Self-Diffusion Measurements of Methanol and 1-Decanol in Supercritical CO_2 by ^{13}C Pulsed Field-Gradient NMR[1]

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ABSTRACT

A sapphire high pressure NMR cell, capable of independently controlling sample pressure, temperature, and concentration, is used to measure self-diffusion coefficients of methanol and 1-decanol in supercritical CO_2. Measurements were made over a range of temperature and pressure utilizing the pulsed field-gradient spin echo technique. The experimental self-diffusion coefficients were interpreted using an extended hard-sphere model with the local solvent density augmentation framework by Anderson and Kauffman (*J. Phys. Chem.* **99**: 13759, 1995). For both alcohols, CO_2 solvent cluster formation is noted and the cluster sizes are estimated by comparing self-diffusion coefficients of CO_2 and alcohols.

KEY WORDS: self-diffusion coefficients; supercritical fluid CO_2, methanol and 1-decanol, pulsed field-gradient NMR.

1. INTRODUCTION

A small amount of a highly polar compound, such as methanol, is frequently added to supercritical fluid (SCF) carbon dioxide to enhance its ability to dissolve polar molecules in SCF separation technology [1,2]. Few diffusion coefficients in SCF mixtures have been reported in the literature [3-8]. The pulsed field-gradient spin-echo technique (PGSE) [9-12] has been used extensively to measure self-diffusion in neat monohydric alcohols under pressure [13-15]. Hurle et al. [14] and Lüdemann et al. [16] showed that the experimental diffusion coefficients of methanol may be explained by a rough hard-sphere model (RHS) with a roughness parameter, *A*. In this paper, diffusion measurements are reported for CO_2-methanol and CO_2-decanol mixtures in supercritical fluids. Since methanol in CO_2 is primarily monomeric at low concentration [17,18], the RHS model, that is accurate for most simple, non-associated liquids [16], should apply. Previous nuclear spin-lattice relaxation studies in SCF CO_2 [19,20] suggest a large local solvent density enhancement, or solvent clustering, near an alcohol solute molecule under SCF conditions. When solvent clustering occurs in the vicinity of alcohol solute molecules, it affects the diffusion coefficients. We have made the requisite measurements and found that they corroborate previous spin-relaxation data.

2. MEASUREMENTS

2.1 Samples and High Pressure Set-Up:

High purity (99.999%) CO_2 was obtained from Air Products Co., and the 99% ^{13}C labeled methanol was purchased from ISOTEC Inc. The previously synthesized 1-decanol, ^{13}C labeled at position 5 [22], was used in this study. A sapphire high pressure NMR cell has been described previously [23]. The CO_2-alcohol mixtures were prepared using methods described previously [18,19]. Alcohol sample volumes of

0.0035 and 0.0025 mL. result in mole fractions of 0.06 and 0.02, for methanol and 1-decanol, respectively.

2.2 Self-Diffusion Coefficient Measurements:

All self-diffusion coefficient measurements were made on a Varian UnityPlus 500 NMR spectrometer with a Nalorac 10-mm broad band gradient probe. The variable temperature control unit in the spectrometer was calibrated with the standard temperature calibration samples of methanol and ethylene glycol. A standard PGSE pulse sequence [10,12], with a gradient pulse separation of 25 ms., was used for diffusion measurements. The pulse sequence was implemented by monitoring the echo amplitude while increasing the length of the two gradient pulses. The self-diffusion coefficient, D, is obtained as a fitting parameter of echo intensity verse gradient pulse duration [10]. The gradient strength is obtained by calibrating the gradient coil using substances with well-known self-diffusion coefficients, such as water [24] and benzene [25]. The typical reproducibility of our diffusion coefficient measurement was ±2-3%.

2.3 Density and Viscosity:

Densities of the CO_2-methanol mixture at a given temperature and pressure were estimated using the software SF-Solver™ [26]. Densities of the CO_2-decanol mixture was calculated using a procedure described by Pitzer *et al.* [27]. The viscosities were evaluated using a procedure described by Jossi *et al.* [28].

3. RESULTS AND DISCUSSION

3.1 Self-Diffusion Coefficients of CO_2-Alcohol Mixtures:

Self-diffusion coefficient isotherms of methanol and 1-decanol in CO_2 measured at pressures ranging from of 8.1 to 19.4 MPa are shown in Fig. 1 and 2. The self-diffusion coefficients for CO_2 were simultaneously determined. Minor differences were noted for CO_2 in CO_2-alcohol mixtures compared to neat CO_2 under similar conditions

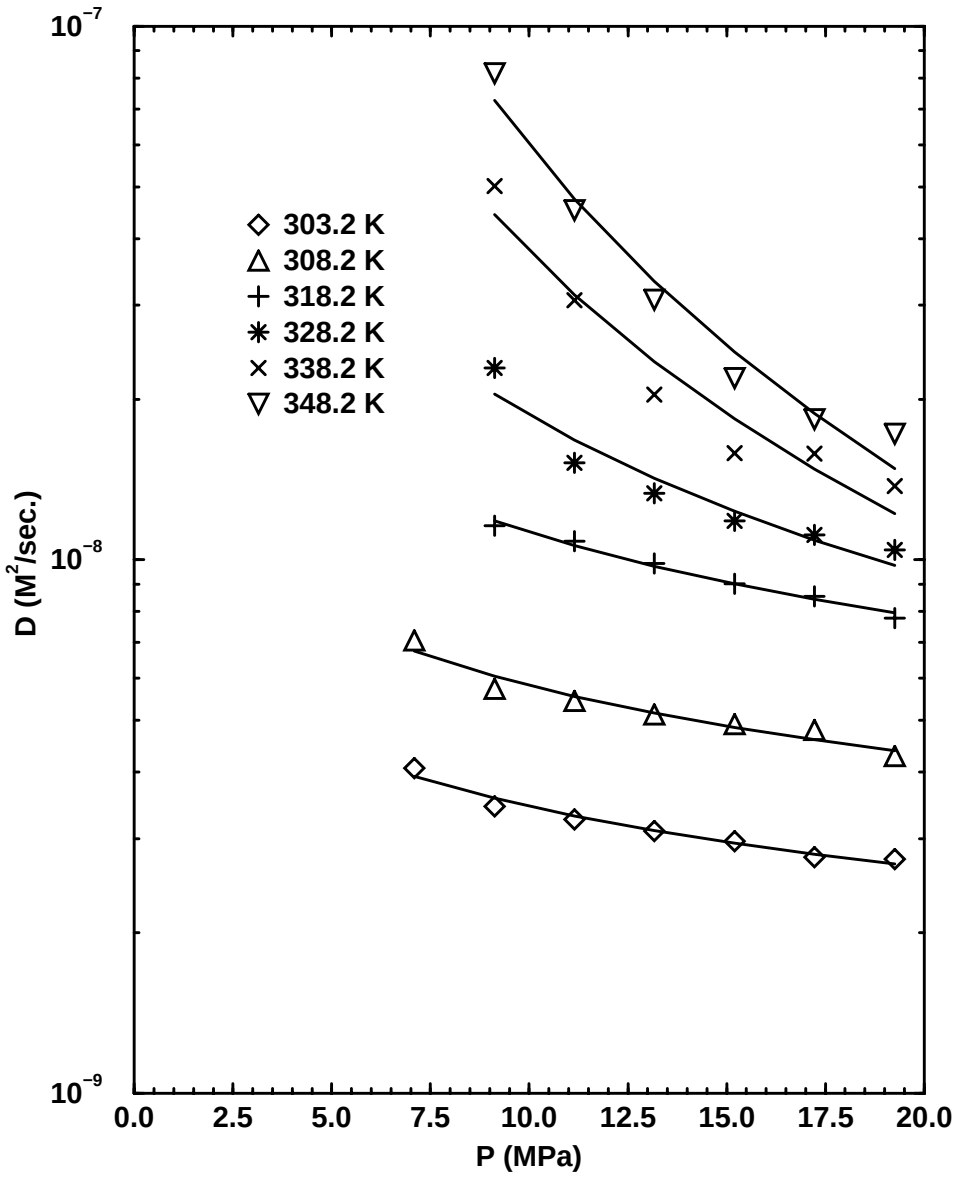

Fig. 1. Methanol self-diffusion coefficient (D_{Exp}) isotherms as a function of sample pressure for a CO_2-methanol mixture

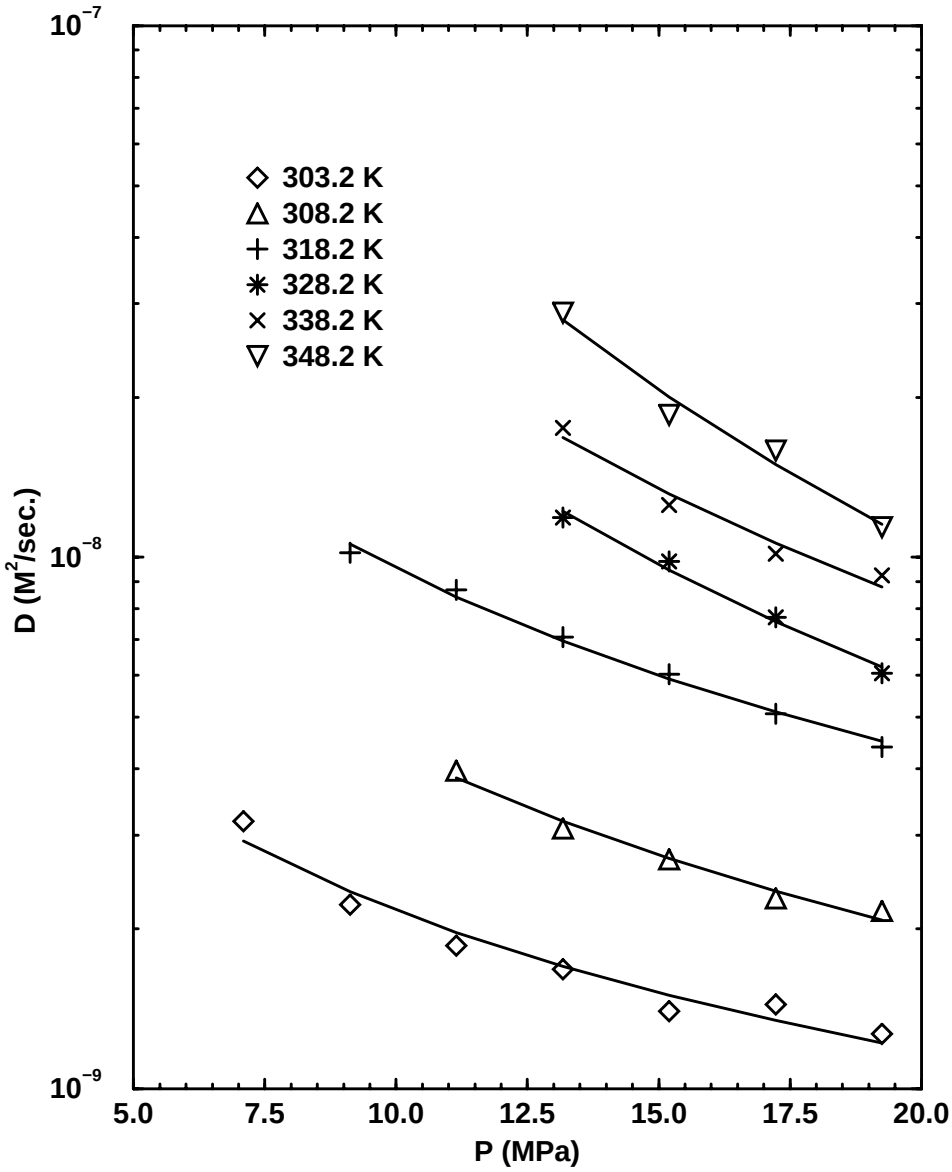

Fig. 2. Decanol self-diffusion coefficient (D_{Exp}) isotherms as a function of sample pressure for a CO_2-methanol mixture.

[8] because of the presence of small concentrations of alcohols. From Figs. 1 and 2, it is noted that the diffusivity values for both methanol and decanol decrease with increasing pressure due to increasing viscosity. At constant pressure, the self-diffusion coefficients of methanol and 1-decanol both increase with temperature. The measured self-diffusion coefficients of methanol in the CO_2-methanol mixture are at least three times greater than those of neat methanol at similar temperature and pressure [16].

3.2 Hard-Sphere Model and Solvent Local Density Enhancement:

Transport of hard-sphere molecules in dense gas by self-diffusion is usually described in terms of the Chapman-Enskog solution of the Boltzmann equation and Speedy's radial distribution function [11, 29]:

$$D_{HS} = \frac{D_o}{\rho}\left(1 - \frac{\rho}{1.09}\right)\left(1 + 0.4\rho^2 - 0.83\rho^4\right) \qquad (1)$$

where $D_o = 3/8\left(kT/\pi m\right)^{1/2}\sigma$, k is the Boltzmann constant, m is the molecular weight, and σ is the hard-sphere diameter. Eq. (1) reproduces the density dependence of the self-diffusion coefficient quite well for most real molecular liquids, but overestimates the numerical values [11]. A rotation-translation coupling parameter, A ($0 < A \leq 1$), is introduced to account for the differences between the experimental self-diffusion coefficient, D_{Exp}, and D_{HS} [30]:

$$D_{Exp} = AD_{HS} \qquad (2)$$

For liquids that hydrogen bond, the empirical quantity, (1-A), is usually interpreted as the degree of hydrogen bonding [13]. The empirical parameter, A, is also a function of the ratio of local to bulk concentrations [31]. In this work the differences between D_{Exp} and D_{HS}, are ascribed to a local solvent interactions and the corresponding density enhancement in the vicinity of the solute molecules. According to our previous study [18], at least 78% of methanol in CO_2 exists in monomeric form in density less than 19,000 $\mathrm{mol \cdot M^{-3}}$. This density limit exceeds the highest density under this study.

Compared with methanol, an even higher percentage of 1-decanol would be monomeric. Thus, it will be assumed that hydrogen bonding is negligible in the studied mixtures. This implies that the empirical parameter A in Eq. (2) approaches unity.

In Eq. (1), $\rho = n\sigma^3$ and n is the bulk number density. According to Anderson and Kauffman [20], a local density, n_{12}^{ℓ}, may be used to replace the bulk density n:

$$n_{12}^{\ell} = n\left[1 + F(g_{12}(r))\right] \tag{3}$$

where F($g_{12}(r)$) is an integral equation in the pair distribution function, $g_{12}(r)$, over the spatial coordinates and r is the distance between solvent and solute molecules. F($g_{12}(r)$) is a measure of the excess solvent density near the solute molecule and is treated as an adjustable parameter in the Anderson and Kauffman (AK) model. When F($g_{12}(r)$)=0, the local density equals the bulk density, and when F($g_{12}(r)$)=1.0, the local density is twice the bulk density. The AK version of the hard-sphere model for self-diffusion coefficients is then established by combining Eqs. (1) and (3). Calculations show that D_{HS} is very sensitive to F($g_{12}(r)$), yet relatively insensitive to changes in temperature in the range from 303 and 384 K. These small temperature effects allow one to use the temperature mid-point (326 K in our case) for calculating the self-diffusion coefficient by Eqs. (1) and (3).

Figs. 3 and 4 compare the experimental self-diffusion coefficients with curves calculated from the AK hard-sphere model as functions of T/η, where η is fluid viscosity. Hard-sphere diameters, σ, for CO_2 (0.36 nm. [8]), methanol (0.36 nm. [14,16]), and n-decane (0.69 nm. [32]) were used. An average σ [33] of 0.36 nm. and 0.49 nm. were used for the CO_2-methanol and CO_2-decanol collision pairs, respectively. The lines in the figures were calculated using Eqs. (1) and (3) at 326 K and values of F($g_{12}(r)$) from 0.0 to 0.5 . From Fig. 3, it is noted that the local density of CO_2 in the vicinity of methanol is about 30±5% more dense than the bulk density at temperatures from 318 to 348 K. This density enhancement increases to 40 to 50% with an error of

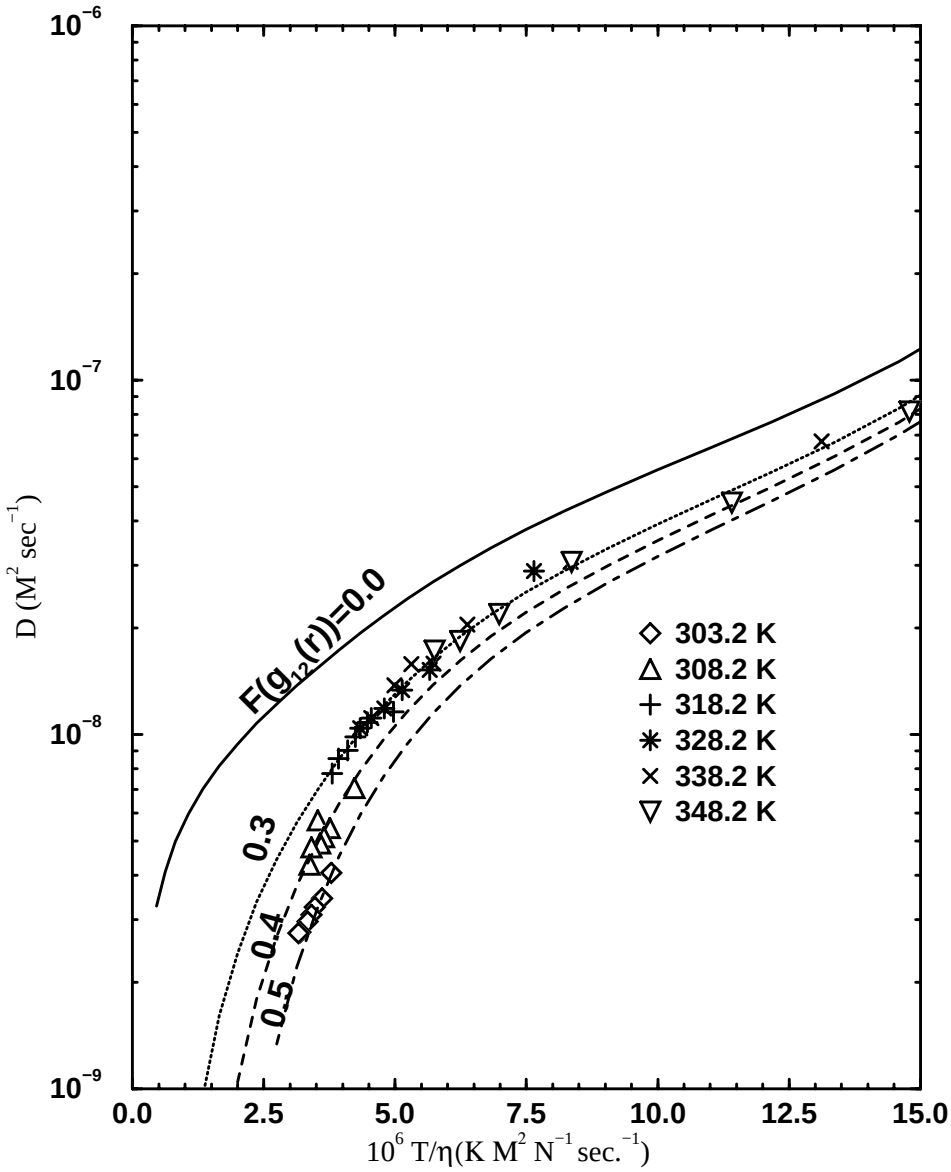

Fig. 3. Experimental self-diffusion coefficients for methanol are compared with the predictions from the AK version of the hard-sphere model (Eqs. (1) and (3)) at 326 K.

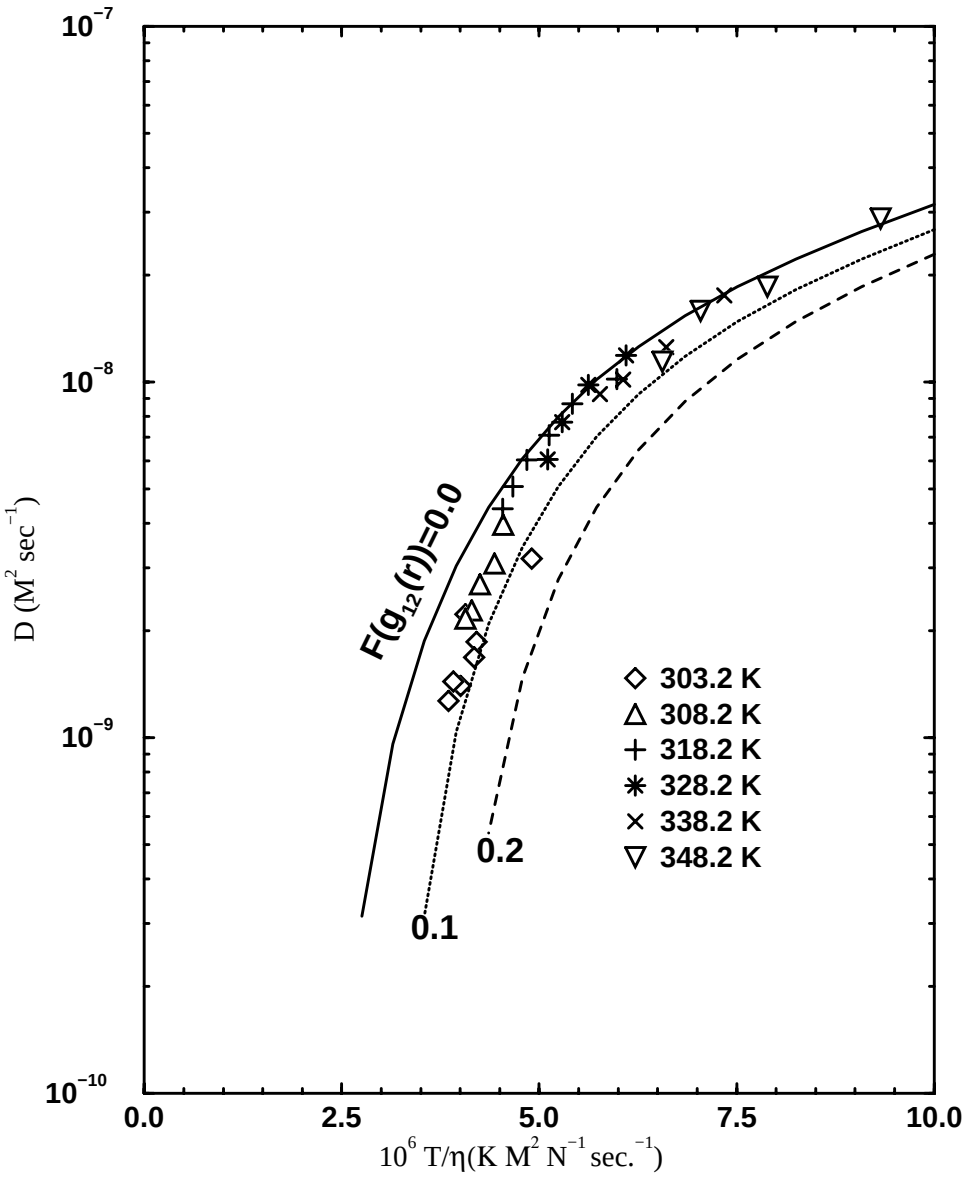

Fig. 4. Experimental self-diffusion coefficients for 1-decanol are compared with the predictions from the AK version of the hard-sphere model (Eqs. (1) and (3)) at 326 K.

±10% within a lower temperature range (303-308 K), suggesting that an enhanced solvent clustering occurs near the critical temperature (312.8 K [26]) of the mixture. From Fig. 4, however, only a 10±5% increase in the CO_2 local densities in the vicinity of a 1-decanol molecule is observed for the temperature range of 303-308 K. At higher temperatures (318-348 K), the bulk density and the local density seem to be equal. The observations presented here are in agreement with our previous spin-lattice relaxation results [19]. A comparable experiment was performed [20] on diphenylbutadiene (DPB) and hyroxy-methylstilbene (HMS) in CO_2. Solvent clustering was observed only in the vicinity of the HMS molecules. Because the extended π-electron systems existing in DPB and HMS are similar, one may conclude that the -OH group in HMS is responsible for the association between the solute and solvent molecules. The one-to-one association between solute and solvent molecules may initiate further CO_2 clustering whenever strong many-body interactions affect the solvent structure in supercritical fluids [20].

3.3 Self-diffusion Coefficient Ratio:

Since measurements were carried out in single phase mixtures using small concentrations of alcohol, the packing fraction, ρ, may be approximated as the same for both CO_2 and alcohols. If an average hard-sphere diameter is used, a resonable approximation of the ratios of self-diffusion coefficients can be made using Eq. (1):

$$D_{CO_2} / D_{alcohol} \approx (m_{alcohol} / m_{CO_2})^{1/2} \qquad (4)$$

where m_i is the molecular weight. Fig. 5 compares the D_{Exp} ratio for CO_2-methanol and CO_2-decanol mixtures with the calculated values of $(m_{alcohol} / m_{CO_2})^{1/2}$ for methanol-CO_2 and decanol-CO_2 pairs as a function of the reduced density, ρ_r. The diffusion ratios are found to be greater than the values of $(m_{alcohol} / m_{CO_2})^{1/2}$ for both alcohols. However, the diffusion ratio approaches that predicted by Eq. (4) at lower densities. The fact that the diffusion ratio is greater than the quantity of $(m_{alcohol} / m_{CO_2})^{1/2}$ may be explained if the "effective" molecular weight of the alcohols is greater than that calculated from atomic

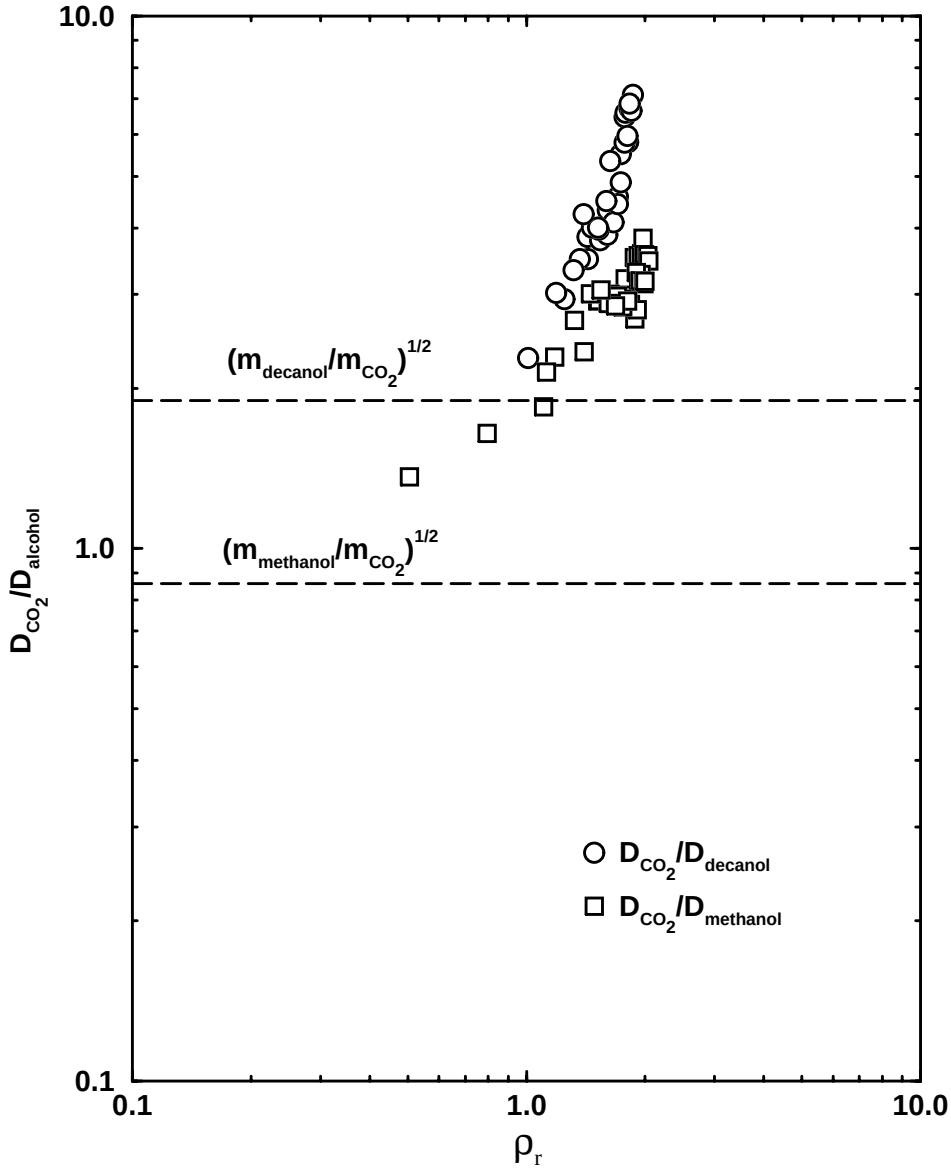

Fig. 5. The measured diffusion constant ratios, $D_{CO_2} / D_{methanol}$ and $D_{CO_2} / D_{decanol}$, are compared to the corresponding molecular weight ratios (see Eq. (4)), indicating significant departure from the hard-sphere model due to solvent clustering.

weights. This may happen when alcohol-CO_2 clusters diffuse in the mixture as a single entity. In this case, one can estimate the average cluster size by assuming that all deviation from the hard-sphere model results from the transport properties of the solute-solvent cluster. For the CO_2-methanol mixture, the maximum diffusion coefficient ratio in this study is 4.4 times larger than $(m_{methanol} / m_{CO_2})^{1/2}$ (see Fig. 5), leading to an "effective" methanol molecular weigh of 0.61 $Kg \cdot mol^{-1}$. If it is assumed that a single methanol molecule participates in such solute-solvent clusters, then the estimated cluster size for CO_2 molecules is 13. The cluster size of CO_2 in the vicinity of 1-decanol is estimated to be 50 at the highest densities studied. Considering the molecular size difference between decanol and methanol, it is understandable that the cluster size is much larger for decanol (50) than for methanol (13). It is interesting to note that the cluster size may be as large as several hundred for pure CO_2 near its critical point [34,35].

The preliminary conclusions reported here depend upon the assumptions that hydrogen bonding is negligible in these CO_2-alcohol mixtures. This simplifying assumption undoubtedly will lead to certain errors in the analysis of solvent local density enhancement and the average cluster size, but this approach provides a semi-quantitative assessment of fluid structures. Further work will address the relative modest effects of hydrogen bonding.

3.4 Summary:

The self-diffusion coefficients for methanol and 1-decanol in supercritical fluid were measured using pulsed field-gradient NMR spectroscopy. Diffusion coefficients derived from the AK version of the hard-sphere model for simple liquids suggest the formation of solvent clustering near the solute molecules. The maximum CO_2 cluster sizes of 13 and 50 for methanol and decanol, respectively, are estimated from ratios of diffusion constants.

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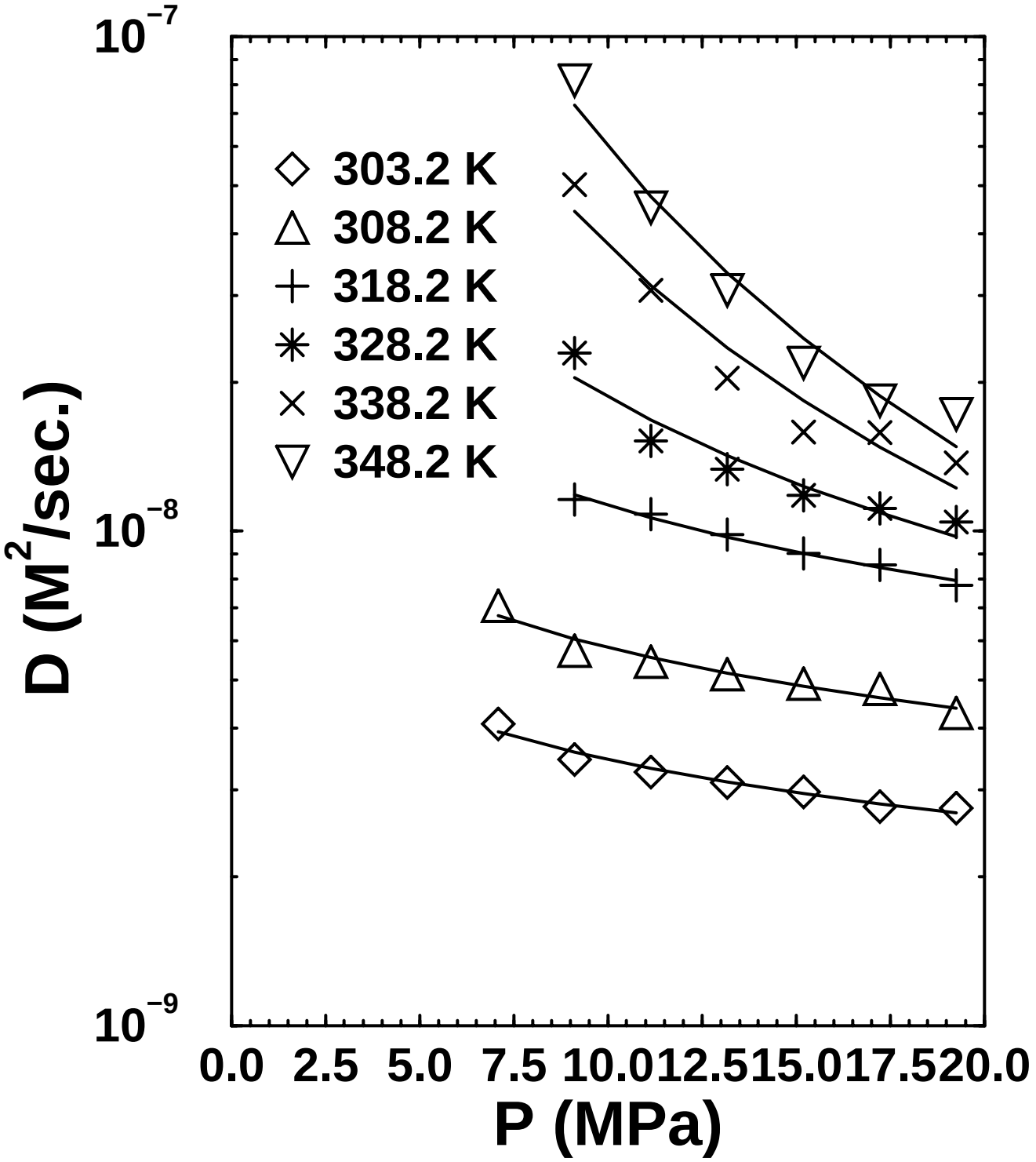
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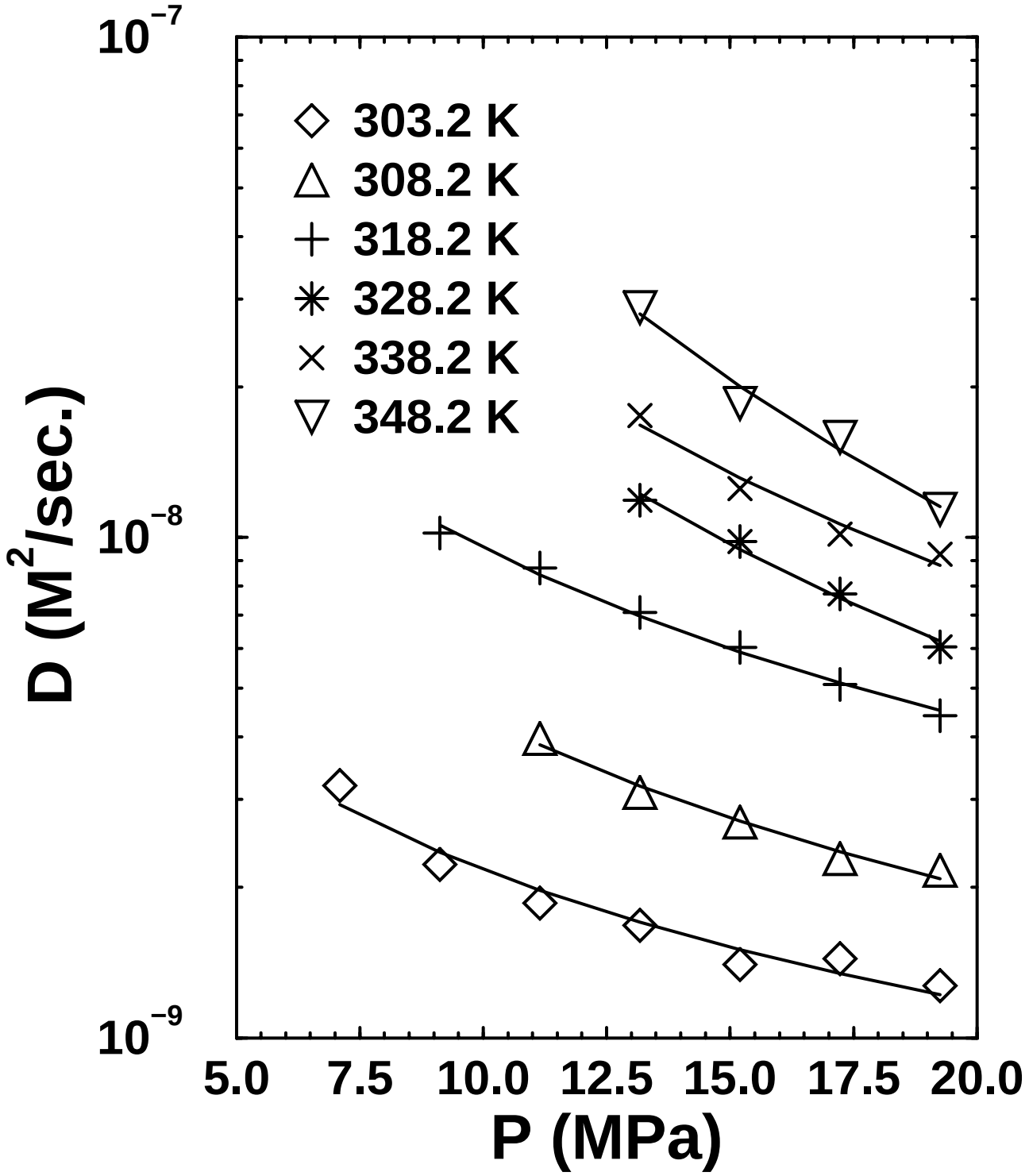
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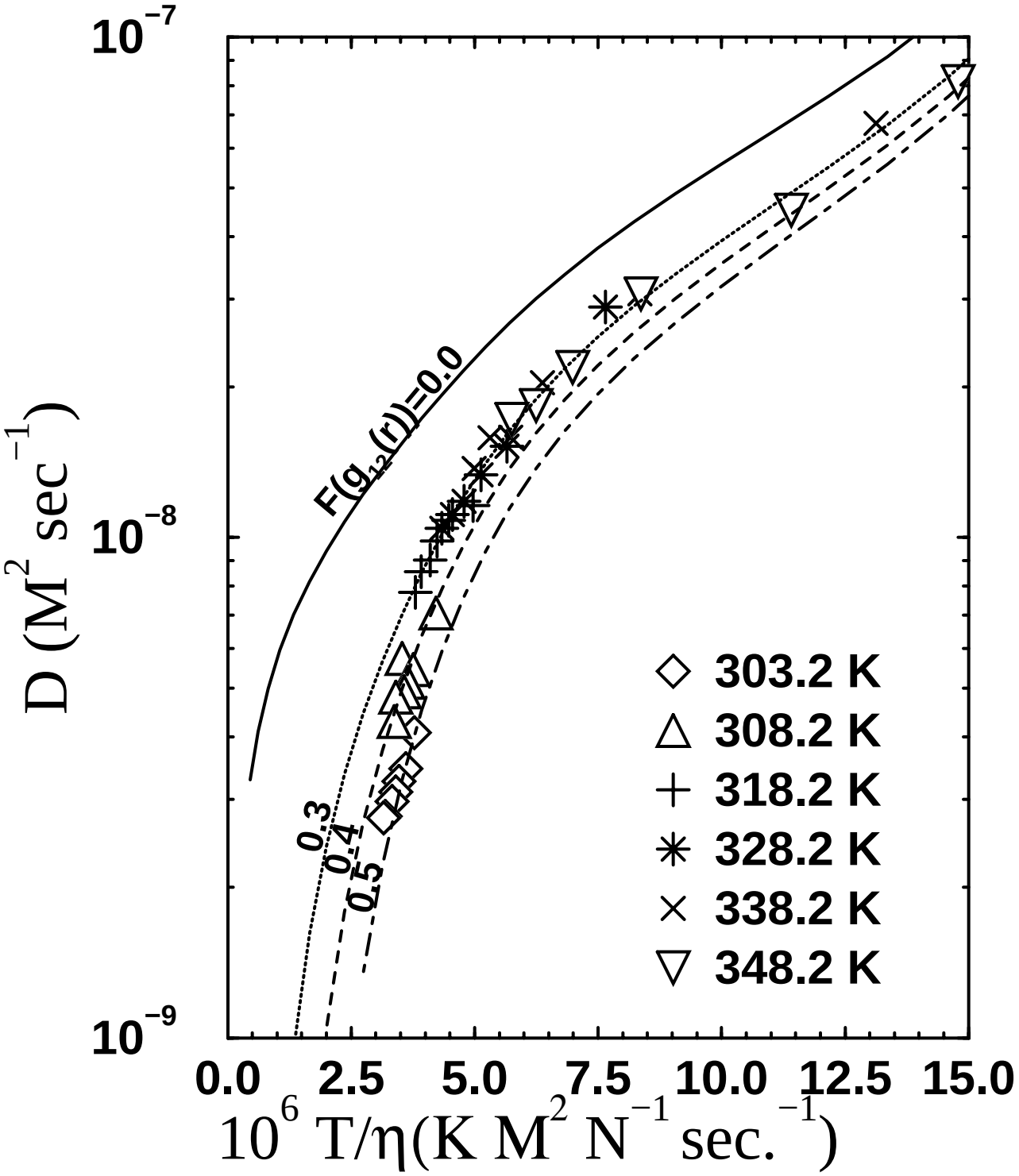
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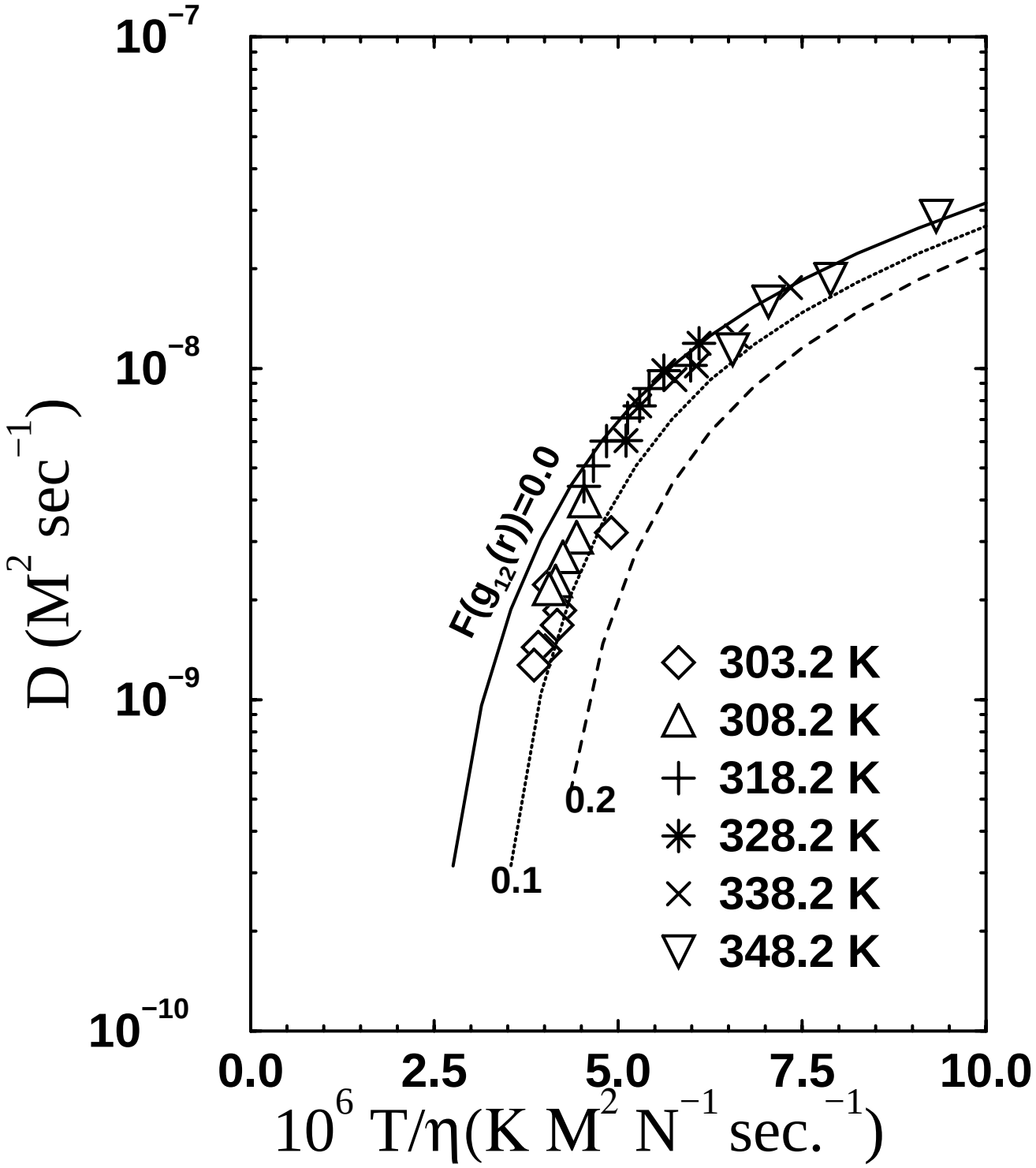
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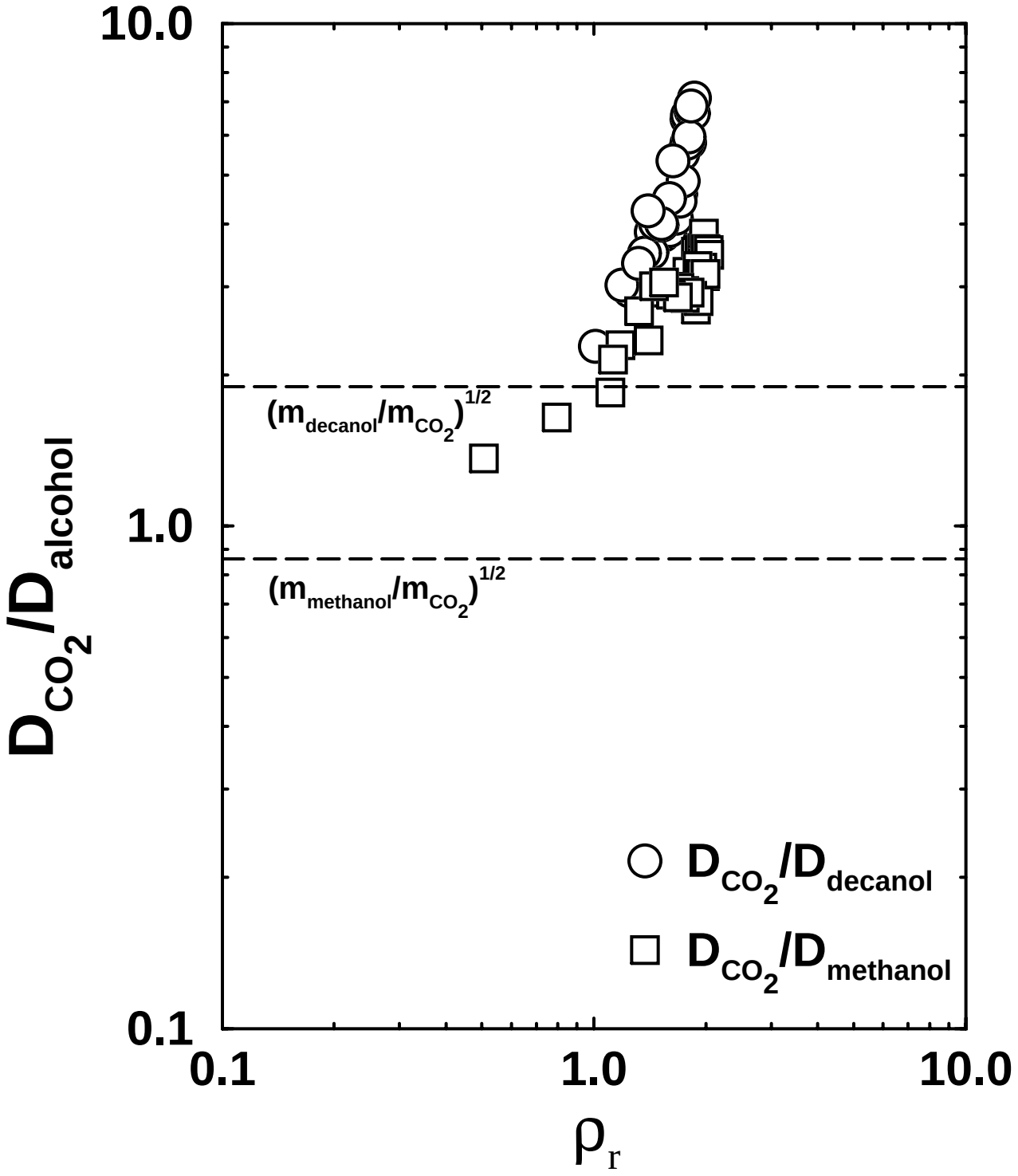
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