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A study on the onset of turbulent conditions with SFC mobile-phases

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ABSTRACT

Following a recent publication [1], the topic of turbulent flow in SFC has generated both interest and questions. Liquid-like density, coupled with significantly low viscosity of CO_2-based mobile-phases may result in high Reynolds number (Re) – higher than what represents laminar flow conditions, reaching the so-called turbulent regions. Although such turbulent flows can form only in the connecting tubings, thus not directly affecting the chromatographic process, it is important to know under many situations, whether the flow inside the tubing is laminar or turbulent.

In this report a comprehensive guideline to identify the possibilities of turbulent flow conditions is provided through a series of charts. Flow properties depend on state conditions (composition, pressure and temperature) and also on the tubing material and geometry. Here guidelines to detect the onset of turbulent conditions is provided for cylindrical stainless-steel tubings of different internal diameters (i.d.) under a wide range of SFC mobile-phase conditions.

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1. Introduction

1.1. Background

Like in liquid chromatography, the main source of pressure-drop in an SFC system was considered to be the packed-bed column till Rajendran et al. [2] demonstrated the important contribution of pressure-drop in connecting tubings. Later Pauw et al. [1] demonstrated that tubing pressure-drops are not only non-negligible, under certain conditions it can be really high – even higher than that offered by the columns. Beyond certain flow velocity, pressure-drop rises non-linearly with flowrate increment. Through their report Pauw et al. demonstrated that this unusual rise in pressure-drop is linked to the occurrence of turbulent flow inside the connecting tubings of an SFC system. Although not directly affecting the chromatography, any loss of usable pressure-drop to the system is a concern, especially when the contribution of the system pressure-drop is higher than that of the column.

1.2. Causes of turbulent flow in SFC

Reynolds number ($Re = \frac{du\rho}{\mu}$, where d is the diameter of the conduit, ρ is the fluid density, μ is the dynamic viscosity and u is the flow velocity) of a flow determines whether the flow is laminar or turbulent. Flows with a value of $Re > 4000$ are typically turbulent and flows with $Re < 2100$ are laminar flow [3]. The region in between is considered a transition or buffer region where the flow could be either laminar or turbulent depending on conditions at the conduit entrance, the surface roughness of the conduit and also the distance from the entrance where this phenomenon is taking place. A discussion on the effect of surface roughness on the onset of turbulence in SFC is available in Ref. [1].

Although it is rare in liquid chromatography except for extreme conditions (see Ref. [4]), turbulent flow can occur in SFC system under common method conditions. The main reason behind is the much lower viscosity of CO_2 based mobile-phases, although the densities remain similar to that of the LC mobile-phases. See in Fig. 1 that viscosity of pure CO_2, even when its density is as high as water's, is almost 3 times smaller than the least viscous solvents used in LC – e.g. hexane, acetonitrile, etc. At lower densities, viscosity is even lower. Note that the lower the μ is, the higher is the Reynolds number. In addition, because of lower μ, SFC is typically run at higher flowrates, which also increases the Re values because u increases. These two factors together increase the *chances* of SFC mobile-phase entering fluidic conditions beyond the laminar limit. The remaining factor that determines whether the flow will be laminar or not, is the diameter of the conduit (d). Even with very favorable solvent properties Re inside SFC columns are too low to be turbulent. Inside connecting tubings, especially in the low-dispersion tubings that are typically used in ultra-performance chromatographic systems, however, flow can become turbulent *depending on* the mobile-phase flowrate, tubing i.d., mobile-phase

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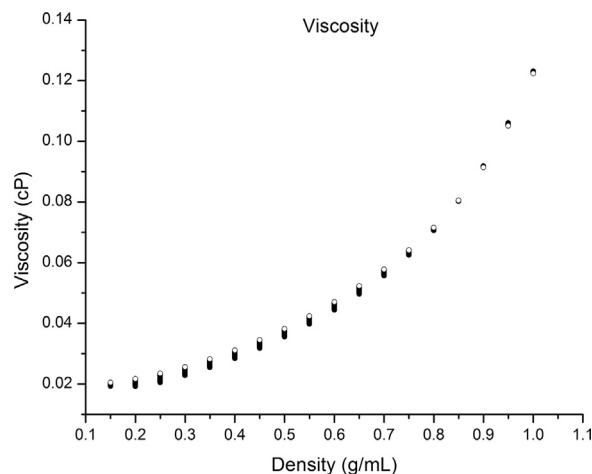E-mail address: abhijit_tarafder@waters.com

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Fig. 1. Variation of viscosity with density of neat CO_2 (from Ref. [9]). More than one viscosity values at certain density points are due to the influence of temperature [9]. At lower densities, CO_2 viscosity can be as low as 0.02 cP, which is 50 times lower than that of water. Even when CO_2 density is equal to that of water its viscosity is 0.122 cP [8], which is about three times lesser than the least viscous solvents of LC, e.g. acetonitrile (=0.34 cP at 27 °C), hexane (=0.3 cP at 25 °C), etc. [10].

temperature and pressure, co-solvent used in the mobile-phase and co-solvent percentage.

1.3. Objective of the current report

In practical situation, it is challenging to identify experimental conditions that maximize experimental objective(s) (e.g. fast analysis) while avoiding turbulent flow – causing excessive pressure-drop in the tubings. For CO_2-based solvents the contour of physical property variation and hence identification of the onset of turbulent conditions, is difficult to describe with words or by presenting tabular set of data. Charts, on the other hand, depicts a global picture of the scenario, which is very important to realize and appreciate the true possibilities of SFC methods.

The objective of the current report is to provide a global picture of the conditions that may lead to the onset of turbulence in SFC system tubing. A series of charts is provided here in that direction. Such charts should be helpful to diagnose, conveniently and instantly, whether an unexpected pressure rise in an SFC system is caused by a turbulent flow or not. The charts may also provide insights regarding the trade-offs in selecting method conditions for better separation while avoiding excessive pressure-drop in tubing.

2. Theory

This section is divided in two parts. The first part describes factors that may lead to non-linear variation of pressure-drop across a system. It will be shown here that turbulent flow is not the only phenomenon that can lead to non-linear variations of pressure-drop with flowrate in SFC. The second part describes construction of the turbulent-flow-identification charts.

2.1. Non-linear variation of pressure-drop with flowrate

In related literature (see Refs. [1,5]), the criterion of a deviation from linear increment of pressure-drop as a function of increasing flowrate has been considered as an indicator of transitioning to turbulent region. While this indeed is the traditional (see Ref. [3]) and also a convenient experimental procedure to detect onset of turbulent conditions and is employed in this report as well, it is important to understand if there are any other factor(s) that may lead to non-linear increment of pressure-drop in a flow system.

The reason behind the linear increment of pressure-drop with flowrate can be understood from the Hagen–Poiseuille equation [3]:

$$\Delta P = C_t \cdot Q \cdot \mu \qquad (1)$$

where ΔP is the pressure-drop, C_t is a constant that characterize the conduit geometry ($= \frac{128L}{\pi d^4}$, where L is length and d is conduit i.d.), Q is the volumetric flowrate and μ is the dynamic viscosity.

Note from Eq. (1), which is valid for laminar flow of a Newtonian fluid, that with liquid (incompressible) mobile-phase, ΔP shall increase linearly with Q for an isocratic and isothermal system because μ or any other physical properties will remain constant. At high enough Q, when the flow enters turbulent regime, there is a rapid increase in pressure-drop – approximately as the square of the velocity [3]. Eq. (1) is no longer valid in the turbulent region.

For SFC mobile-phases, which are more compressible than liquid, there will be non-negligible variation of physical properties with pressure even when high concentration of co-solvents are present. This indicates, in SFC ΔP will increase non-linearly even under laminar conditions. *The extent of this non-linearity, however, will depend on the state conditions and the extent of pressure-drop.* For example, neat CO_2, which is the most compressible among SFC mobile-phases, will demonstrate highest non-linearity. Increasing co-solvent percent, on the other hand, will decrease the non-linearity. A brief explanation of this issue is presented below.

The first point is, to apply Eq. (1) in SFC we need modifications. The Q delivered by the SFC pump(s) do not remain constant throughout the system – it varies depending on local fluid density. On the other hand, the mass flowrate(s) delivered by the pump(s) remain constant. Hence, for SFC Eq. (1) can be re-written as:

$$\Delta P = C_t \cdot G \cdot \kappa \qquad (2)$$

where G is the mass flowrate anywhere in the conduit and κ is the average kinematic viscosity.

The second point is, when SFC pumps deliver a set volumetric flowrate (Q) independent to the pump-outlet pressure (constant-flow mode), which is normally done by most pumps of commercial SFC systems, G increases non-linearly with Q. Note that for liquid solvents ρ remains constant, hence mass flowrate varies with the same multiples as the volumetric flowrate ($G = \rho Q$). For CO_2 (compressible), however, increasing Q leads to increased pump-outlet pressure (caused by increased pressure-drop in the system) and hence increased CO_2 density at pump-outlet ($\rho_{CO_2,PO}$) and vice-versa. So mass flowrate variation depends also on how $\rho_{CO_2,PO}$ varies with Q (see Ref. [6] for more details). If $\rho_{CO_2,PO}$ variation is considerable enough, variation of Q leads to non-linear variation of G. Similarly, with rising average pressure of the system caused by increased Q, κ will also vary. Variation of both factors with Q result in non-linear variation of ΔP with increasing Q (see Eq. (2)). To emphasize again, the extent of this variation will depend on how $\rho_{CO_2,PO}$ and κ vary during particular experimental runs.

Fig. 2 demonstrates the extent of possible variation of $\rho_{CO_2,PO}$ at two different pump-head temperatures and variation of κ of neat CO_2 as function of temperature and pressure. Temperatures 4 and 13 °C represent settings of two different commercial instruments. Although both figures (Fig. 2a and b) demonstrate considerable variation of $\rho_{CO_2,PO}$ and κ with pressure, *their net effect on ΔP variation in SFC may not be significant.* The main reason being – to impart a considerable variation in $\rho_{CO_2,PO}$ and κ during an experimental run, the pressure-drop has to be very high. For example, at 13 °C, to increase $\rho_{CO_2,PO}$ from 0.9 to 1.0 g/mL (i.e. by 11%) ΔP has to be increased from 10 to 200 bar (i.e. by 2000%). Similar observation can be made regarding the variation of κ too.

A detailed discussion on this topic is outside the scope of current report. However, to provide an approximate idea regarding the extent of possible non-linearity imparted by varying CO_2 proper-