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COMMUNICATION

Mass Separation Due to the Rapid Expansion of Supercritical Carbon Dioxide Fluid across a Radial Thermal Gradient

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ABSTRACT

Enhanced mass transport and compound selectivity are possible for low molecular weight components solubilized in a carrier media of supercritical carbon dioxide fluid and subjected to radial thermal field-flow fractionation. In preliminary studies we observed separation of methanol and benzophenone through rapid expansion of carrier fluid at 135 bar from a 100-μm diameter capillary tube into a larger-bore tube that extended across a 20°C radial thermal gradient. We can only assume that the localized drop in pressure imposed by the rapid expansion of fluid coupled with its behavior when subjected to the thermal gradient have enormous effects on fluid density which appear to be more effective in mass transport than conventional liquid solvents for extending field-flow fractionation to a range of low molecular weight compounds that classically could only be separated by chromatography.

INTRODUCTION

Supercritical and fluidized gases have found widespread use in numerous industrial and analytical applications as solvents for material extraction (1–4), and as solvents for material separation through chromatography (5–7) and thermal field-flow fractionation (8). The enormous utility of a supercritical fluid can be attributed to the fact that it retains many of the characteristics of both its liquid and gaseous states at around the

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critical point for that substance, even though it is neither a gas nor a liquid in the strictest sense. At the critical point, defined by the critical pressure and critical temperature for a substance, the densities of the liquid and gaseous states become identical, and therefore, the two states are indistinguishable. However, slight changes in pressure and temperature around the critical values can have profound effects on fluid density as well as on the dielectric constant, thus affecting the solvating strength of the fluid.

Carbon dioxide is one of several gases that can be compressed and used as a dense fluidized media in its supercritical state. It possesses critical valves of $T_c = 31.3°C$ and $T_p = 73$ bar. Both density and dielectric constant increase drastically with pressure between 70 and 150 bar (Fig. 1) but change very little thereafter (9). A similar dependence can be seen between fluid density and temperature (Fig. 2) as well. Also, the dielectric constant for carbon dioxide is strongly dependent on temperature as exemplified by the fact that at 50 bar this parameter will decrease drastically from 1.6 at 20°C (10) to 0.06 at 40°C.

The utility of supercritical fluids in thermal field-flow fractionation has been previously addressed from both a theoretical and experimental per-

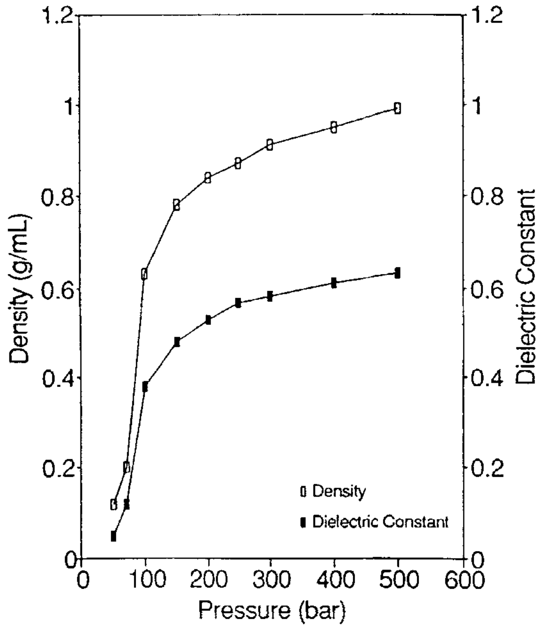

FIG. 1 Relationship between density and dielectric constant of carbon dioxide with increasing pressure and at 40°C.

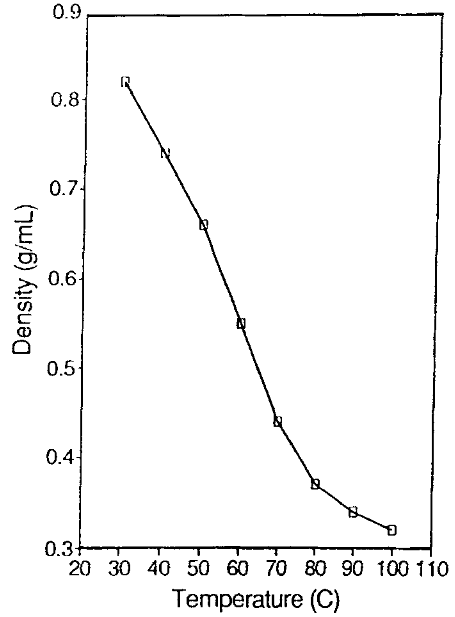

FIG. 2 Relationship between density of carbon dioxide with increasing temperature and at 135 bar.

spective (8). In fact, this earlier work demonstrated that retention of low molecular weight polymers was considerably greater using supercritical fluids than conventional liquid solvents. A model based on solubility gradients in supercritical fluids was developed to explain the thermal diffusion process of material under these circumstances. Much of this model was based on the Hildebrand solubility parameter concept which describes the enhancement of solute solubility caused by the densification of fluidized gas. Of course, an underlying assumption here was that nonvolatile solutes would seek out regions of the carrier fluid possessing the highest density, which typically would be the cold wall of the fractionation channel.

Interestingly, a recent paper reported that when tested, certain nonvolatile organic solutes, in fact, exhibited increased solubility in supercritical carbon dioxide fluid at constant pressure as the temperature of the fluid was increased from 50 to 200°C (11). These observations are in sharp contrast to conventional wisdom regarding solubility and fluid density. However, these observations may not have a direct bearing on the above model and its implications to supercritical fluid thermal field-flow fractionation at around the critical temperature of the fluid. Of course, other factors yet known to us involving *solute–solvent* interactions may play a more important role at elevated temperatures than that of the fluid's density in affecting solute solubility.

The present communication reports on an application of thermal field-flow fractionation utilizing supercritical carbon dioxide fluid as a carrier media to enhance mass transport and compound selectivity. Unlike conventional methodologies employed within this technology, where gradient fields are applied perpendicular to the velocity vector of the carrier media across a ribbonlike channel created between two parallel walls, we were able to observe simple mass separation utilizing an open tubular column that was subjected to a radial thermal gradient. It is not the intention of this preliminary communication to delve into the theoretical implications of these observations, but merely to report and explain results in a way that seem compatible with existing models.

EXPERIMENTAL

A single-stage expansion column was constructed from a 15 cm × 4.1 mm i.d. empty stainless steel high pressure liquid chromatography (HPLC) column (Phenomenex Inc., Empty Column Assembly, PN AQO-0184). Fused silica capillary tubing was used for the inlet as well as for the outlet tubes. The inlet tube possessed a 100-μm i.d. while the outlet tube possessed a 20-μm i.d. Connection of the capillary tubes to the empty HPLC column was made using 0.25 mm i.d., 1/16 to 1/32" stainless steel reducing couplings (Suprex Corp., PN FI-00007) and Vespel ferrules (Suprex Corp., PN GF-03203). Fluid pressures were maintained and measured using an ISCO syringe pump (Model 260D: Omaha, NE).

The stainless steel column was heated by forced air using a gas chromatograph (GC) oven (Hewlett-Packard Model 5890 Series II GC). In all measurements the hot air temperature was ramped from ambient to 51°C while the inside core temperature of the expansion tube was monitored as a function of time using a miniature thermocouple thermometer (Omega Engineering, Inc., Model 660 with J Type thermocouple). Samples were injected at predetermined times roughly corresponding to the desired thermal gradient. The largest thermal gradient of 20°C provided an inside core temperature equivalent to the critical temperature for carbon dioxide. No attempt was made to profile the thermal gradients beyond those measurements described.

Samples were introduced to the expansion column via a standard HPLC injection valve (Rheodyne model 7125) possessing a stainless steel 20 μL volume loop. The valve was of a top-loading design to allow sample introduction via a syringe.

The outlet capillary tube was connected to a GC flame ionization detector (Hewlett-Packard Model 5890 Series II GC) for measurement of compound resolution. This detector is insensitive to the carbon dioxide fluid.

RESULTS AND DISCUSSION

Studies were carried out using samples of benzophenone (molecular weight 182) mixed in methanol (molecular weight 32). Results are shown in Fig. 3 for imposed thermal gradients of 20, 10, and 0°C extending up from the critical temperature. Initial fluid pressures were maintained at 135 bar. Unfortunately, the present experimental configuration made it impossible to determine what the localized pressure change was when the

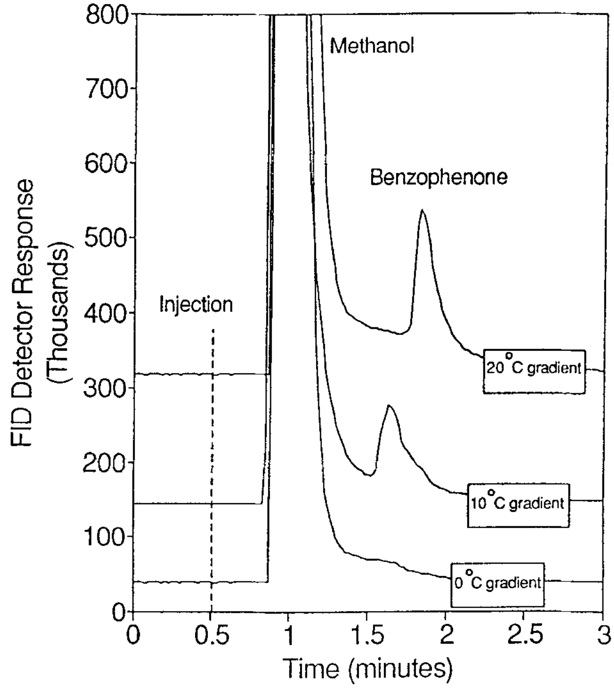

FIG. 3 Mass separation of methanol (MW 32) and benzophenone (MW 182) resulting from the rapid expansion of supercritical carbon dioxide fluid initially at 135 bar pressure across radial thermal gradients of 20, 10, and 0°C.

fluid expanded into the larger-bore tube. We can only assume that it was something less than the source pressure.

A 0.8-minute separation was achieved between the eluting methanol and eluting benzophenone peaks from the higher thermal gradient. This separation decreased with decreasing thermal gradients and disappeared entirely as the thermal gradient was decreased to zero.

It is apparent from the above observations that the thermal gradient is essential for material separation to occur under the present circumstances. However, the thermal gradient field does not directly drive separation of components, since it works at right angles to the carrier fluid's flow axis. Instead, the field drives components into different stream laminae of the carrier fluid to a degree that depends on their coupling with the field. Separation occurs because of the unequal velocities within the different stream laminae.

One must assume that the flow velocity profile for carrier fluid is parabolic in shape to be consistent with hydrodynamic considerations. One must also assume that since the thermal gradient is applied radially, then the change in viscosity as a function of temperature is uniform, thus allowing the flow velocity profile to maintain a symmetric shape. However, the applied thermal gradient will cause viscosity to increase from the outer wall region to the core region, and therefore, blunt the parabolic profile somewhat. Some evidence for this behavior can be seen by the fact that there was not as much peak broadening for benzophenone with the 20°C gradient as with the 10°C gradient.

From the general framework laid out to describe the differing separation mechanisms occurring within field-flow fractionation (12), it becomes obvious that a single applied field can typically cause ancillary forces to form strong ties to the solute components and work either in unison or in opposition to the initial applied field. The balance between these field-driven forces then dictates the positional distribution of components within the different laminae streams, which ultimately controls the degree of component retention.

Under the present circumstances the thermal gradient will establish a field-driven motion involving thermal diffusion as well as diffusion due to a solubility gradient caused by the fluid density dependence on temperature which serve to drive components toward the center core region. However, the concentration gradient established by this action may in fact be opposed by a reciprocating force that is more selective for the heavier benzophenone component owing to the compound's stronger solubility dependence on fluid density. In the outer wall region where fluid density is at its lowest value, a compound like benzophenone could fall out of solution and aggragate. This behavior may set up a strong enough opposing force to actually *pull* additional material to the outer boundary, thus allowing benzophenone to experience more of the slower flow laminae and be retained longer within the tube.

The efficacy of this methodology as a general separation tool cannot be answered until additional studies are carried out. For example, the mass resolution needs to be measured with compounds of differing molecular weights for the present configuration of expansion tubes used, and for the identical operating conditions of fluid pressure and thermal gradients used. In addition, the effect of fluid pressure change on compound separation during expansion, as well as the effect of fluid linear flow velocity profile on compound separation, must be investigated with the intent to discern the interrelation of these features with hardware geometry and operating parameters.

Compound solubility within the supercritical fluid is another issue that needs to be addressed. The present work was carried out in a region of fluid temperature and pressure where the dependency of fluid density on these parameters was very strong. Therefore, one might expect solvating strength of the fluid to be an important factor here. In order to verify this, we need to explore whether this methodology can separate two components of a mixture whose molecular weights are similar but whose solubilities within the fluid are very different. We also need to explore the effect of thermal gradients on compound retention at much higher temperatures. Although fluid density will decrease, there is clear evidence in the literature demonstrating that compound solubility actually increases, and quite drastically.

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