: (B) and (D). Pe=59.07; a=0.515; b=7.92

one run of Szabo's [1] experimental data which will be described later on.

Figs. 2A and 2C show the effect of inlet boundary conditions. When the solute mass flux is kept constant at inlet, injected concentration C_o is not attained instantaneously (Fig. 2C). Therefore, dimensionless concentration profiles as a function of distance, are delayed (Fig. 2A).

Fig. 2B and 2D show the influence of the four boundary conditions at outlet. The conservation of mass solute at inlet delays the concentration profiles. This effect is partly compensated when considering a finite porous media whose derivative of concentration with respect to distance equals zero at outlet. Because of that, three curves corresponding respectively to boundary conditions (8), (5) (which coincides with (7')), and (6) appear in Fig. 2D. Eq.(8) gives the concentration distribution which travels fastest and Eq.(6) gives the slowest.

In order to represent the boundary condition at infinity, $y = 5.0$ was chosen.

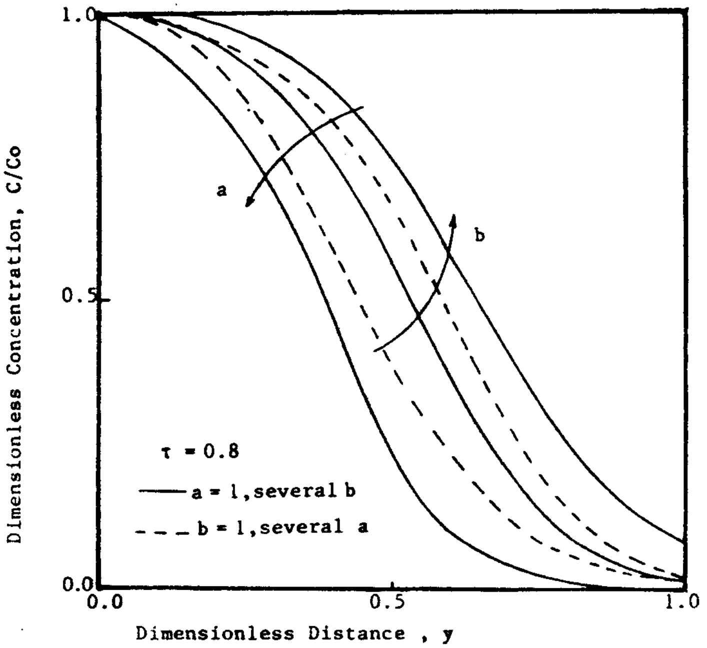

Fig. 3. Effect of adsorption parameters a and b. Dimensionless concentration as a function of dimensionless distance. P_e = 100. , τ = 0.8.

Influence of adsorption parameters

The influence of adsorption parameters is represented in Fig. 3. Dimensionless concentration distributions as a function of distance from inlet are delayed by adsorption. Consequently they go slower as the parameter a increases and as the parameter b decreases.

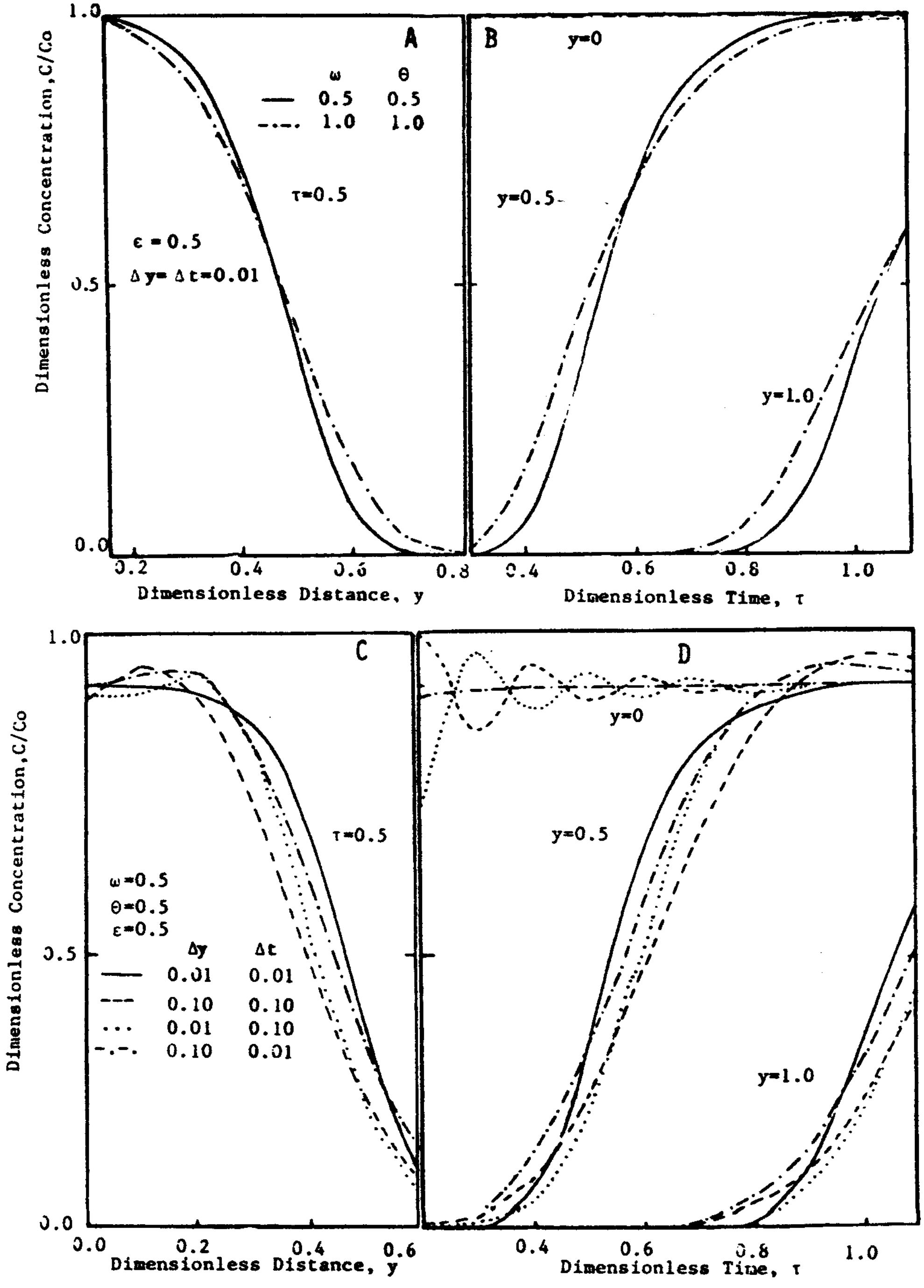

Fig.4: Dimensionless concentration profiles for Pe=59.07; a=0.515 and b=7.92. A and C show the influence of weighting parameters (ω, θ) and numerical dispersion. B and D show the influence of distance and time increments ($\Delta y, \Delta z$).

Influence of numerical parameters

In the linear adsorption case, the lowest truncation error is obtained with $\varepsilon = w = \Theta = 0.5$. Furthermore, concentration profiles do not show oscillations with time and space increments $\Delta y = \Delta\tau = 0.01$. Thus, this combination of parameters is considered to give the best numerical solution for the convection/dispersion/Langmuir type adsorption equation (12).

The effect of weighting parameters ε, w and Θ has been analyzed. The modification of $\varepsilon = 0.5$ or $\varepsilon = 1.0$ does not produce noteworthy differences. Furthermore, zero values of either w, Θ or ε create conditional stability. Therefore, every combination of w, Θ taking values 0.5 or 1. has been studied.

Figs. 4A, 4B show dimensionless concentration profiles for $(w,\Theta) = (0.5,0.5)$ and $(w,\Theta) = (1.0,1.0)$. The last combination gives the highest numerical dispersion in the linear adsorption case: $\mathcal{D}_{num} = 0.01$. $(w,\Theta) = (0.5,1.0)$ and $(w,\Theta) = (1.0,0.5)$ are not drawn because they lie between the two profiles already shown. For these combinations $\mathcal{D}_{num} = 0.005$ in the linear adsorption case. However, $(w,\Theta) = (1.0,0.5)$ produces lesser smearing than the other, consequently it lies closer to the $(w,\Theta) = (0.5,0.5)$ curve.

The effect already described can be shown in Fig. 4A for C/C_0 vs. y, at 0.5 porous volumes injected. It can also be seen in Fig. 4B for C/C_0 vs. τ, at dimensionless distance corresponding to inlet, midpoint and outlet. At inlet, all the solutions agree.

Moreover, the influence of time and space increments $(\Delta y, \Delta\tau)$ has been studied. Again the combination $\varepsilon = \Theta = w = 0.5$ and $\Delta\tau = \Delta y = 0.01$ is taken as the best solution.

Dimensionless concentration profiles as a function of dimensionless distance for 0.5 porous volumes injected are presented in Fig. 4C The combination $(\Delta y, \Delta\tau) = (0.1,0.1)$ shows oscillations, with overshoot occurring behind the moving front. The oscillations are similar to those found by Peaceman [6] for the convection/dispersion case.

The combinations $(\Delta y, \Delta\tau) = (0.1,0.01)$ and $(\Delta y, \Delta\tau) = (0.01,0.1)$ also produce numerical solutions with some oscillations. The first one creates smaller oscillations than the last one. This effect can also be seen in Fig. 4D, where C/C_0 vs. τ has been drawn for inlet, midpoint and outlet. At inlet, the pair $(\Delta y, \Delta\tau) = (0.01,0.1)$ shows noticeable oscillations, similar to those produced by $(\Delta y, \Delta\tau) = (0.1,0.1)$. However, the combination $(\Delta y, \Delta\tau) = (0.1,0.01)$ has better behaviour.

One might expect that if $\Delta\tau$ tends to zero, it should produce numerical solutions without oscillations. However, oscillations appeared with the pair $(\Delta y, \Delta\tau) = (0.1,0.001)$. Consequently, both distance and time increments should be carefully chosen.

EXPERIMENTAL VERIFICATION

Polymer flooding

Szabo [1] performed single flow experiments in unconsolidated sands using C^{14}-tagged partially hydrolyzed polyacrylamide and a commercial product, Calgon Polymer 454. The experiments have been carried out using sandpacks completelly saturated with brine, at a constant flow rate (6 ft/day). Produced and adsorbed polymer were measured using radioactivity.

The same author also performed static adsorption tests. Results of polymer adsorption in a silica sand as a function of equilibrium polymer concentration are shown in Fig.(2) of his paper [1]. The static adsorption isotherm corresponding to brine is well described by Langmuir's equation (3). We have obtained

$$a = 0.515 \quad , \qquad b = 0.0132\ (\text{ppm})^{-1} \qquad (23)$$

by handling eq.(3), with C_R and C expressed in ppm of polymer in brine.

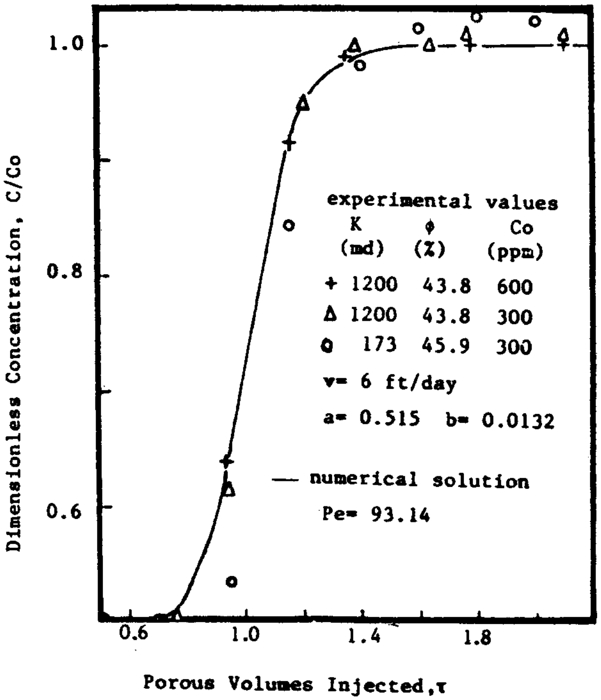

Fig. 5. Comparison between numerical solution and experimental results from Szabo [1]. Effluent polymer concentration as a function of the number of porous volumes injected for three different runs.

Fig. 5 reproduces Szabo's results of effluent polymer concentrations during polymer flow through sandpacks previously saturated with 100-percent brine, for three runs, all of them at approximately the same intersticial velocity. The first and the second have been performed on the highest permeability (1200 md) sand. The first at $C_0 = 600$ ppm and the second at $C_0 = 300$ ppm. The third has been carried out in a lower permeability sand (173 md) at $C_0 = 300$ ppm.

If the three runs were represented in terms of dimensionless concentration, C/C_0, the measured values should coincide. This is because polymer concentration in effluent ought not to depend on permeability. In fact, their differences are not greater than experimental errors. Notice that the effluent concentration should not be higher than the injected concentration. Therefore, C/C_0 values higher than one could be caused either by a reversible hydrodynamic retention, or by measurement errors. Anyway, they cannot be simulated by this model.

Experimental results are simulated by eq.(12) and boundary conditions are given by eq.(6) using the adsorption parameters written above. Numerical solution can be seen in Fig. 5. Péclet number was obtained by Fibonacci [9] optimization technique for the purpose of minimizing differences between the experimental measurements (from the three runs) and the numerical solution. A good match is obtained.

CONCLUSIONS

Numerical solutions of the partial differential nonlinear equation representing one-dimensional flow of miscible fluids through porous media with dispersion and Langmuir equilibrium adsorption are obtained. The procedure is entirely general. It is based on a finite-differences scheme which uses time-weighting and distance-weighting parameters.

The best combination of these parameters is (0.5,0.5,0.5) as it provides a well-behaved solution without oscillations, it is unconditionally stable, without numerical dispersion for the linear adsorption case, and it shows the best agreement with experimental results. This combination of parameters corresponds to the Crank-Nicolson method.

Four boundary conditions have been studied. The differences among them are noteworthy only at narrow ranges of time and space: at inlet for very early times and at outlet when the number of porous volumes injected is around 1.0 ± 0.4; and it increases if the adsorption becomes greater. In most cases their differences are within the range of experimental errors.

The proposed numerical solution shows excellent agreement with the exact solution for the linear adsorption case. It also coincides satisfactorily with experimental results obtained from different runs of polymer flooding tests.

A further application of the numerical solution is to determine the dispersion coefficient from displacement laboratory experiments when there is adsorption. The most representative dispersion parameter of a porous medium is obtained, when adsorption parameters are known, by minimizing the differences between experimental and numerical results applying the Fibonacci optimization method.

NOMENCLATURE

a, a', b : parameters for Langmuir adsorption model.
C : solute concentration [m/L^3].
C_o : inlet concentration of solute [m/L^3].
C_R : amount of solute adsorbed/volume of fluid [m/L^3].
C_s : exit concentration of solute [m/L^3].
D : longitudinal dispersion coefficient [L^2/t].

D_{num} : numerical dispersion $[L^2/t]$.
e_t : local truncation error.
g : derivative of the adsorption with respect to C
L : length of porous medium [L].
P_ℓ : dimensionless dispersion coefficient, defined by eq.(11).
P_e^r : dimensionless dispersion coefficient, defined by eq.(13).
t : time [t] .
v : average intersticial velocity [L/t].
x : distance [L].
y : dimensionless distance, defined by eq.(10).
y' : dimensionless distance, defined by eq.(13).

Greek letters

$\Delta\tau$: increment of τ .
Δy : increment of y .
ε : time-weighting parameter.
θ : time-weighting parameter.
ρ_R : rock density $[m/L^3]$.
τ : dimensionless time.
ϕ : porosity, % .
ω : distance-weighting parameter.

Subscripts and superscripts

i : index in y-direction.
k : iteration count.
m : fractional index in τ-direction, $=(1-\theta)n+\theta(n+1)$.
n : index in τ-direction.

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APPENDIX A

Truncation Error Analysis

In order to analyze the truncation error associated with the linear difference eq.(18), we can expand $C(y\pm\Delta y,\tau)$ and $C(y,\tau+\Delta\tau)$ in Taylor series,

$$C^n_{i\pm 1} = C^n_i \pm \Delta y \frac{\partial C_i}{\partial y} + \frac{\Delta y^2}{2}\frac{\partial^2 C^n_i}{\partial y^2} \pm \frac{\Delta y^3}{6}\frac{\partial^3 C^n_i}{\partial y^3} + O(\Delta y^4) \qquad \text{(A.1)}$$

$$C^{n+1}_i = C^n_i + \bar{\Theta}\Delta\tau \frac{\partial C^m_i}{\partial \tau} + \frac{\bar{\Theta}^2}{2}\Delta\tau^2 \frac{\partial^2 C^m_i}{\partial \tau^2} + O(\Delta\tau^2) \qquad \text{(A.2)}$$

where $m = (1-\Theta)n + \Theta(n+1)$
$\bar{\Theta} = -\Theta,\ 1-\Theta$
$\Theta = 0.,\ 0.5,\ 1.$
$C^n_i = C(y_i,\tau_n)$
$y_i = i\,\Delta y\ ,\ 0 \leq i \leq I$
$\tau_n = n\,\Delta\tau\ ;\ \ n \geq 0$

From (A.1) and (A.2) we obtain the expressions:

$$\frac{\Delta_y^2 C_i^n}{\Delta y^2} = \frac{C_{i-1}^n - 2C_i^n + C_{i+1}^n}{\Delta y^2} = \frac{\partial^2 C_i^n}{\partial y^2} + O(\Delta y^2) \tag{A.3}$$

$$\frac{\Delta_\tau C_i^n}{\Delta\tau} = \frac{C_i^{n+1} - C_i^n}{\Delta\tau} = \frac{\partial C_i^m}{\partial\tau} + (\tfrac{1}{2}-\Theta)\Delta\tau\frac{\partial^2 C_i^m}{\partial\tau} + O(\Delta\tau^2) \tag{A.4}$$

$$\frac{\Delta_y C_i^n}{\Delta y} = \frac{-w\, C_{i-1}^n + (2w-1)C_i^n + (1-w)C_{i+1}^n}{\Delta y} = \frac{\partial C_i^n}{\partial y} + O(\Delta y^2) + (\tfrac{1}{2}-w)\Delta y\,\frac{\partial^2 C_i^n}{\partial y^2} \tag{A.5}$$

$$\frac{\partial^\alpha C_i^\beta}{\partial y^\alpha} = \frac{\partial^\alpha C_i^m}{\partial y^\alpha} + \overline{\Theta}\Delta\tau\,\frac{\partial^{\alpha+1} C_i^m}{\partial y^\alpha\,\partial\tau} + O(\Delta\tau^2) \tag{A.6}$$

with $\alpha = 1, 2$
$(\beta,\overline{\Theta}) = (n,-\Theta),\ (n+1, 1-\Theta)$

Details to deduce (A.3), (A.4), (A.5) and (A.6) can be seen in Peaceman [6] (chapter 4).

It should be pointed out that, if $C \in C^{k,\ell}$ means that the derivatives of C with respect to y and τ are continuous up to orders k and ℓ respectively, then in the present problem, we require $C \in C^{4,2}$ in order to define the truncation error.

The local truncation error, ε_t, can be defined by the difference operator applied to the exact solution of the partial differential equation at the point (y_i, τ_m). Then,

$$\varepsilon_t = \frac{\varepsilon\,\Delta_y^2 C_i^{n+1} + (1-\varepsilon)\,\Delta_y^2 C_i^n}{P_e\,\Delta y^2} - \frac{\Theta\,\Delta_y C_i^{n+1} + (1-\Theta)\Delta_y C_i^n}{\Delta y} - \frac{\Delta_\tau C_i^n}{\Delta\tau} \tag{A.7}$$

By substituting eqs.(A.3), (A.4), (A.5) and (A.6) with appropriate values of α, β and $\overline{\Theta}$, we can write,

$$\varepsilon_t = \frac{\Delta\tau\ (\varepsilon-\Theta)}{P_e}\frac{\partial^2 C_i^m}{\partial y^2\,\partial\tau} + \Delta y(w-\tfrac{1}{2})\,\frac{\partial^2 C_i^m}{\partial y^2} + (\Theta-\tfrac{1}{2})\Delta\tau\frac{\partial^2 C_i^m}{\partial\tau^2} + O(\Delta\tau^2) + O(\Delta y^2) \tag{A.8}$$

Differentiation of eq.(14) with respect to τ gives,

$$\frac{1}{P_e}\,\frac{\partial^3 C_i^m}{\partial y^2\,\partial\tau} - \frac{\partial^2 C_i^m}{\partial y\,\partial\tau} = \frac{\partial^2 C_i^m}{\partial\tau^2}$$

while differentiation with respect to y yields

$$\frac{1}{P_e}\frac{\partial^3 C_i^m}{\partial y^3} - \frac{\partial^2 C_i^m}{\partial y^2} = \frac{\partial^2 C_i^m}{\partial y\,\partial \tau} \tag{A.9}$$

so that,

$$\frac{\partial^2 C_i^m}{\partial \tau^2} = \frac{1}{P_e}\frac{\partial^3 C_i^m}{\partial y^2\,\partial \tau} - \frac{1}{P_e}\frac{\partial^3 C_i^m}{\partial y^3} + \frac{\partial^2 C_i^m}{\partial y^2} \tag{A.10}$$

Now, differentiating eq.(A.9) with respect to y, it results

$$\frac{\partial^3 C_i^m}{\partial y^2\,\partial \tau} = \frac{1}{P_e}\frac{\partial^4 C_i^m}{\partial y^4} - \frac{\partial^3 C_i^m}{\partial y^3} \tag{A.11}$$

Thus, substitution of eqs.(A.10) and (A.11) into eq.(A.8) gives the final form for the local truncation error

$$\begin{aligned}\varepsilon_t = \frac{\Delta\tau}{P_e}\left(\varepsilon-\tfrac{1}{2}\right)\frac{\partial^4 C_i^m}{\partial y^4} + \frac{\Delta\tau}{P_e}\left[\left(\tfrac{1}{2}-\varepsilon\right) + \left(\tfrac{1}{2}-\theta\right)\right]\frac{\partial^3 C_i^m}{\partial y^3} + \\ +\left[\Delta y\left(w-\tfrac{1}{2}\right) + \left(\theta-\tfrac{1}{2}\right)\Delta\tau\right]\frac{\partial^2 C_i^m}{\partial y^2} + O(\Delta y^2) + O(\Delta\tau^2)\end{aligned} \tag{A.12}$$

It is immediately obvious that we must choose w, ε and θ equal to 0.5 in order to obtain the minimum local truncation error.

But, if the derivatives of third and fourth order are neglected, ε_t does not depend on ε, and the choice of convenient w, θ, Δy and $\Delta\tau$ gives a local truncation error that is $O(\Delta y^2) + O(\Delta\tau^2)$.

The factor of the derivative of second order is called D_{num},

$$D_{num} = \Delta y\,\left(w-\tfrac{1}{2}\right) + \Delta\tau\,\left(\theta-\tfrac{1}{2}\right)$$

APPENDIX B

Stability

We proceed with a von Neumann stability analysis of eq.(18). We assume that the homogeneous difference equation has a solution of the form

$$E_j^n = \rho^n e^{i\beta j} \quad ; \quad \beta = p\,\Delta y \quad ; \quad i^2 = -1 \tag{B.1}$$

The von Neumann criterion for stability states that the modulus of the amplification factor must be less than or equal to one, that is

$$\left|\frac{\rho^{n+1}}{\rho^n}\right| \leq 1 \tag{B.2}$$

Letting $$a = \frac{\Delta\tau}{\Delta y^2 P_e} \quad , \qquad b = \frac{\Delta\tau}{\Delta y} \tag{B.3}$$

and upon substituting eqs.(B.1) and (B.3) into eq.(18), we have,

$$a\left[\varepsilon\Delta y^2(\rho^{n+1}e^{i\beta j}) + (1-\varepsilon)\Delta y^2(\rho^n e^{i\beta j})\right] - b\left[\Theta\Delta y(\rho^{n+1}e^{i\beta j}) + (1-\Theta)\Delta y(\rho^n e^{i\beta j})\right] = \rho^{n+1}e^{i\beta j} - \rho^n e^{i\beta j} \tag{B.4}$$

After cancelling the common factor $e^{i\beta j}$, and making use of the identities

$$e^{-i\beta} - 2 + e^{i\beta} = -4 sen^2\alpha$$

$$e^{i\beta} - 1 = -2 sen^2\alpha + 2i\ sen\alpha\ cos\alpha; \quad \alpha = \beta/2$$

we can obtain the modulus of the amplification factor. The condition (B.2) leads to

$$4a^2(1-2\varepsilon)sen^2\alpha + b^2(1-2\Theta)sen^2\alpha(2w-1)^2 + b^2(1-2\Theta)cos^2\alpha - b(2w-1) + 4ab\ sen^2\alpha(2w-1)(1-\Theta-\varepsilon) \leq 2a \tag{B.5}$$

So as to analyze (B.5) we must combine all the possible values of weighting parameters (0., 0.5 and 1.). From the 27 possible combinations, only 8 give unconditional stability.They are those which do not contain w, Θ or ε equal to 0.. .

Two examples will show how to analyze (B.5):

Example 1 : $w = 0.5$ $\quad\Theta = 1.$ $\quad\varepsilon = 0.5$

(B.5) results $$-b^2 cos^2\alpha \leq 2a$$

since $a > 0$, w, Θ and ε do not influence on stability. Thus, we have unconditional stability. But $D_{num} = \Delta\tau/2$, leads to

$$\varepsilon_t = O(\Delta y^2) + O(\Delta\tau)$$

that it is not the optimum local truncation error.

Example 2 : $w = 0.5$ $\quad\Theta = 0.5$ $\quad\varepsilon = 0.$

(B.5) results $$4a^2 sen^2\alpha \leq 2a$$

then $$a \leq \frac{1}{2}$$

or $$\frac{\Delta\tau}{\Delta y^2} \leq \frac{P_e}{2}$$

Thus, we have conditional stability. However, the weighting factors give $D_{num} = 0$ and

$$\varepsilon_{t} = O(\Delta y^{2}) + O(\Delta\tau^{2})$$

The examples 1 and 2 suggest that the weighting factors w, θ and ε should be carefully selected, in order to obtain unconditional stability and the optimum local truncation error.