ether, 111-43-3; dibutyl ether, 142-96-1; dipentyl ether, 693-65-2; 2,4-dioxapentane, 109-87-5; 3,5-dioxaheptane, 462-95-3; 2,5-dioxahexane, 110-71-4; 3,6-dioxaoctane, 629-14-1; 2,5,8-trioxanonane, 111-96-6; 3,6,9-trioxaundecane, 112-36-7; 2,5,8,11-tetraoxadodecane, 112-49-2.

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Infinite Dilution Diffusion Coefficients of Methanol and 2-Propanol in Water

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Infinite dilution diffusion coefficients of methanol and 2-propanol in water have been measured by the Taylor dispersion technique over the temperature range 30–120 °C. Using the data of Pratt and Wakeham and Esteal and Woolf at lower temperatures, we examined the Othmar and Thakar equation (1953) over the entire temperature range. It is found that there are significant deviations above 75 °C.

Introduction

Diffusion coefficients in water are of significance in evaluating theories of diffusion and the liquid state since water/alcohol systems exhibit strong hydrogen bonding. Data in the literature are limited in the temperature range with most measurements being at ambient conditions. The objective of this work was to measure the diffusion coefficients of methanol and 2-propanol in water at a temperature range from 30 to 120 °C. In order to prevent water from boiling, the measurements were made at a pressure of 400 kPa (about 58 psia). Our previous studies indicate that the diffusion coefficients in liquids are independent of pressure in a narrow pressure range of 14.7–500 psia (*1*).

Experimental Technique

Mutual diffusion coefficients of the alcohols were measured by the Taylor dispersion method (*2*). In this method, a narrow pulse of solute diluted in the solvent is injected into a tube in which the solvent is moving in slow laminar flow. The pulse ultimately assumes a Gaussian distribution whose temporal variance is dependent on both the average flow velocity and molecular diffusivity D_{12}. At the end of the diffusion tube the concentration versus time data is recorded as the peak elutes. The normalized first and second temporal moments are calculated from which the diffusion coefficient is obtained. The apparatus and working equations have been described previously (*1*, *3*).

Table I. Infinite Dilution Diffusion Coefficients of Methanol and 2-Propanol in Water

	$D_{12} \times 10^5$, cm^2/s	
T, °C	MeOH	i-PrOH
30	1.83	1.43
56	3.42	2.21
81	4.91	3.32
120	7.73	5.82

Results and Discussion

Measured infinite dilution diffusion coefficients of methanol and 2-propanol in water are given in Table I. A 95% confidence interval of ±5% of the mean is generally sufficient for the data. Previous measurements on diffusion of alcohols in water were performed at temperatures below 65 °C, so this work almost doubles the temperature range of available data. Figure 1 shows data from this work along with those of Pratt and Wakeham (*4*) for 2-propanol in water and those of Esteal and Woolf (*5*) for methanol in water. Pratt and Wakeham also

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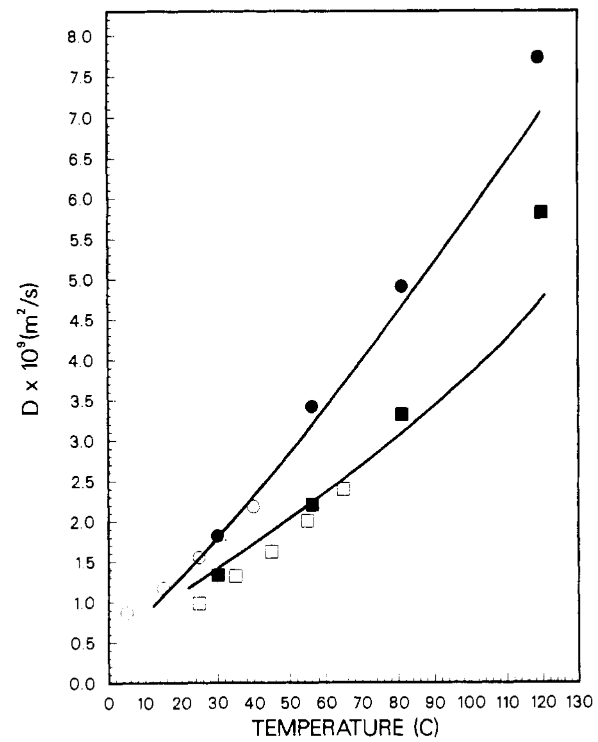

Figure 1. Infinte dilution diffusion coefficients of methanol and 2-propanol in water: (●) methanol, this work; (■) 2-propanol, this work; (○) methanol, ref *5*; (□) 2-propanol, ref *4*; (—) predictions of Othmar and Thakar (*6*).

used the Taylor dispersion method to make their measurements. Esteal and Woolf used a magnetically stirred diaphragm cell technique. Our low-temperature data agrees well within experimental accuracy with data of Pratt and Wakeham and Esteal and Woolf.

Diffusion in water as been well correlated with the Othmar and Thakar equation (*5*). For diffusion in water this empirical correlation reduces to

$$D_{12} = 14.0 \times 10^{-5} \eta_2^{-1.1} V_1^{-0.6} \qquad (1)$$

where the water viscosity η_2 is in centipoise, the molar volume of the alcohol is in cm^3/(g mol), and the diffusivity is in cm^2/s. This equation is also plotted in Figure 1. As can be seen from the figure, the agreement is good at low temperatures; however, there is a significant deviation from the data at high temperatures. Clearly there is a danger in extrapolating this predictive equation beyond its temperature range.

Glossary

D_{12}	diffusivity of solute 1 in solvent 2
V_1	molar volume of solute, cm^3/(g mol)
η_2	solvent viscosity

Registry No. Methanol, 67-56-1; 2-propanol, 67-63-0; water, 7732-18-5.

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Vapor–Liquid Equilibria of Nitrogen–Hydrocarbon Systems at Elevated Pressures

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The phase equilibria behavior of nitrogen + hydrocarbon binary, ternary, and quaternary systems was studied. Measurements were made over the temperature range from 305.4 K (90 °F) to 373.2 K (212 °F) at pressures up to 35.85 MPa (5200 psia). The binary systems studied included nitrogen + *n*-heptane, nitrogen + *n*-octane, nitrogen + *n*-nonane, nitrogen + *n*-decane, nitrogen + *n*-dodecane, nitrogen + benzene, and nitrogen + toluene. The methane + *n*-butane + *n*-decane, nitrogen + *n*-butane + *n*-decane, and nitrogen + methane + *n*-butane + *n*-decane systems are also reported. Comparisons with binary data from the literature show good agreement and consistency of a new experimental vapor–liquid equilibrium (VLE) measurement design.

Introduction

Nitrogen has been widely used in oilfield operations for reservoir pressure maintenance, gas cycling, and gas lift. In recent years, the use of nitrogen for enhanced oil and gas recovery has become an attractive method for some high-pressure reservoirs.

A thorough understanding of the phase behavior of the nitrogen gas and the crude oil is essential for applications of nitrogen in enhanced oil recovery. The equilibrium phase diagram of nitrogen–crude oil systems can be used to establish whether a miscible or immiscible condition will occur.

Ideally, the phase behavior of complex systems can be predicted by using equations of state (EOS) such as the Soave–Redlich–Kwong (SRK) or Peng–Robinson (PR) EOS. However, the use of EOS for the prediction of these multicomponent systems will face a possible problem—the lack of experimental phase behavior information needed to optimize these equations of state for more accurate predictions.

Most of the information on this subject in the literature is about binary nitrogen–light alkane systems. Binary system studies involving nitrogen and methane, ethane, or propane have been concentrated mostly on operations under cryogenic conditions. Most data for ternary and a few quaternary systems