EXACT SOLUTIONS IN IDEAL CHROMATOGRAPHY VIA DIFFERENTIAL CONSTRAINTS METHOD

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ABSTRACT. A differential constraints analysis is worked out for a quasilinear hyperbolic system of first order PDEs written in terms of Riemann invariants which models multi-component ideal chromatography. Depending on the appended constraints, different exact solutions can be obtained which exhibit inherent wave features. Among others, there are determined generalized simple wave solutions which are parameterized by an arbitrary function so that they may also fit suitable boundary value problems. Within the latter framework an example is given.

1. Introduction

Along the years a variety of mathematical methods for finding exact solutions to nonlinear partial differential equations have been proposed. Among others the approach based on the use of differential constraints is of relevant interest. The method is based upon appending a set of PDEs to a given governing system of field equations and it was first applied by Janenko (1964) to the gas dynamics model. The auxiliary equations play the role of differential constraints because they select classes of solutions of the system under interest. The procedure is based on two steps: first the compatibility of the over determined set of equations consisting of the governing equations along with the differential constraints must be assured, then exact solutions to the entire set of equations to which correspond particular solutions of the original field equations can be obtained.

In view of solving problems of interest in the applications, the key question is on the form of differential constraints which can be appended to the given system of equations. That aspect can be considered by means of "ad hoc" requirements on the reduction procedure to be developed or on the form of exact solutions which are to be expected (see Fusco and Manganaro 1994a,b, 1996, 2008; Manganaro and Meleshko 2002; Meleshko and Shapeev 1999).

Along the latter lines of investigation, reduction procedures based on the use of differential constraints have been proposed for studying soliton-like interactions described by homogeneous and non homogeneous hyperbolic 2×2 systems (Currò, Fusco, and Manganaro 2012c, 2013, 2015) as well as for solving problems of interest in wave propagation (Currò, Fusco, and Manganaro 2012a,b; Currò and Manganaro 2013).

Here the attention is focussed on a system of conservation laws which was considered by Rhee Hyun-Ku, Aris, and Amundson (1970) and Rhee Hyun-Ku, Aris, and Amundson (1971) to model the dynamics of multicomponent chromatography. Actually, it has to be noticed that Hankins and Helfferich (1999), Helfferich and Whitley (1996), Helfferich (1997), and Ting and Helfferich (1999) worked out an exhaustive study of the experimental validation of theoretical predictions as those provided by the model in point. Therefore, in fields of chemical engineering application this system of PDEs has played a prominent role over the years (Butté, Storti, and Mazzotti 2008; Canon 2012; Canon and James 1992; Golshan-Shirazi and Guiochon 1989; Gritti and Guiochon 2013; Hankins and Helfferich 1999; Helfferich 1997; Helfferich and Whitley 1996; Helfreich and Klein 1970; Rhee Hyun-Ku, Aris, and Amundson 1970; Mazzotti and Rajendran 2013; Rhee Hyun-Ku, Aris, and Amundson 1971, 2001; Rouchon *et al.* 1987; Seidel-Morgenstein 2004; Shen and Smith 1968; Siitonen and Sainio 2011; Ting and Helfferich 1999; Urbach 1992; Urbach and Bokx 1992).

As significant mathematical aspect of distinguishing, the system under interest belongs to the class of homogeneous semi-hamiltonian systems of hydrodynamic type which can be diagonalized in terms of suitable field variables which represent, in fact, Riemann invariants. Hence via the generalized hodograph method, solutions of these systems can be obtained by integrating, in principle, a linear set of equations (Tsarev 1991, 2000). Further, in a very recent paper Curró, Fusco, and Manganaro (2015) performed an accurate and exact description of the hyperbolic wave interaction processes which are associated to the governing model proposed by Rhee Hyun-Ku, Aris, and Amundson (1970, 1971).

In order to accomplish an exhaustive validation of the model of ideal chromatography in terms of exact solutions, in this paper a differential constraints analysis is developed. These solutions in suitable space-time domains behave as regular solutions of nonlinear hyperbolic models until they do not evolve into a shock (Jeffrey 1976; Whitham 1974). It has to be remarked that the appended constraints select given families of characteristic curves along which the resulting solutions are defined. Thus, within the well established nonlinear hyperbolic wave theory, the solutions in point have inherent wave features since they may describe propagating signals. Apart from their own theoretical value, these solutions can be also useful for testing numerical procedures for the quasilinear hyperbolic system of PDEs under interest.

The paper is organized as follows. In section 2 we give a short survey of the main results which are related to the differential constraints method for quasilinear hyperbolic systems. In section 3 we introduce the governing system of ideal chromatography which is the subject of our study. In section 4 we analyse the possible cases of differential constraints which are consistent with the model under interest. Depending on the appended constraints, different exact solutions can be obtained. Among others, a class of generalized simple wave solutions are obtained. Since the latter solutions are parameterized by an arbitrary function, they are flexible to fit suitable boundary value problems.

2. Differential Constraints Method

Let us consider the system

$$\mathbf{U}_t + A(\mathbf{U})\mathbf{U}_x = \mathbf{B}(\mathbf{U}), \tag{1}$$

where x and t are space and time coordinates, respectively; $\mathbf{U} \in R^{\mathrm{N}}$ is a column vector denoting the dependent field variables; $A(\mathbf{U})$ and $\mathbf{B}(\mathbf{U})$ are matrix coefficients. Hereafter a subscript denotes a derivative with respect to the indicated variable. The system (1) is assumed to be strictly hyperbolic, namely the N–th order matrix A is required to admit N real eigenvalues so that $\lambda^{(i)} \neq \lambda^{(j)}, \forall i, j = 1...N$ to which there correspond N right eigenvectors $\mathbf{d}^{(i)}$ and N left eigenvectors $\mathbf{l}^{(i)}$ spanning the Euclidean space E^{N}. Moreover we assume, without loss of generality, $\mathbf{l}^{(i)} \cdot \mathbf{d}^{(j)} = \delta^{(ij)}$.

Along the lines of investigation carried out by Janenko (1964), Meleshko and Shapeev (1999), and Meleshko (1980) we append to system (1) the set of differential constraints

$$\mathbf{l}^{(i)} \cdot \mathbf{U}_x = q^{(i)}(x, t, \mathbf{U}), \qquad i = 1...M \leq N, \tag{2}$$

where the functions $q^{(i)}$ have to be determined through later consistency requirement to the given governing model. Relations (2) represent the most general set of first order differential constraints which can be appended to strictly hyperbolic first order quasilinear systems of PDEs (Meleshko 1980).

The first step in the procedure at hand is to require the differential compatibility between equations (1) and (2). That leads to an overdetermined set of conditions to be fulfilled by the functions $q^{(i)}$ which also impose restrictions on the structural form of the matrix coefficients A and $\mathbf{B}$, whereupon classes of material response functions (Model Constitutive Laws) are characterized in order that the approach under interest holds. In current literature on the subject of group or reduction approaches, the expression "Model Constitutive Laws" refers to special forms to be adopted by the material response functions which are involved in a class of Constitutive Laws. Once the consistency conditions have been satisfied, then a class of exact solutions to a given governing model can be obtained by integrating the overdetermined system (1), (2). Thus the differential constraints (2) select particular exact solutions to the original system (1).

The solutions resulting from the differential constraints method depend on $N - M$ arbitrary functions so that they generalize the so-called multiple wave solutions and may be useful to solve suitable classes of initial and/or boundary value problems. The two limiting cases $M = N$ and $M = N - 1$ are of a certain theoretical interest (Fusco and Manganaro 1996; Manganaro and Meleshko 2002; Meleshko and Shapeev 1999).

Actually, for $M = N$ the equations (1) and (2) assume, respectively, the form

$$\mathbf{U}_t = -A(\mathbf{U})\mathbf{P}(x, t, \mathbf{U}) + \mathbf{B}(\mathbf{U}), \qquad \mathbf{U}_x = \mathbf{P}(x, t, \mathbf{U}). \tag{3}$$

Owing to the special structure of system (3), we can integrate separately the set of differential equations $(3)_1$, or alternatively $(3)_2$, so that later substitution into the remaining set of equations provides to (1) a class of exact solutions parameterized by N arbitrary constants. It is simple to prove that such a class of solutions include the well known "nonclassical similarity solutions" (Bluman and Cole 1969; Fusco and Manganaro 1996).

When $M = N - 1$ it is straigtforward to ascertain that (1) and (2) lead to

$$\mathbf{U}_t + \lambda^{(\mathrm{N})}\mathbf{U}_x = \mathbf{B} + \sum_{i=1}^{N-1} q^{(i)}\left(\lambda^{(\mathrm{N})} - \lambda^{(i)}\right)\mathbf{d}^{(i)}, \tag{4}$$

so that the searched solutions of the governing equations can be obtained through integration along the characteristic curves associated to the eigenvalue $\lambda^{(\mathrm{N})}$, namely along the family of

characteristics selected by the equations (2) which must be also satisfied by the initial data $\mathbf{U}(x,0)$. In passing we notice that when in (1) and (2) $\mathbf{B} = 0$ and $q^{(i)} = 0$ then (4) determines the classical simple wave solution to a homogeneous hyperbolic model. Therefore the solutions of (1) defined by (4) and (2) inherit all the main features of simple waves and also take into account source-like effects in hyperbolic wave processes.

3. The governing model

Chromatographic separation processes are based on the adsorption of the components of a mixture. In gas or liquid chromatograhy the separation is achieved by injecting a pulse of the solute mixture into a column containing an active sorption material (solid phase). The components move with different velocities through the column in function of their affinity for the solid phase. Hence, as the low retained component exits the column earlier than the more retained one, the separation is achieved. Under the assumption of an "ideal column" the chromatographic separation of different chemical species in the case of *Langmuir sorption* is described by the following first order quasilinear strictly hyperbolic PDEs system (Rhee Hyun-Ku, Aris, and Amundson 1970; Rozhdestvenskii and Janenko 1990)

$$V\frac{\partial v_i}{\partial x} + \frac{\partial}{\partial t}\left(v_i + \frac{\Gamma_i v_i}{p}\right) = 0, \qquad i = 1,..n, \tag{5}$$

where x and t are space and time coordinates, v_i are the normalized concentrations of the components in the mixture and V is the constant rate of motion of the mixture in the column. Furthermore $p = 1 + v_1 + .. + v_n$ whereas $\Gamma_1 < .. < \Gamma_n$ are characteristic parameters named the Henry coefficients. The quasilinear system pf PDEs (5) results to be strictly hyperbolic (see, for instance, Janenko 1964).

The equations (5) have been studied by Rhee Hyun-Ku, Aris, and Amundson (1970) who used the method of characteristics to solve several Riemann problems. Integrability of (5) was also established by Tsarev (1991) with a generalized hodograph method suitable for reducing the problem of solution of the above system to a linear problem was given. The concentrations v_i can be expressed as (Rhee Hyun-Ku, Aris, and Amundson 1970):

$$v_i = \left(\frac{\Gamma_i}{\omega_i} - 1\right)\prod_{j=1,\,j\neq i}^{n}\frac{(\Gamma_i - \omega_j)\Gamma_j}{(\Gamma_i - \Gamma_j)\,\omega_j}, \tag{6}$$

being ω_j Riemann invariants satisfying the characteristic equations

$$\frac{\partial \omega_k}{\partial \eta} - \widehat{\lambda}_k\frac{\partial \omega_k}{\partial \tau} = 0, \qquad (k = 1,..,n), \tag{7}$$

$$\widehat{\lambda}_k = \omega_k\left(\prod_{j=1}^{n}\omega_j\right), \tag{8}$$

where

$$\eta = x\left(\prod_{j=1}^{n}\Gamma_j\right)^{-1}, \quad \tau = x - Vt. \tag{9}$$

Owing to the hyperbolicity of (5), the Riemann invariants ω_k fulfil the conditions:

$$0 < \omega_1 < \Gamma_1 < \omega_2 < \Gamma_2 < ... < \omega_n < \Gamma_n. \tag{10}$$

For the sake of simplicity in the following we consider the case of a mixture of three solutes and we set

$$\omega_1 = R, \quad \omega_2 = S, \quad \omega_3 = P, \tag{11}$$

so that equations (7) specializes to the homogeneous system

$$R_\eta - \lambda R_\tau = 0,$$
$$S_\eta - \mu S_\tau = 0, \tag{12}$$
$$P_\eta - \nu P_\tau = 0,$$

where

$$\lambda = R^2 S P, \quad \mu = R S^2 P, \quad \nu = R S P^2, \tag{13}$$

which belongs to the class of hyperbolic models (1) with

$$\mathbf{U} = \begin{bmatrix} R \\ S \\ P \end{bmatrix}, \qquad A = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & \mu & 0 \\ 0 & 0 & \nu \end{bmatrix}, \qquad \mathbf{B} = 0. \tag{14}$$

Therefore, the integration of the system of equations (12) give rise, through (6), to exact solutions of the governing model (5).

Finally, inserting into (2) the left eigenvectors $\mathbf{l}^{(i)}$ $(i = 1, 2, 3)$ associated to the diagonal matrix $(14)_2$, the only possible first order differential constraints whoch can be compatible with (12) are

$$R_\tau = \alpha(\eta, \tau, R, S, P), \tag{15}$$
$$S_\tau = \beta(\eta, \tau, R, S, P), \tag{16}$$
$$P_\tau = \gamma(\eta, \tau, R, S, P). \tag{17}$$

4. Differential Constraints Analysis

For the overdetermined system resulting from (12) and (15), (16), (17) three possible cases arise.

1. *Three constraints.*
First we append to the system (12) the differential constraints (15), (16) and (17) whereupon, by cross differentiation the resulting consistency conditions specialize to

$$\alpha_\eta - \lambda \alpha_\tau = \lambda_R \alpha^2 + ((\lambda - \mu)\alpha_S + \lambda_S \alpha)\beta + ((\lambda - \nu)\alpha_P + \lambda_P \alpha)\gamma, \tag{18}$$
$$\beta_\eta - \mu \beta_\tau = \mu_S \beta^2 + ((\mu - \lambda)\beta_R + \mu_R \beta)\alpha + ((\mu - \nu)\beta_P + \mu_P \beta)\gamma, \tag{19}$$
$$\gamma_\eta - \nu \gamma_\tau = \nu_P \gamma^2 + ((\nu - \lambda)\gamma_R + \nu_R \gamma)\alpha + ((\nu - \mu)\gamma_S + \nu_S \gamma)\beta. \tag{20}$$

In order to determine solutions of (18), (19) and (20), we assume $\alpha(\eta, \tau, R)$, $\beta(\eta, \tau, S)$ and $\gamma(\eta, \tau, P)$. Double differentiation of equation (18) with respect to S and further differentation with respect to P gives rise to

$$\beta = \beta_0(\eta, \tau)S + \beta_1(\eta, \tau). \tag{21}$$

In a similar way, multiple differentiations of the equations (19) and (20) lead to

$$\alpha = \alpha_0(\eta, \tau)R + \alpha_1(\eta, \tau), \qquad \gamma = \gamma_0(\eta, \tau)P + \gamma_1(\eta, \tau), \tag{22}$$

where α_0, α_1, β_0, β_1, γ_0 and γ_1 are functions to be determine.

Finally, by inserting (21) and (22) into (18), (19), (20) and requiring the resulting conditions to be fulfilled $\forall R, S, P$, after some simple calculations, we obtain

$$\alpha = \frac{a'(\tau)}{a(\tau)}R, \quad \beta = \frac{a'(\tau)}{a(\tau)+k_1}S, \quad \gamma = \frac{a'(\tau)}{a(\tau)+k_2}P, \tag{23}$$

where k_1 and k_2 are arbitrary constants, while the function $a(\tau)$ must satisfy the equation

$$a(\tau)\left(a(\tau)+k_1\right)\left(a(\tau)+k_2\right)a'(\tau) = c_0. \tag{24}$$

being c_0 an arbitrary constant and the prime means for ordinary differentiation.

Next, by taking (23) into account, the set of Riemann equations (12) and the constraint equations (15), (16), (17) specialize, respectively to

$$R_\eta = R^3 S P \frac{a'}{a}, \quad S_\eta = R S^3 P \frac{a'}{a+k_1}, \quad P_\eta = R S P^3 \frac{a'}{a+k_2}, \tag{25}$$

and

$$R_\tau = \frac{a'}{a}R, \quad S_\tau = \frac{a'}{a+k_1}S, \quad P_\tau = \frac{a'}{a+k_2}. \tag{26}$$

Thus, after some elementary algebra the integration of (25) and (26) leads to

$$R = \frac{a(\tau)}{f(\eta)}, \quad S = \frac{a(\tau)+k_1}{f(\eta)+m_1}, \quad P = \frac{a(\tau)+k_2}{f(\eta)+m_2}, \tag{27}$$

where m_1 and m_2 are arbitrary constants while the function $f(\eta)$ is determined by the equation

$$f(\eta)\left(f(\eta)+m_1\right)\left(f(\eta)+m_2\right)f'(\eta) = -c_0. \tag{28}$$

Finally the integration of (24) and (28) give rise to the relations

$$a^4 + \frac{4}{3}(k_1+k_2)a^3 + 2k_1k_2a^2 = c_0\tau, \tag{29}$$

$$f^4 + \frac{4}{3}(m_1+m_2)f^3 + 2m_1m_2f^2 = -c_0\eta, \tag{30}$$

which define the functions $a(\tau)$ and $f(\eta)$. Once $a(\tau)$ and $f(\eta)$ are specified according to (29) and (30), respectively, an exact solution of (12) parameterized by arbitrary constants is obtained.

2. *One constraint*

Here we add to the equations (12) one of the possible constraints, say (15). In this case the resulting compatibility conditions take the form

$$\begin{aligned}
(\mu - \lambda)\alpha_S &= \lambda_S \alpha, \\
(v - \lambda)\alpha_P &= \lambda_P \alpha, \\
\alpha_\eta - \lambda \alpha_\tau &= \lambda_R \alpha^2.
\end{aligned} \tag{31}$$

Now we prove that, if $\alpha \neq 0$, then the overdetermined system (31) does not admit any solution. In fact by introducing the variable transformation

$$\alpha = e^b,$$

the equations (31), taking (13) into account, assume the form

$$b_S = \frac{R}{S(S-R)},$$

$$b_P = \frac{R}{P(P-R)}, \tag{32}$$

$$b_\eta = R^2 S P b_\tau + 2RSP e^b.$$

Finally, from (32) it is simple matter to verify that the equations $b_{S\eta} = b_{\eta S}$ and $b_{P\eta} = b_{\eta P}$ are not compatible so that the equations (31) are not consistent. Therefore, if $\alpha \neq 0$, the governing system (12) is not compatible with only one appended constraint.

Hence the equations (31) admit only the solution $\alpha = 0$. In this case the constraint (15), along with (12), leads to $R = const.$. In terms of the original variables v_1, v_2, v_3 the latter result characterizes an exact solution belonging to the well known class of double wave (i. e. a solution depending on two parameters).

3. *Two constraints*

In the present case we append to the system (12) the differential constraints (15) and (16) so that the resulting consistency conditions are

$$(v - \lambda)\alpha_P = \lambda_P \alpha, \tag{33}$$

$$\alpha_\eta - \lambda \alpha_\tau = \lambda_R \alpha^2 + ((\lambda - \mu)\alpha_S + \lambda_S \alpha)\beta, \tag{34}$$

$$(v - \mu)\beta_P = \mu_P \beta, \tag{35}$$

$$\beta_\eta - \mu \beta_\tau = \mu_S \beta^2 + ((\mu - \lambda)\beta_R + \mu_R \beta)\alpha. \tag{36}$$

Along the some line of approach outlined in the case 1, after some algebra the solution of (33), (34), (35) and (36) is given by

$$\alpha = \frac{1}{2RS(R-S)\eta + A(R,S,\sigma)} \frac{P-R}{P}, \tag{37}$$

$$\beta = \frac{1}{2RS(S-R)\eta + B(R,S,\sigma)} \frac{P-S}{P}, \tag{38}$$

where the functions $A(R,S,\sigma)$ and $B(R,S,\sigma)$ satisfy the system

$$A(2R - RSB_\sigma) + R(R-S)B_R + SB = 0, \tag{39}$$

$$B(2S - RSA_\sigma) + S(S-R)A_S + RA = 0, \tag{40}$$

being $\sigma = \tau + R^2 S^2 \eta$.

Several cases of integration in a closed form can be considered for the pair of conditions (39) and (40). Here we limit our attention on the particular solution of form

$$A = kRS(R-S), \qquad B = kRS(S-R), \tag{41}$$

where k is an arbitrary constant. In this case, owing to (4) and by taking (37) and (38) into account, the system (12) can be recast as

$$R_\eta - v R_\tau = -\frac{(R-P)^2}{(R-S)(2\eta+k)}, \tag{42}$$

$$S_\eta - v S_\tau = \frac{(S-P)^2}{(R-S)(2\eta+k)}, \tag{43}$$

$$P_\eta - v P_\tau = 0, \tag{44}$$

while the constraints (15) and (16) specialize, respectively, to

$$R_\tau = \frac{1}{RS(R-S)(2\eta+k)}\frac{P-R}{P}, \tag{45}$$

$$S_\tau = \frac{1}{RS(S-R)(2\eta+k)}\frac{P-S}{P}. \tag{46}$$

The next step is to integrate (42), (43), (44) along with (45) and (46) under the initial conditions

$$R(\tau,0) = R_0(\tau), \quad S(\tau,0) = S_0(\tau), \quad P(\tau,0) = P_0(\tau). \tag{47}$$

We remark that, owing to (9), in terms of the original variables x and t the initial data (47) correspond to boundary data. Therefore the solution we are looking for will fit a boundary value problem for the model (5).

Equations (42), (43) and (44) involve the directional derivative of R, S, and P along the characteristic associated to v, so that in order to integrate them, we can use the standard method of characteristics. In particular from (44) we find

$$P = P_0(z), \tag{48}$$

where z is the parameter determining the curves of the characteristics family, while from (42) and (43) we have

$$(R+S)_\eta - v(R+S)_\tau = \frac{2P_0 - (R+S)}{2\eta+k}, \tag{49}$$

$$(RS)_\eta - v(RS)_\tau = \frac{RS - P_0^2}{2\eta+k}, \tag{50}$$

whose solution is given by

$$R+S = 2P_0(z) + (R_0(z) + S_0(z) - 2P_0(z))\sqrt{\frac{k}{2\eta+k}}, \tag{51}$$

$$RS = P_0^2(z) + (R_0(z)S_0(z) - P_0^2(z))\sqrt{\frac{k}{2\eta+k}}, \tag{52}$$

along with

$$\tau = P_0^4(z)\eta - k\left(R_0(z)S_0(z)P_0^2(z) - P_0^4(z)\right)\left(\sqrt{\frac{2\eta+k}{k}} - 1\right) + z. \tag{53}$$

Finally, in view of integrating the equations (45) and (46), it is more convenient to rewrite them under the form

$$(R+S)_\tau = -\frac{1}{PRS(2\eta+k)}, \tag{54}$$

$$(RS)_\tau = -\frac{1}{RS(2\eta+k)}. \tag{55}$$

According to the differential constraints theory and by taking (53) into account, later substitution of (48), (49) and (50) into (54) and (55) yields

$$\frac{d(R_0+S_0)}{dz} = -\frac{1}{kP_0R_0S_0}, \tag{56}$$

$$\frac{d(R_0S_0)}{dz} = -\frac{1}{kR_0S_0}, \tag{57}$$

which select the class of initial data (47) allowing the present procedure to hold. Therefore the relations (48), (49) and (50) along with (53), (56) and (57) provide an exact solution of (12) parameterized by one arbitrary function. In fact from (56), (57) one of the three initial functions R_0, S_0, P_0 results to be arbitrary so that the corresponding solution generalizes the well known simple wave solution.

In order to get a deeper insight into the method which was developed hitherto, now we determine an exact solution to the governing model (12) in a case where the wavelet parameter z can be explicitly calculated from (53).

Actually, by requiring

$$R_0S_0 = cP_0^2, \tag{58}$$

with c an arbitrary constant, from (53) and (57) we obtain

$$P_0^2 = \mp\frac{1}{c}\sqrt{-\frac{2}{k}z}, \tag{59}$$

$$R_0S_0 = \mp\sqrt{-\frac{2}{k}z}, \tag{60}$$

$$z = \frac{c^2k\tau}{2\left(-\eta+(c-1)\left(\sqrt{k(2\eta+k)}-k\right)\right)+c^2k}, \tag{61}$$

while, by assuming $c > 0$, from (56) we deduce

$$R_0+S_0 = \mp2\sqrt{c}\left(-\frac{2}{k}z\right)^{\frac{1}{4}}. \tag{62}$$

Thus, relations (48), (54) and (55), supplemented by (59)-(62) provide an exact solution of the set of equations (12) which, through (6), give rise to an explicit solution of the governing system (5) provided that the conditions (10) are satisfied. The intrinsic wave features of the solution under interest are highlighted by its 3D-plot shown in fig. 1 and which describes the propagation of a single concentration of the mixture. The resulting behavior fits with that one reported by Helfferich and Whitley (1996) for the case in point.
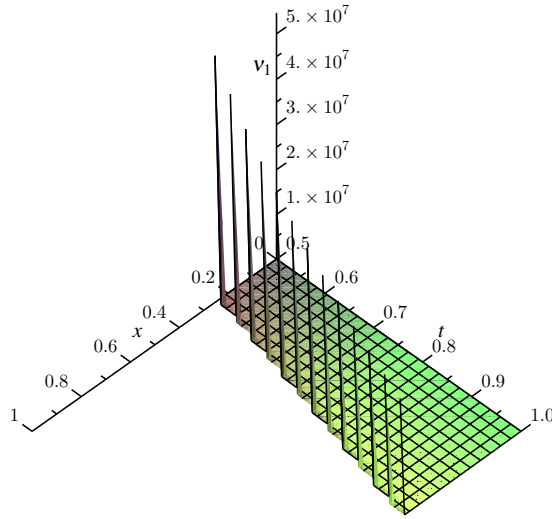
FIGURE 1. 3-D-plot of v_1 concentration given by (6) with $\Gamma_1 = 6$, $\Gamma_2 = 7$ and $\Gamma_3 = 8$,

5. Conclusion and final remarks

Along the lines of the differential constraints method, in this paper a comprehensive analysis has been worked out for the quasilinear hyperbolic system of first order PDEs (5) which was proposed by Rhee Hyun-Ku, Aris, and Amundson (1970, 1971) to model multicomponent chromatography for an ideal column in terms of wave processes. Actually, in fields of chemical engineering application this mathematical model played a prominent role over the years, because its leading assumptions represented the very first step to derive updated and more accurate models for describing interactions between different solutes in multicomponent systems (Butté, Storti, and Mazzotti 2008; Canon 2012; Canon and James 1992; Golshan-Shirazi and Guiochon 1989; Gritti and Guiochon 2013; Hankins and Helfferich 1999; Helfferich 1997; Helfferich and Whitley 1996; Helfreich and Klein

1970; Rhee Hyun-Ku, Aris, and Amundson 1970; Mazzotti and Rajendran 2013; Rhee Hyun-Ku, Aris, and Amundson 1971, 2001; Rouchon *et al.* 1987; Seidel-Morgenstein 2004; Shen and Smith 1968; Siitonen and Sainio 2011; Ting and Helfferich 1999; Urbach 1992; Urbach and Bokx 1992). Apart from its own theoretical value, as significant mathematical aspect of distinguishing the system under interest belongs to the class of homogeneous semi-hamiltonian systems of hydrodynamic type involving $N > 2$ dependent variables and which, nevertheless, can be diagonalized in terms of Riemann invariants.

Very recent papers (Curró, Fusco, and Manganaro 2015) have been devoted to perform an accurate and exact description of the hyperbolic wave interaction processes which are associated to the hyperbolic governing system (5). The results obtained therein by means of a generalized hodograph method (Tsarev 1991) were in line with the main theoretical predictions which are expected from the model in point (Hankins and Helfferich 1999; Helfferich 1997; Helfferich and Whitley 1996; Ting and Helfferich 1999).

Here in order to accomplish an exhaustive theoretical validation, exact solutions to the model (12) are searched by means of the differential constraints method. In section 4 there have been considered the possible constraints which can be appended to system (12). The case 1 provides exact solutions which are parameterized by arbitrary constants and that induces a strong restriction on the initial data which can be fitted. Next, the consistency of (12) and (18) gives rise to the trivial solution $R = const$. Finally in case 3 the resulting solutions are parameterized by an arbitrary function so that they are flexible to fit suitable boundary value problems. Since these solutions are obtained by integrating along characteristic curves they have inherent wave features. Apart from their own theoretical value, all these solutions can be also useful for testing numerical procedures for the quasilinear hyperbolic system of PDEs under interest.

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