

# Determination of Partial Molar Volumes at Infinite Dilution Using SFC Technique

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The use of supercritical-fluid chromatography for determining partial molar volumes of some substances (linear, cyclic and aromatic hydrocarbons, benzaldehyde) at infinite dilution in supercritical CO<sub>2</sub> is presented and discussed. Partial molar volumes at infinite dilution are obtained from the variation of the retention properties with the density of mobile phase at 313.15 K and in the pressure range from 80 to 280 bar.

**Keywords:** partial molar volume at infinite dilution, supercritical-fluid chromatography, carbon dioxide, hydrocarbons, aromatics

## INTRODUCTION

In the recent years, supercritical fluids (SFs) have become more and more important, not only as extraction media, but also as carriers for the modification of the properties of a condensed phase (e.g., impregnation of polymers<sup>1</sup>) or in connection with high-pressure micronization. Several applications of SFs have been developed so far and several processes have been set up at industrial scale.<sup>2</sup>

Nevertheless, a basic understanding of equilibrium properties and the partitioning of a given substance between the phases is required for a quantitative description of the process and in order to establish the optimum operating conditions. Unfortunately, thermodynamic properties in the close vicinity of the mixture critical point are hard to predict and to describe because of the very strong nonidealities that exist at this point, such as, the abnormal behavior of partial molar properties.

Among the thermodynamic properties that can be measured to understand the behavior of mixtures in the vicinity of the critical point, partial molar volume is important in describing the pressure dependence of the fugacity coefficient (and consequently solubility), which is the basis for many separation processes. The large negative partial molar volumes of solutes at infinite dilution in

SFs physically indicate a large volume decrease when a molecule of a solute is added to the pure solvent.

Measurements of partial molar volumes may be performed by using classical methods or using supercritical-fluid chromatography (SFC). Generally speaking, the experimental methods employed may be roughly divided in two categories: direct and indirect methods. The direct methods are normally based on density or volume determinations and the partial molar properties are derived directly from their definitions. This group of methods requires very precise measurements and special care is needed when operating in the vicinity of the critical point. Eckert et al.<sup>3</sup> determined  $\bar{v}^{\infty}$  naphthalene and other substances in supercritical CO<sub>2</sub> and ethane on the basis of very precise density determinations of the supercritical solutions. Foster et al.<sup>4</sup> determined  $\bar{v}^{\infty}$  of benzaldehyde in supercritical CO<sub>2</sub> by using a constant-volume apparatus. Wu and Ehrlich<sup>5</sup> actually determined partial molar volumes of ethane and heptane by measuring volume change of mixing of the binary mixture.

Indirect methods are all based measuring the variation of a given equilibrium property (e.g., solubility, K factor) with pressure. In this respect the determination is easier, but requires a very accurate method for the determination of the equilibrium property over a wide range of

pressures, since the partial molar property is obtained from a slope measurement.

A possible choice for experimentally determining thermodynamic properties and partial molar properties is inverse chromatography, which has been widely used at low-to-moderate pressures. Supercritical-fluid chromatography may be used at high pressure in almost the same fashion as inverse chromatography. This technique has several advantages with respect to static or dynamic methods for the determination of thermodynamic properties in the vicinity of the critical point: small quantities of the solute are required, the method is rapid and it uses standard equipment. Several authors have focused on distribution coefficients and partial molar quantities (such as partial molar volume and enthalpy).<sup>1,6</sup> Among others, van Wasen and Schneider<sup>7</sup> employed SCF to determine  $\bar{v}^{\infty}$  of naphthalene and fluorene in supercritical CO<sub>2</sub> based on an adsorption retention mechanism. The same approach has been used also by Erkey and Akgerman<sup>8</sup> who calculated the partial molar volumes of naphthalene at infinite dilution in supercritical CO<sub>2</sub>. Shim and Johnston<sup>1</sup> used SFC to measure K factors, partial molar volumes, and partial molar enthalpies of naphthalene and phenanthrene in supercritical CO<sub>2</sub>. K factors (partition coefficients defined as the ratio of the concentration in the liquid over the concentration in the fluid phase) have been determined by Olesik et al.<sup>6</sup>

In this work, partial molar volumes at infinite dilution are determined by applying the procedure used by Shim and Johnston<sup>1</sup> for packed columns to capillary columns and using SFC to measure the variation with pressure of the retention properties of 17 different solutes in supercritical CO<sub>2</sub>.

## THEORY

The theoretical background for applying the SFC technique for the determination of  $\bar{v}^{\infty}$  is briefly reviewed in this section. According to standard chromatographic terminology, the capacity factor  $k_i$  is defined (per unit of bed volume) as

$$k_i = \frac{t_i - t_0}{t_0} \quad (1)$$

where  $t_i$  is the retention time of component  $i$  and  $t_0$  is the retention time of an unretained solute. The capacity factor is related to the equilibrium compositions in the mobile phase ( $y$ ) and in the stationary phase ( $x$ ) through the relationship<sup>9</sup>

$$k_i = \frac{x_i V_s v_m}{y_i V_m v_s} \quad (2)$$

where  $V_m$  and  $V_s$  represent the total volumes of the mobile and stationary phases respectively, and  $v_m$  and  $v_s$  are molar volumes.

If the fugacity in each phase is expressed by means of the well-known relationship<sup>10</sup>

$$f_i = x_i \phi_i P \quad (3)$$

then, at equilibrium

$$k_i = \frac{\phi_{im} V_s v_m}{\phi_{is} V_m v_s} \quad (4)$$

If the stationary phase does not swell and its composition remains constant,  $V_s$ ,  $V_m$ , and  $v_s$  are constant. Under these assumption the variation of the  $k$  factor with temperature, pressure, and density may be calculated. The effect of temperature and pressure on  $k_i$  are given by the following derivatives expressed in terms of partial molar quantities (in the hypothesis of infinite dilution)

$$\left( \frac{\partial \ln k_i}{\partial P} \right)_T = \frac{\bar{v}_{im}^{\infty} - \bar{v}_{is}^{\infty}}{RT} - \kappa \quad (5)$$

$$\left( \frac{\partial \ln k_i}{\partial T} \right)_P = -\frac{\bar{h}_{im} - \bar{h}_{is}}{RT^2} + \beta \quad (6)$$

where  $\kappa$  is the mobile phase isothermal compressibility and  $\beta$  the isobaric thermal expansion coefficient. All the derivatives are taken at infinite dilution of the solute.

The derivative of the capacity factor with respect to the density is expressed, still at infinite dilution, by the following relationship

$$\left( \frac{\partial \ln k}{\partial \rho} \right)_T = \left( \frac{\partial P}{\partial \rho} \right)_T \left( \frac{\bar{v}_{im}^{\infty} - \bar{v}_{is}^{\infty}}{RT} - \kappa \right) \quad (7)$$

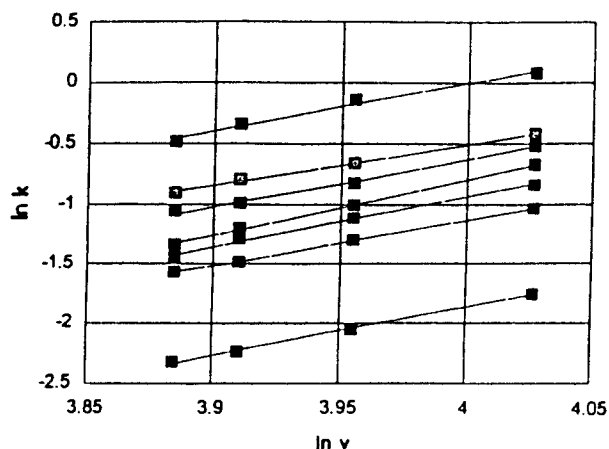
Transforming the above expression we achieve

$$\left( \frac{\partial \ln k}{\partial \ln \rho} \right)_T = \left( \frac{\bar{v}_{im}^{\infty} - \bar{v}_{is}^{\infty}}{RT\kappa} - 1 \right) \quad (8)$$

Near the solvent critical point,  $\bar{v}_{im}^{\infty}$  is much larger than  $\bar{v}_{is}^{\infty}$  and consequently, the latter can be neglected, thus giving the following relationship:

$$\left( \frac{\partial \ln k_i}{\partial \ln \rho} \right)_T = - \left( 1 - \frac{\bar{v}_{im}^{\infty}}{RT\kappa} \right) \quad (9)$$

This equation has been derived by Chimowitz and Kelley<sup>11</sup> on the basis of theoretical developments of Kumar and Johnston,<sup>12</sup> and it is strictly valid only very close to the solvent critical point. Rearranging this relationship the partial molar volume can be easily obtained. The behavior of the derivative in eq 9 with density, in the regime of interest, is determined by the variation of the ratio of



**Figure 1.** Plot of  $\ln k$  vs.  $\ln v$  for naphthalene at 313.15 K in different stationary phases.<sup>13</sup>

the partial molar volume and isothermal compressibility with density. It has been shown<sup>12</sup> that on the critical isotherm, very close to the solvent's critical point, this ratio is independent of density since both, the partial molar volume and the isothermal compressibility have the same scaling.

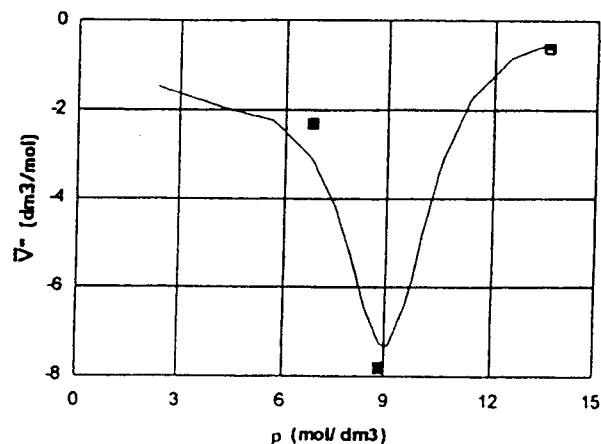
However, by looking at the different terms of this equation, it appears that the derivative strictly depends upon the properties of the mobile phase ( $\kappa$ ) and of the mixture of the solute and the mobile phase. The derivative is independent of the stationary phase used and this can be confirmed using the data of Jinno and Niimi.<sup>13</sup> Figure 1 illustrates retention data of naphthalene at 313.15 K as a function of molar volume for several different stationary phases.<sup>13</sup> The parallel lines indicate that the derivative is independent of the stationary phase.

Equation 9 is strictly valid only in proximity of the critical point. However, Chimowitz and Kelly<sup>11</sup> present capacity factor data and conclude that the linear relationship is still valid across a broader range of conditions and not only along the critical isotherm (see eq 8).

Since  $\kappa$  is a function of the pure mobile phase and it is easily calculated from experimental data for pure  $\text{CO}_2$  (see for example IUPAC tables<sup>14</sup>), isothermal capacity factor data at different densities can be successfully used for the determination of the partial molar volumes of the solute in the mobile phase. The partial molar volumes of naphthalene in supercritical  $\text{CO}_2$  were calculated on the basis of the above mentioned theory using published retention data.<sup>13</sup> These results are illustrated in Figure 2 and are in good agreement with existing partial molar volume data.<sup>3</sup>

## EXPERIMENTAL

The experimental procedure that was employed in this study was based on the measurement of solute retention times using SFC and is similar to that used by other workers. The experiments were performed with a super-



**Figure 2.** Partial molar volumes of naphthalene at infinite dilution vs. molar density of carbon dioxide. (■) data from the literature<sup>3</sup> at 308.38 K; - - - calculated data at 313.15 K. Retention data taken from the literature.<sup>13</sup>

critical-fluid chromatograph Model 3000 (Carlo Erba), equipped with a flame ionization detector, using carbon dioxide as the mobile phase. A fused-silica capillary column, coated with SE-52 (10-m column, 100- $\mu\text{m}$  i.d., 0.45- $\mu\text{m}$  coating thickness) was used. Temperature was monitored using a Systemtechnik 1220 sensor accurate to  $\pm 0.001$  K and the oven temperature was maintained to within  $\pm 0.1$  K. The system pressure was maintained to within  $\pm 1.0$  bar.

The determinations were carried out at 313.15 K and in the range of 80 to 280 bar. The column was stabilized overnight before each set of isobaric measurements, thus allowing uniform flow conditions to be achieved throughout the column. A constant flow-rate was used at each pressure and it was measured using a bubble soap meter. Injections were made with an air actuated preheated valve with a 1- $\mu\text{L}$  loop. The pressure reduction, necessary for using FID detector, was obtained by means of a 15-cm straight restrictor with 8- $\mu\text{m}$  i.d. The chromatographic data were collected and analyzed by Maxima software running on an Intel 80386 personal computer.

The measured pressure drop in the column at 100 bar is negligible while at 280 bar is about 6 bars. These figures when reported in terms of density of the mobile phase, which is relevant for this work, give an effect lower than 1% of the density.

The selected solutes were 99.7% purity, obtained from Riedel de Haen, Fluka, or Aldrich and were used without further purification. The carbon dioxide was obtained from SIAD at a purity of 99.98%.

## RESULTS AND DISCUSSION

For each experimental run, the following quantities were measured: the retention time of the solute, temperature, pressure, and flow rate of the mobile phase. The retention time of the unretained solute,  $t_0$ , used in eq 1, was determined from the retention time of ethane. Repeated

TABLE I  
*k*-Values (–) and Partial Molar Volumes (dm<sup>3</sup> mol<sup>-1</sup>) at Infinite Dilution of Various Solutes at 313.15 K

Solute	Pressure [bar]									
	100		125		130		150		180	
	<i>k</i>	$\bar{v}^{\infty}$	<i>k</i>	$\bar{v}^{\infty}$	<i>k</i>	$\bar{v}^{\infty}$	<i>k</i>	$\bar{v}^{\infty}$	<i>k</i>	$\bar{v}^{\infty}$
Benzene	0.063	-0.81	0.052	-0.26						
Toluene	0.007	-0.83	0.057	-0.27			0.036	-0.14	0.029	-0.09
Ethylbenzene	0.136	-1.14	0.060	-0.37			0.038	-0.15	0.034	-0.10
1-Phenyl-octane	0.242	-1.30	0.089	-0.42			0.042	-0.20	0.036	-0.13
Hexane	0.059	-0.80	0.032	-0.26			0.067	-0.23	0.058	-0.15
Octane	0.082	-0.90	0.041	-0.29			0.024	-0.14	0.021	-0.09
Nonane	0.107	-1.02	0.051	-0.33			0.032	-0.16	0.027	-0.11
Decane	0.128	-1.08	0.057	-0.35			0.037	-0.18	0.031	-0.12
Dodecane	0.165	-1.15	0.074	-0.37			0.043	-0.19	0.034	-0.13
Hexadecane	0.239	-1.21	0.102	-0.39			0.050	-0.20	0.040	-0.13
Benzaldehyde	0.027	-0.48			0.017	-0.13	0.069	-0.21	0.058	-0.14
Hexene	0.014	-0.39			0.009	-0.11	0.016	-0.09	0.013	-0.06
Heptene	0.018	-0.40			0.011	-0.11	0.008	-0.07	0.007	-0.05
Cyclohexane	0.032	-0.36			0.020	-0.10	0.010	-0.07	0.010	-0.05
Methylcyclohexane	0.030	-0.36			0.019	-0.10	0.020	-0.06	0.018	-0.04
Ethylcyclohexane	0.049	-0.60			0.019	-0.10	0.019	-0.06	0.016	-0.04
Decalene	0.093	-0.66			0.028	-0.17	0.024	-0.11	0.021	-0.07
					0.051	-0.18	0.044	-0.12	0.038	-0.08
	200		220		250		280			
	<i>k</i>	$\bar{v}^{\infty}$	<i>k</i>	$\bar{v}^{\infty}$	<i>k</i>	$\bar{v}^{\infty}$	<i>k</i>	$\bar{v}^{\infty}$		
Benzene	0.023	-0.08	0.020	-0.07	0.020	-0.05	0.016	-0.05		
Toluene	0.026	-0.08	0.022	-0.07	0.021	-0.06	0.017	-0.05		
Ethylbenzene	0.029	-0.11	0.026	-0.09	0.025	-0.08	0.022	-0.06		
1-Phenyl-octane	0.049	-0.13	0.044	-0.11	0.035	-0.09	0.027	-0.07		
Hexane	0.018	-0.08	0.017	-0.07	0.016	-0.05	0.027	-0.07		
Octane	0.022	-0.09	0.021	-0.07	0.020	-0.06	0.015	-0.05		
Nonane	0.025	-0.10	0.024	-0.08	0.023	-0.07	0.018	-0.05		
Decane	0.030	-0.10	0.027	-0.09	0.025	-0.07	0.020	-0.06		
Dodecane	0.035	-0.11	0.032	-0.09	0.025	-0.07	0.022	-0.06		
Hexadecane	0.050	-0.12	0.044	-0.10	0.031	-0.08	0.026	-0.07		
Benzaldehyde	0.012	-0.05	0.011	-0.04	0.039	-0.08	0.035	-0.07		
Hexene	0.006	-0.04	0.006	-0.03	0.011	-0.03	0.010	-0.03		
Heptene	0.009	-0.04	0.008	-0.03	0.006	-0.03	0.006	-0.02		
Cyclohexane	0.016	-0.03	0.016	-0.03	0.008	-0.03	0.007	-0.02		
Methylcyclohexane	0.014	-0.03	0.014	-0.03	0.014	-0.02	0.014	-0.02		
Ethylcyclohexane	0.019	-0.06	0.018	-0.05	0.014	-0.02	0.014	-0.02		
Decalene	0.033	-0.06	0.032	-0.05	0.017	-0.04	0.016	-0.03		
					0.030	-0.04	0.028	-0.04		

experiments were performed to determine the retention times of the solute with higher precision: the mean value of these measurements (not differing more than 0.3 %) was used for further calculations. The distribution factors (*k* values) and solute partial molar volumes are reported in Tables I and II as a function of pressure for all the systems investigated.

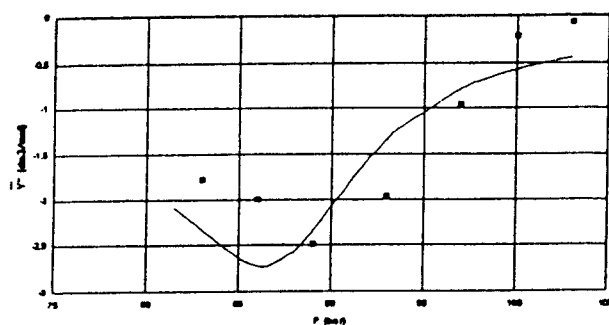
Pure carbon dioxide density calculations were performed using the data from the IUPAC tables.<sup>14</sup> Calculations with other empirical equations<sup>15</sup> (e.g., Bender equation), produced similar results in terms of the density of

pure carbon dioxide the variation in the value of the calculated partial molar volume was less than 3%. The slope of the capacity factor vs. density curve was used together with the isothermal compressibility of pure carbon dioxide to give the partial molar volume (see eq 9).

The experimental uncertainty of the reported  $\bar{v}^{\infty}$  data has been estimated as  $\pm 15\%$ . This figure has been estimated by repeating experiments for the determination of the retention time and application of the error propagation law to the *k* factors. The *k* factor uncertainty is less than 1.2%. From the logarithmic plot of the *k* factor vs.

**TABLE II**  
 **$k$ -Values (-) and Partial Molar Volumes ( $\text{dm}^3 \text{mol}^{-1}$ ) at Infinite Dilution of Various Solutes at 313.15 K and a Pressure Range of 80–95 bar. Data are Plotted in Figures 3 and 4.**

Solute	Pressure [bar]									
	80		85		87.5		90		95	
	$k$	$\bar{v}^\infty$	$k$	$\bar{v}^\infty$	$k$	$\bar{v}^\infty$	$k$	$\bar{v}^\infty$	$k$	$\bar{v}^\infty$
Hexane	0.944	-3.03	0.392	-3.80	0.228	-4.41	0.131	-3.65	0.070	-1.49
Octane	1.676	-3.40	0.641	-4.26	0.356	-4.94	0.195	-4.09	0.099	-1.67
Decane	4.049	-4.08	1.353	-5.10	0.687	-5.93	0.344	-4.90	0.158	-2.00
Dodecane	6.274	-4.35	1.978	-5.45	0.969	-6.33	0.467	-5.24	0.206	-2.13
Hexadecane	10.479	-4.57	3.159	-5.72	1.505	-6.64	0.706	-5.49	0.301	-2.24
Benzaldehyde	0.195	-1.81	0.105	-2.27	0.071	-2.64	0.048	-2.18	0.031	-0.89



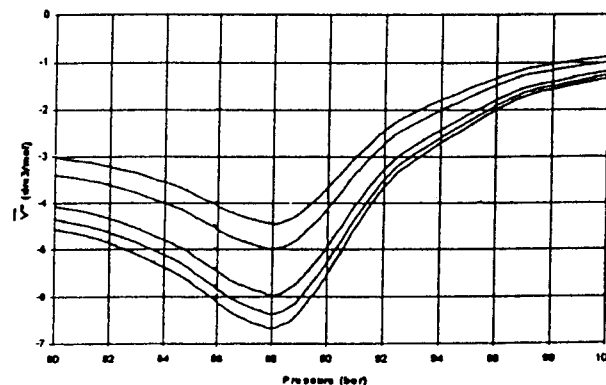
**Figure 3.** Comparison of the  $\bar{v}^\infty$  data for benzaldehyde (— measured in this work, ■ literature<sup>4</sup>).

the density, the slopes have been determined by regressing the experimental data. The uncertainty in the estimated slopes have been evaluated by statistical manipulation of the Hessian matrix at the minimum. The error in the estimated parameters (i.e., the slope of the logarithmic plot of  $k$  vs. density) is lower than 8%.

The swelling effect has not been experimentally evaluated, even though several authors<sup>1</sup> pointed out that a precise evaluation of swelling improves the global precision of the data. Nevertheless, the total uncertainty of the partial molar volumes obtained in this work, without correcting for swelling, is estimated to be lower than 15%. Naturally, this figure could be reduced by measuring the swelling of the stationary phase. The estimated accuracy is in agreement with those reported in the literature for experimental determinations of partial molar volumes<sup>1,3,4</sup> by using different methods.

A comparison with literature results may be done for the benzaldehyde-carbon dioxide system.<sup>4</sup> Figure 3 shows the data obtained in the present work (at 313.15 K) compared with literature results at 314.95 K. The agreement is good, considering the difference in the temperature (1.8 K) for the two sets of data.

Figure 4 illustrates the measured partial molar volume data for a series of normal alkanes ranging from hex-



**Figure 4.**  $\bar{v}^\infty$  experimental data measured in this work for  $n$ -alkanes in the vicinity of the critical point. The curves from top to bottom refer to hexane, octane, decane, dodecane, and hexadecane, respectively.

ane to hexadecane as a function of pressure in the vicinity of the critical point. As expected the absolute magnitude of the partial molar volume increases with increasing carbon chain length.

## CONCLUSIONS

Using the technique outlined in this paper, straightforward and rapid determinations of partial molar volumes are possible. The data measured are in good agreement with partial molar volumes determined by direct methods and the precision of the experimental determinations is comparable to that of previous studies.

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**Symbols**

$f_i$	= fugacity
$h$	= enthalpy
$k_i$	= capacity factor
$P$	= pressure
$R$	= gas constant
$T$	= temperature
$t_0$	= retention time of an unretained solute
$t_i$	= retention time of component $i$
$v_m$	= molar volume of the mobile phase
$V_m$	= volume of the mobile phase
$v_s$	= molar volume of the stationary phase
$V_s$	= volume of the stationary phase
$x_i$	= equilibrium composition of the stationary phase
$y_i$	= equilibrium composition of the mobile phase

**Greek letters**

$\beta$	= isobaric thermal expansion coefficient
$\phi_i$	= fugacity coefficient of the component
$\kappa$	= isothermal compressibility
$\rho$	= density

**Superscript**

—	= partial molar property
$\infty$	= infinite dilution property

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