Elution parameters in constant-pressure, single-ramp temperature-programmed gas chromatography

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Abstract

The dependence of the degree of interaction of a solute with the stationary phase at the time of its elution from the column in temperature-programmed GC is best described by interaction level of the solute. The latter represents the fraction of a solute residing in the stationary phase relative to the total amount of the solute. A simple approach to the evaluation of interaction levels of eluting solutes in a single-ramp temperature program is proposed. In a single-ramp temperature program having no preceding temperature plateau, all solutes that elute at temperatures that are about 60°C higher than the initial temperature of the heating ramp elute with nearly the same interaction levels that can be found as $\exp(-r)$, where r is dimensionless heating rate. A specially designed temperature plateau preceding the ramp causes all solutes eluting during the entire time of the ramp to elute with nearly the same interaction levels equal to $\exp(-r)$. A transformation of the interaction level of a solute into its retention factor or mobility factor (a fraction of a solute in a mobile phase in relation to the total amount of the solute) and vice versa is also described.   © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Gas chromatography; Temperature programming; Mobility factor; Retention factor

1. Introduction

In chromatography, the relationship between the solute and the mobile phase velocities is typically expressed by the solute retention factor [1], k, or by the quantity $\mu = 1/(1 + k)$, introduced by Consden et al. in 1944 [2]. Sometimes, it can be more convenient to use quantity $\lambda = 1 - \mu$ instead of k or μ (for the interpretation of μ and λ, see analysis below). In this study, we evaluate the values, k_e, λ_e and μ_e, of k, λ and μ at the time of solute elution from the column in temperature programmed GC (gas chromatography).

A detailed study of a temperature-programmed GC is mathematically complex [3,4], and the details frequently obscure the general picture. Here we pursue a limited goal of evaluation of the major trends in k_e, λ_e and μ_e. To find the simple results, we not only narrow the scope of this study as outlined in its title (constant pressure, single-ramp temperature program), but we also choose to ignore the dependence of a gas viscosity on the temperature, T, and

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assumed that the retention factor, k, of a solute can be expressed as [5]:

$$\ln k = (T_{char} - T)/\theta_{char} \qquad (1)$$

where $\theta_{char} = -\,dT/dk$ at $k=1$ (inverse of the slope in k vs. $-T$ at $k=1$) is characteristic thermal constant of a solute, and T_{char} is its characteristic elution temperature (the temperature at which the solute elutes with $k=1$).

The linear dependence of $\ln k$ on T in Eq. (1) is a first approximation [5] to the thermodynamically more meaningful [3,4,6–8], but non-linear dependence:

$$\ln k = a + bT^{-1} \qquad (2)$$

The non-linearity of this function is the main cause of the complications in known studies of the temperature-programmed GC. In addition to that, parameters a and b of Eq. (2) have no direct chromatographic meaning [5].

The mathematical aspects of the approximation of Eq. (2) by Eq. (1) were discussed elsewhere [5]. However, there are also the practical ones.

Parameters a and b of Eq. (2) can change [9,10] with the temperature. At the same time, the measurement of these parameters for large values of k, is time consuming. As a result, the measurements are typically done [5,11–14] for relatively small k values confined within a narrow (typically, less than 100°C) temperature range. From that point of view, both Eq. (2) with fixed a and b, and Eq. (1) are just two different approaches to curve fitting experimental data. While both yield very close $\ln k$ values within experimental temperature range [5], it is not certain that, in a wide temperature range (hundreds of°C), Eq. (2) gives substantially more accurate results.

There is another important aspect of solute migration in temperature programmed GC. During a long linear heating ramp, retention factor, k_e, of each eluting solute converges to the value that is primarily affected by the dependence of k on $(T-T_e)$ in the vicinity of the solute's elution temperature, T_e [3–5]. This magnifies the importance of describing k vs. T for each solute in the vicinity of its own elution temperature, T_e. An optimum value of k_e depends [5,15,16] on specific optimization constraints, but it

is usually in the vicinity of $k_e=1$. Eq. (1), describing k in the vicinity of T_{char} which is T_e at $k=1$, focuses exactly on this region and, thereby, can better fit the experimental data than Eq. (2).

The last argument also provides a reason for ignoring the gas viscosity dependence on temperature [17,18]. As the elution parameters of each solute in temperature programmed GC are mostly affected by its migration during a relatively short time period immediately preceding the elution, the change in a gas viscosity during that short period does not significantly affect elution parameters. We shall ignore this effect in favor of the simplicity of the results.

The net effect of these approximations is graphically illustrated, at the end of this study.

2. Theory

2.1. Migration of a solute relative to the mobile phase

As we mentioned in the beginning of the Introduction, the relationship between the velocities of a solute and the mobile phase can be described in several ways. Retention factor [1], k (the ratio of the amount of solute in the stationary phase to that in the mobile phase) is the most frequently used one. While k most directly relates to the solute thermodynamic properties, Eqs. (1) and (2), the separation of given solutes eventually depends on the difference in their velocities:

$$u_s = \mu u \qquad (3)$$

as they migrate through the column (u is velocity of the mobile phase). Introduced by Consden et al. in 1944 [2] and known from other workers [1,4,6–8,19–25], the quantity $\mu = 1/(1 + k)$ represents a fraction of the solute in a mobile phase in relation to its total amount. When $\mu=0$, no solute is in the mobile phase and, hence, has a zero mobility. In the other extreme, when $\mu=1$, the solute is entirely in the mobile phase and, therefore, migrates with the velocity of the mobile phase and has maximum mobility. We will refer to μ as to the solute mobility

factor.[1] Giddings suggested [8] (p. 233, different symbols were used for μ and k in the original text) that ''most equations describing chromatography are simpler when expressed in terms of μ rather than k.'' Eq. (3) is a good example of that.

Complimentary to μ is the quantity $\lambda = 1 - \mu$ which represents the fraction of solute in the stationary phase in relation to the total amount of the solute. One might think of λ as a measure of the level of interaction of the solute with the stationary phase. This level can change from 0 for the solutes that have no interaction with the stationary phase (i.e. have 100% presence in the mobile phase) to 1 for the solutes that totally reside in the stationary phase. Some chromatographic equations become simpler and have more transparent interpretation (see below) when expressed via λ rather than via k or μ.

It follows directly from their definitions that quantities k, μ, and λ relate as:

$$k = \frac{\lambda}{1 + \lambda} = \frac{1 - \mu}{\mu}, \quad \lambda = \frac{k}{1 - k} = 1 - \mu,$$

$$\mu = \frac{1}{1 + k} = 1 - \lambda \tag{4}$$

2.2. Elution parameters

Consider a single-ramp temperature program:

$$T = T_{\text{init}} + R_{\text{T}}t \tag{5}$$

where T_{init} is initial temperature, R_{T} is heating rate, and t is time from the solute injection into the column. This program has no preceding temperature plateau.

It will be useful for subsequent derivation to treat the initial retention factor, k_{init}, of each solute rather than the initial temperature, T_{init}, in Eq. (5) as an a

priori known independent parameter. Eq. (1), allows one to express T_{init} via k_{init} as:

$$T_{\text{init}} = T_{\text{char}} - \theta_{\text{char}} \ln k_{\text{init}} \tag{6}$$

Earlier [5,24], we introduced dimensionless temperature, x, dimensionless heating rate, r, dimensionless time, τ, and dimensionless retention time, τ_{R}, defined as:

$$x = T/\theta_{\text{char}}, \quad r = R_{\text{T}}t_{\text{M}}/\theta_{\text{char}}, \quad \tau = t/t_{\text{M}},$$

$$\tau_{\text{R}} = t_{\text{R}}/t_{\text{M}} \tag{7}$$

where t_{M} and t_{R} are void time and retention time, respectively. Accounting for Eqs. (5) and (6), one can rewrite Eq. (1) as:

$$\ln k = \ln k_{\text{init}} - r\tau, \quad \text{or} \quad k = k_{\text{init}}e^{-r\tau} \tag{8}$$

Let k_{e} be elution retention factor of a solute, i.e. the solute retention factor at the time, τ_{R}, of its elution from the column. Eq. (8) yields:

$$\tau_{\text{R}} = (\ln k_{\text{init}} - \ln k_{\text{e}})/r \tag{9}$$

Ignoring the temperature dependence of a gas viscosity, one can write elution equation [24] for a constant column pressure as $\int_0^{\tau_{\text{R}}} \mu \, d\tau = 1$ which, due to Eq. (4), can be written as $\int_0^{\tau_{\text{R}}} d\tau/(1 + k) = 1$. Coupled with Eq. (8), this becomes $\int_0^{\tau_{\text{R}}} d\tau/(1 + k_{\text{init}}e^{-r\tau}) = 1$. Integration of this equation yields:

$$r\tau_{\text{R}} + \ln \frac{1 + k_{\text{init}} \exp(-r\tau_{\text{R}})}{1 + k_{\text{init}}} = r \tag{10}$$

Several useful relations can be derived from this equation. Its solution for τ_{R} is:

$$\tau_{\text{R}} = \frac{\ln[e^r + (e^r - 1) k_{\text{init}}]}{r} \tag{11}$$

where, due to Eq. (4), k_{init} can be expressed via λ_{init} as:

$$k_{\text{init}} = \lambda_{\text{init}}/(1 - \lambda_{\text{init}}) \tag{12}$$

A result of the substitution of Eq. (9) in Eqs. (10) or (11) can be expressed as:

$$\lambda_{\text{e}} = \lambda_{\text{init}}e^{-r} \tag{13}$$

where, according to Eq. (4), $\lambda_{\text{init}} = k_{\text{init}}/(1 + k_{\text{init}})$ and $\lambda_{\text{e}} = k_{\text{e}}/(1 + k_{\text{e}})$ are initial and elution interaction levels of a solute, respectively. Finally, substi-

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[1]This quantity is also known as a retardation factor [1,6,19–21,23], retention ratio [8,22,25], and propagation factor [24]. In our view, the terms retardation factor and retention ratio are counterintuitive. They assign the highest retardation or retention values to the least retained (i.e. the most mobile) solutes. In addition to that, retention ratio can be confused with retention factor, k. The term propagation factor that we previously proposed [24] is sufficiently descriptive and somewhat intuitive. However, this term seems to be less suitable for chromatography than the term mobility factor, proposed herein.

tution of Eq. (12) in Eq. (11) followed by the cancellation of λ_{init} between the result and Eq. (13) leads to the expression:

$$\lambda_e = \frac{e^{r(\tau_R - 1)} - 1}{e^{r\tau_R} - 1} \qquad (14)$$

Eqs. (11) and (13) describe the parameters (the dimensionless retention time, τ_R, and elution inter-action level, λ_e) of each specific solute via its initial conditions, k_{init} or λ_{init}, and via the heating rate, r, of a temperature program. Eq. (14) describes elution interaction levels of all solutes as a function of their retention times and the heating rate. Using Eq. (7) to convert dimensionless parameters, r and τ_R, in Eqs. (11)–(14) into their absolute equivalents, R_T and t_R, one can express the behavior of the solutes in those absolute terms. Also, using Eqs. (7) and (5), one can express λ_e in Eq. (14) as a function (Fig. 1) of the solute elution temperature, T_e, rather than its elution time.

Due to its simplicity, Eq. (13) deserves additional attention. It indicates that (Figs. 1 and 2):

(1) During a linear heating ramp, interaction levels, λ_e, of the eluting solutes asymptotically approach a stable value:
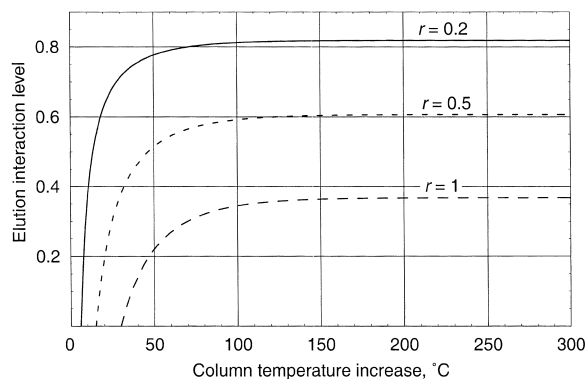

Fig. 1. Elution interaction levels, λ_e, vs. a column temperature increase, $T - T_{init}$, from the beginning of a heating ramp. Each solute elutes with the interaction level $\lambda_e = \lambda_{init} e^{-r}$, Eq. (13), that depends only on the initial interaction level, λ_{init}, of the solute, and on the dimensionless heating rate, r. When the column temperature increases, the interaction levels, λ_e, of the eluting solutes asymptotically approach a stable value, e^{-r}, that depends only on r. Assumptions: (a) no initial temperature plateau prior to the heating ramp, and (b) all solutes have the same characteristic thermal constant, $\theta_{char} = 30°C$ [5].
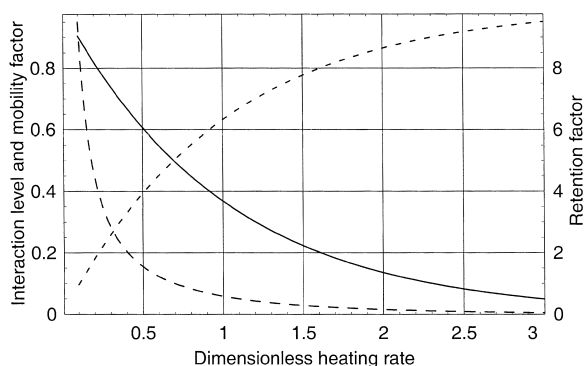

Fig. 2. Stable elution parameters: (—) interaction level, $\lambda_{eo} = e^{-r}$; (- - -) mobility factor, $\mu_{eo} = 1 - e^{-r}$; and (— — —) retention factor, $k_{eo} = 1/(e^r - 1)$, resulting from heating ramp with dimensionless rate, r.

$$\lambda_{eo} = e^{-r} \qquad (15)$$

that depends only on the dimensionless heating rate, r

(2) All solutes that are substantially retained at the beginning of the ramp ($\lambda_{init} \approx 1$) elute with nearly the same interaction level approaching λ_{eo} in Eq. (15).

In view of Eq. (15), one can write Eq. (13) as:

$$\lambda_e = \lambda_{init} \lambda_{eo} \qquad (16)$$

For all solutes that are substantially retained at the beginning of the temperature program ($\lambda_{init} \approx 1$), Eq. (16) can be approximated (Fig. 2) as:

$$\lambda_e \approx \lambda_{eo} = e^{-r} \qquad (17)$$

The same follows for the large τ_R values from Eq. (14) confirming that, as the heating ramp progresses, the interaction levels, λ_e, of the eluting solutes asymptotically approaches the stable level of e^{-r} (Figs. 1 and 2).

For the other two elution parameters in Eq. (4), one has from Eq. (13):

$$k_e = \frac{k_{init}}{e^r + (e^r - 1) k_{init}},$$
$$\mu_e = 1 - (1 - \mu_{init}) e^{-r} \qquad (18)$$

For solutes that are substantially retained at the beginning of the ramp (i.e. $|\mu_{init}| \ll 1$, $k_{init} \gg 1$), μ_e and k_e also approach their own stable levels (Fig. 2):

$$k_{eo} = 1/(e^r - 1), \quad \mu_{eo} = 1 - e^{-r} \qquad (19)$$

corresponding to k_e and μ_e at $k_{init} = \infty$ and $\mu_{init} = 0$, respectively. Notice that Eqs. (18) and (19) are not as simple as their counterparts, Eqs. (13), (15)–(17), for λ_e and λ_{eo}.

3. Discussion

In the theoretical section, we have established, Eqs. (13), (15)–(17) that, in a single-ramp temperature program with no preceding temperature plateau, the elution interaction level, λ_e, of a solute is a product of its initial, λ_{init}, and the stable, λ_{eo}, interaction levels (Eq. (15)). These expressions quantify an experimentally known fact that the higher the heating rate in temperature programmed GC, the lower the retention of solutes during their last stages of migration in general, and during their elution in particular. Eqs. (13), (15)–(17) show that λ_e drops exponentially (Fig. 2) with an increase in the heating rate, r. It is important to emphasize that it is not the absolute heating rate, R_T, that counts, but rather its relation, r, Eq. (7), to void time, t_M, and to characteristic thermal constant, θ_{char}, (typically, 30–40°C [5,26]) of the solute.

Example 1. According to Eq. (7), $R_T = r\theta_{char}/t_M$. Assuming that $T_{init} = 50$°C, $\theta_{char} = 30$°C, $r = 0.5$, one has for a 5-m × 100-μm column with $t_M \approx 0.075$ min (1 ml/min of hydrogen at T_{init} [27]) a value of $R_T \approx 200$°C/min. On the other hand, for a 100-m × 530-μm column with $t_M \approx 6.5$ min (4.2 ml/min of helium at T_{init} [27]), $R_T \approx 2.3$°C/min. This shows how different the absolute heating rates, R_T, can be for the same dimensionless heating rate, r, depending on column dimensions, carrier gas type and its flow-rate.

It follows from Eq. (16) that, when λ_{init} is high ($\lambda_{init} \approx 1$), its actual value (whether it is, say, 0.9, 0.99 or 0.999) does not have significant effect. Only when λ_{init} is substantially lower than 1, its impact can be significant.

The time after which λ_e becomes close to its stable level λ_{eo} can be found from Eqs. (11) and (12). Unfortunately, the initial elution parameters, λ_{init} or k_{init}, of the solutes in these expressions are typically unknown. Fortunately, however, this problem can be easily avoided due to the following two facts. First, as we have experimentally shown earlier [15,16],

depending on optimization constraints, optimal dimensionless heating rate can have different values that are below unity, but not very far from it. Secondly, we have also shown [5] by computer simulation that, when $0.1 \leq r \leq 1$, all solutes that elute after the temperature becomes about $2\theta_{char}$ (about 60°C) higher than T_{init}, elute with nearly the same λ_e. Expressed as a direct function of T, this asymptotic behavior of λ_e (Fig. 1) follows from Eq. (14). Practically speaking, this means that about 60°C after the start of a heating ramp, all solutes elute with nearly the same elution interaction level, λ_e, that can be found as e^{-r} (Fig. 2). The most remarkable property of the solutes eluting after about 60°C from the start of a heating ramp is that their elution parameters essentially depend only on the dimensionless heating rate, Eqs. (15) and (16) (Fig. 1), regardless of initial values of these parameters.

Example 2. Assume that, as in Example 1, $r = 0.5$. The elution interaction levels, λ_e, of all solutes that elute after the column temperature becomes about 60°C higher than T_{init}, are close to $\lambda_{eo} = e^{-r} \approx 0.6$.

In one important practical case, all solutes eluting during the heating ramp, including the ones that elute during the early portion of the ramp, have $\lambda_e \approx \lambda_{eo}$.

In practice, some solutes in a sample mixture might just barely interact with the stationary phase at T_{init}. A temperature increase during migration of these solutes further diminishes their interaction with the phase, and, hence, their already potentially low separability. It can be beneficial for the separation of these solutes to provide a temperature plateau at T_{init} (isothermal section) that lasts through the elution of these solutes. By freeing a column of these solutes before the initiation of the ramp, a short temperature plateau reduces the transitional portion of the ramp where $\lambda_e < \lambda_{eo}$. On the other hand, if the plateau is so long that the highly interactive solutes elute before the ramp, it might take a significant portion of the ramp before λ_e gets down to λ_{eo}. Using too long a plateau can also substantially increase the total analysis time. These two extremes suggest that there might be a middle ground — a temperature plateau that has such a duration, t_{po}, that is just long enough to essentially eliminate the deviations of λ_e from λ_{eo} during its initial portion. Finding the best rule for selecting such t_{po} is beyond the scope of this report. However, it seems natural to choose $t_{po} = (1 +$

k_{eo}) t_M as the first approximation. The ramp that follows after such a plateau starts at the time when the solute eluting at the end of the isothermal section elutes with the retention factor, k_{eo}, which is the same as the stable retention factor for solutes eluting during the subsequent ramp.

Due to Eq. (19), t_{po} can be found as:

$$t_{po} = (1 + k_{eo}) t_M = t_M/(1 - e^{-r}) \qquad (20)$$

To reflect the fact that dimensionless measure, t_{po}/t_M, of t_{po} depends only on dimensional heating rate, we will say that the temperature plateau matches the heating rate. Quantities t_{po}/t_M, k_{eo}, λ_{eo} and μ_{eo}, at the end, t_{po}, of the matching plateau for several heating rates are listed in Table 1. A balanced single-ramp temperature program consisting of a linear heating ramp preceded by the matching temperature plateau can be described as:

$$T = \begin{cases} T_{init}, & \text{when } t \le t_{po} \\ T_{init} + (t - t_{po}) R_T, & \text{when } t > t_{po} \end{cases} \qquad (21)$$

A computer simulation [28] of λ_e values in a balanced temperature program are shown in Fig. 3. Because the distribution of the solutes in the column prior to the start of the ramp results from isothermal conditions, some departures of λ_e from their stable vales, λ_{eo}, do occur during the early portion of the ramp (see Fig. 3). However, the departures are relatively small and can be ignored as a first approximation. One can conclude that, in a balanced single-ramp temperature program, Eqs. (21) and (20), elution parameters, λ_e, k_e, and μ_e, of all solutes eluting during the heating ramp remain nearly constant, and can be approximately described by Eqs. (15) and (19).
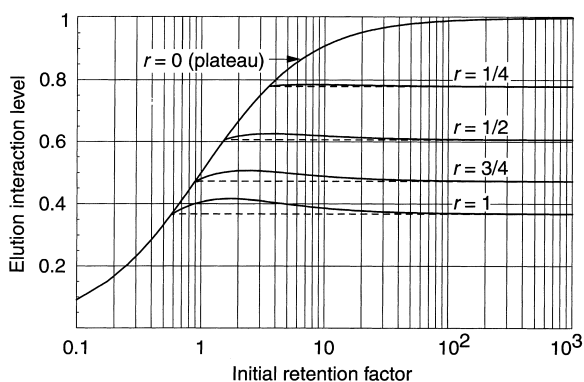

Fig. 3. Elution interaction levels, λ_e, in a balanced single-ramp temperature program, Eqs. (21) and (20). A solute eluting during the temperature plateau elutes at dimensionless time $\tau_R = 1 + k_{init}$, and, hence, has interaction level $\lambda_e = k_{init}/(1 + k_{init}) = (\tau_R - 1)/\tau_R$. For the ramp, solid lines (—) show results of a computer simulation [28] of λ_e vs. k_{init} for k vs. T described in Eq. (1). Dashed lines (- - -) mark asymptotic levels, $\lambda_{eo} = e^{-r}$, for the λ_e values at the same dimensionless heating rates, r. In view of a relatively small departures of λ_e from λ_{eo}, one can reasonably assume that, during the ramp, $\lambda_e \approx \lambda_{eo}$.

3.3. Approximations

This study is based on two simplifying assumptions. Eq. (1) was used instead of the widely known [3,4,6–8] and thermodynamically more meaningful formulae in Eq. (2). Also, the temperature dependence [17,18] of a gas viscosity, η, was ignored. The effect of these simplifications on the value of λ_e is shown in Fig. 4. A justification for the choice of the range of the dimensionless heating rate, r, in Fig. 4 can be found in our previous studies [15,16] where, using experimental data, we have shown that the optimal r values (that depend on the optimization constraints) are lower than unity, but not very far from it. The data in Fig. 4 allow one to conclude that the simple expression in Eq. (16) and other related formulae provide an adequate representation of the dependence of elution parameters in a temperature programmed GC on the dimensionless heating rate, r, in a wide range of useful values of r.

4. Conclusion

There are several alternative ways — solute

Table 1
Dimensionless duration, t_{po}/t_M, Eq. (20), of a matching temperature plateau, and parameters of a solute eluting at the end, t_{po}, of the plateau vs. dimensionless heating rate, r

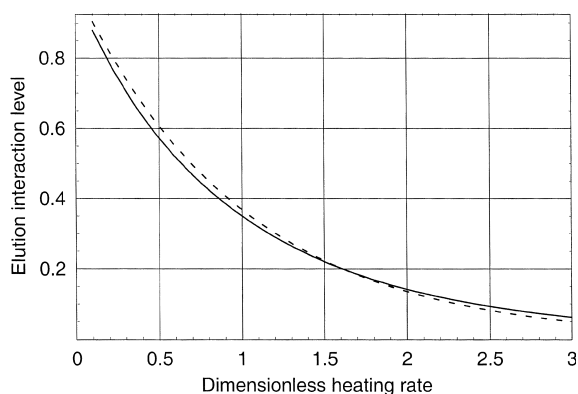| r	t_{po}/t_M	k_{eo}	λ_{eo}	μ_{eo}
0.25	4.52	3.52	0.78	0.27
0.5	2.54	1.54	0.68	0.39
0.75	1.9	0.9	0.47	0.53
1	1.58	0.58	0.37	0.63

Fig. 4. Elution interaction level, λ_e, vs. dimensionless heating rate, r, Eq. (7), for a solute that has been substantially retained ($\lambda_{init} \approx 1$) at the beginning of a linear heating ramp: (—) numerical solution [28] of elution equation [24] (see also Appendix in Ref. [5] for details) for k in Eq. (2) and for gas viscosity proportional to $T^{0.7}$ [17,18], (- - -) $\lambda_{eo} = e^{-r}$, Eq. (15).

retention factor, mobility factor, interaction level — to describe the relationship between the velocity of migration of a solute and that of a mobile phase in chromatography. We found that the interaction level, λ, is the most suitable for analytical description of dependence of the elution properties of the solutes on the heating rate in a single-ramp temperature programmed GC. We have shown that, in a single-ramp temperature program with no preceding temperature plateau, all solutes eluting about 60°C above the initial temperature, T_{init}, of the heating ramp, elute with nearly the same elution interaction level, λ_e, that can be found, Eq. (17), as e^{-r} where r is dimensionless heating rate, Eq. (7). For the same conditions, we have also found, Eq. (19), the retention factor, k_e, and the mobility factor, μ_e.

We have also described a balanced single-ramp temperature program, Eqs. (21) and (20), where duration, t_{po}, of a temperature plateau preceding the heating ramp matches the heating rate in a certain way. For that temperature program, elution parameters, λ_e, k_e, and μ_e, of all solutes eluting during the heating ramp remain nearly constant, and can be approximately described by Eqs. (15) and (19).

The study was based on two simplifying assumptions described in the Introduction. A graphic evaluation of the approximation errors has been provided.

5. Nomenclature

Symbol	Description (measured in units of)
k	retention factor (–)
r	dimensionless heating rate, Eq. (7) (–)
R_T	heating rate (temperature/time)
T	column temperature (temperature)
t	time (time)
T_{char}	characteristic elution temperature [5] (temperature)
t_M	void time (time)
t_{po}	duration of matching temperature plateau, Eq. (20) (time)
t_R	retention time (time)
u	carrier gas velocity (length/time)
u_s	solute velocity (length/time)
x	dimensionless temperature, Eq. (7) (–)
λ	interaction level, Eqs. (4) (–)
μ	mobility factor, Eqs. (4) (–)
θ_{char}	characteristic thermal constant [5] (temperature)
τ	dimensionless time, Eq. (7) (–)
τ_R	dimensionless retention time, Eq. (7) (–)
Subscript	*Definition*
char	characteristic
e	elution
init	initial
o	stable values, Eqs. (15) and (19)

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