

Corresponding States Correlation of Dissolved-Gas Diffusion in Normal Alkanes

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INTRODUCTION

The diffusion of gases dissolved in liquids plays a key role in mass transfer with or without chemical reactions across the gas-liquid interface (Danckwerts, 1970). Existing tabulations of binary diffusivities of gases slightly soluble in liquids (or simply tracer diffusivities) are mostly limited to temperatures not far removed from 298 K.

Recently the Taylor dispersion technique has been applied (Chen, Davis and Evans, 1981) for measuring the tracer diffusivities of rare gases and methane in a series of liquid normal alkanes from 298 to 433 K. This method proves to be more accurate and versatile in its application than other techniques such as flow over a sphere (Davidson and Cullen, 1957), diaphragm cell (Hildebrand and Ross, 1964), bubble collapse (Wise and Houghton, 1966), wetted column (Mazarci and Sandall, 1980), constant bubble size (DeBlock and Fortuin, 1981), and so on.

This paper is concerned with the application of corresponding state principle (CSP) to the correlation of tracer diffusivities. A pseudocritical method will be followed in which the square root of the solute gas and solvent liquid critical temperatures is taken as the critical temperature, T_c , of the solute-solvent pair. The critical diffusivity D_c (i.e., tracer diffusivity at T_c) will be interpolated or extrapolated from the experimental data over a range of temperature. So determined T_c 's and corresponding D_c 's will serve as reducing parameters for developing a generalized correlation.

Although the CSP has been successfully utilized to correlate transport properties including viscosity, thermal conductivity (Tham and Gubbins, 1970), and self-diffusivity (Riazi and Daubert, 1980) in dense fluids, its application to tracer diffusivity will represent a significant extension of previous work.

CORRELATION DEVELOPMENT

The Arrhenius equation (Chen, Davis and Evans, 1982) was found to reproduce to within $\pm 1\%$ of the observed diffusivities of argon, krypton, xenon, methane in n-octane, n-decane, and n-tetradecane from 298 to 433 K. For a specific solute-solvent pair, D_c is evaluated from the Arrhenius equation at T_c , which is simply the square root of the solute and solvent critical temperatures. So determined T_c 's and D_c 's for all solute-solvent pairs are given in Table 1. Figure 1 shows the experimental diffusivities reduced with critical values vs. the reciprocal of corresponding reduced temperatures. The linear relationship between $\ln(D/D_c)$ and T_c/T , namely

$$\ln(D/D_c) = -3.651 (T_c/T) + 3.682 \quad (1)$$

with a correlation coefficient of 0.9960, is capable of reproducing the observed diffusivities to within 5%.

This generalized correlation has both practical and theoretical implications. In practice, it permits the tracer diffusivity to be predicted over wide temperature ranges from a single diffusivity D_c which can be readily measured with the Taylor dispersion technique. From the molecular point of view, it suggests that the

diffusion of inert solutes in nonpolar solvents is comparable at the same reduced temperature.

DISCUSSION

The generalized correlation, Eq. 1, is reminiscent of what Tham and Gubbins (1970) developed for self-diffusivities in saturated

TABLE 1. T_c AND D_c FOR BINARY DIFFUSION OF RARE GASES AND METHANE IN NORMAL ALKANES

	Ar	Kr	Xe	CH ₄
T_c (K)	293	345	406	329
$10^9 D_c$ (m ² /s)	6.28	8.51	12.0	9.01
n-C ₈ H ₁₈	305	360	423	343
n-C ₁₀ H ₂₂	5.41	7.62	11.2	8.00
n-C ₁₄ H ₃₀	324	381	448	364
	4.80	6.69	9.88	6.87

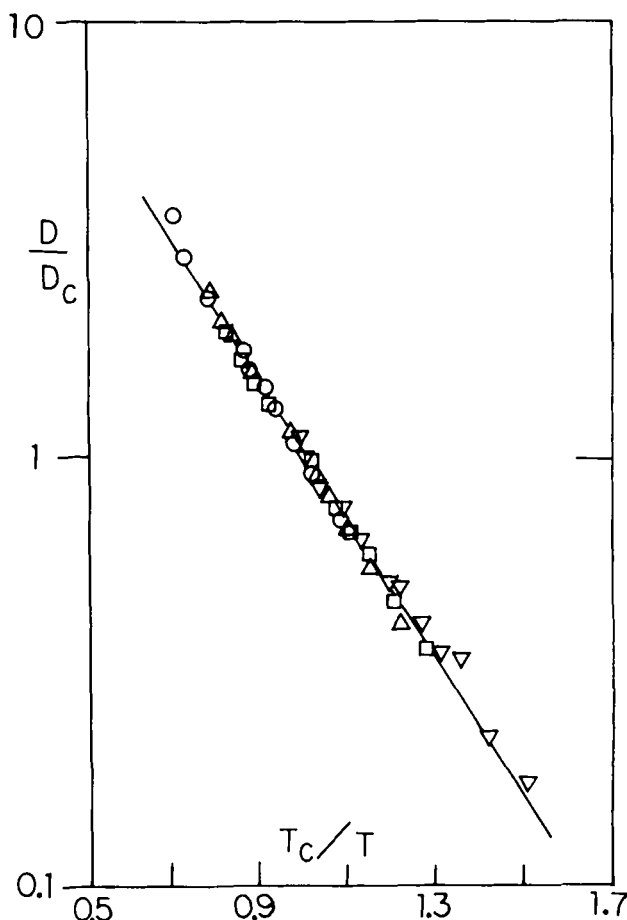


Figure 1. Tracer Diffusivities of argon (○), krypton (Δ), xenon (▽), and methane (□) in n-octane, n-decane, and n-tetradecane from 298 to 433 K.

liquids involving parameters for intermolecular potential energy and for molecular rotation. When applied to binary diffusion, this procedure entails rational mixing rules for the parameters associated with both components. It is obvious that the pseudocritical method is advantageous owing to its simplicity as well as generality.

It is noted that pressure does not play a role simply because slight pressures (less than 5×10^5 N/m²) were applied only when required to prevent the liquid from vaporizing as the temperature was raised above its normal boiling point; diffusivity in liquid is known to be a weak function of pressure.

Further studies are under way which will help to establish the conditions for the applicability of the proposed correlation. For example, restrictions on the shape and polarity of both solute and solvent molecules can be removed and the range of molecular weights extended to test the validity of Eq. 1.

NOTATION

D = tracer diffusivity of gases in liquids, m²/s
 T = absolute temperature, K

Subscripts

c = pseudocritical conditions

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Manuscript received March 11, 1982; revision received June 23, and accepted July 20, 1982.

Local Heat Transfer Coefficients for a Horizontal Tube in a Large-Particle Fluidized Bed at Elevated Temperature

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Current interest in large-particle fluidized beds stems from the development of several new processes. The fluidized combustion of coal, in which crushed coal is burned in a bed of dolomite or limestone particles, is possibly the most important. Recent studies (Leon et al., 1980; Tang and Howe, 1980; Goblirsch et al., 1980; Skinner, 1971) all report promising results based on pilot-plant studies. Heating of process fluids (e.g., crude oil) is being studied by Cherrington et al. (1977).

In all of the above-mentioned applications, horizontal tube arrays have proven to be a practical configuration for the immersed heat exchanger surface. A review of literature on the topic of heat transfer to tubes immersed in fluidized beds is given by Saxena et al. (1978).

The present publication reports local heat transfer coefficients for a single 50.8 mm diameter horizontal tube in a large-particle ($d_p = 3.23$ mm maximum), high-temperature ($T_B = 1,053$ K maximum) fluidized bed. Both the thermal stress problem for the tube wall and the analysis of coking of process fluids within the tube require local bed-to-tube heat transfer information.

Details concerning the instrumentation used as well as data acquisition and data reduction techniques appear elsewhere (George, 1981). Some useful information about the fluidized-bed facility used in the study are given below.

FLUIDIZED BED

Cross-sectional dimensions of the fluidized bed were 0.60 m \times 0.30 m. Combustion products of propane were used to heat the bed. A proportional-type controller regulated the propane flow rate to maintain the desired combustion chamber exit temperature. No combustion occurred in the bed itself. A complete description of the fluidized-bed facility, including engineering drawings, is given by Welty (1978). The design of the distributor plate is given by George (1981).

Granular refractory material, with commercial designation Ione Grain A, was used for bed material. Chemical composition of this material was given by the supplier as: 53.5% silica, 43.8% alumina, 2.3% titania, and 0.4% other. The particles had a smooth surface and fairly spherical shape from several previous test runs. Particle density was 2,700 kg/m³.

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