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A Mixing Rule of Self-Diffusivities in Methane Hydrocarbon Mixtures and the Determination of GOR and Oil Viscosities from NMR Log Data

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Abstract

A new mixing rule is described for the prediction of the self-diffusivities of gas and liquid hydrocarbon molecules in methane-oil mixtures. Unlike macroscopic fluid properties such as density and viscosity, molecule self-diffusivity is a microscopic parameter associated with individual molecule species. Thus, a self-diffusivity of a binary mixture of gas and oil is non-existent. Instead, the self-diffusivity of each species in the binary system is affected by presence of the other species. For that reason, the commonly used log-mean based mixing rule that applies to macroscopic properties of the mixtures is unsuitable for self-diffusivity when the reference states are pure Component 1 and pure Component 2. We found that it is necessary to introduce two new reference states: one is the infinite dilution of Component 1 in Component 2; the other is the infinite dilution of Component 2 in Component 1. The component can be a single-molecule species or a mixture; as long as its self-diffusivity or self-diffusivity distribution can be measured. Using this approach, the self-diffusivity of each component in the mixture follows the log-mean based mixing rule. This new mixing rule is verified with literature data of methane-hexane, ethane-hexane, methane-octane, ethane-octane, methane-decane, and ethane-decane mixtures over a wide range of temperatures, pressures, and solution gas concentrations.

The new mixing rule is applied, and a detailed procedure is developed, to determine the Gas Oil Ratio (GOR) and the live-oil viscosity for in-situ volatile oils from NMR log data. First, the self-diffusivities and proton fraction of the methane and oil mixture are determined by fitting the NMR-measured diffusivity distribution with a bi-modal distribution. Then, the self-diffusivities for the four reference states are calculated using the mixing rule. Finally, the GOR is calculated from the proton ratio; while the live-oil viscosity is calculated from the self-diffusivity of pure oil and GOR. The calculated GOR and oil viscosities are compared with the PVT measurement of the oil sample taken from downhole and show good agreement. GOR and oil viscosities from this new technique can be used for optimizing testing and sampling programs, for reservoir stimulation studies, and for the design of surface production facilities.

Introduction

Molecule diffusion occurs due to the concentration gradient (ordinary diffusion), the pressure gradient (pressure diffusion), the thermal gradient (thermal diffusion), unequal external forces (forced diffusion), or Brownian motion (self-diffusion) (Bird et al., 1960). In a binary system with Component 1 and 2, the mutual diffusion coefficient ($D_{12} = D_{21}$) due to concentration gradient is defined by Fick's (1855) first law of diffusion.

$$J_i = -c \cdot D_{12} \nabla x_i \tag{1}$$

where J_i is the molar diffusion flux of component i; c is the molar concentration of the mixture; x_i is the molar fraction of component i in the mixture. In a homogeneous binary system where there is no macroscopic concentration gradient, molecules diffuse due to random Brownian motion; the self-diffusivity, D_i, of component i is defined as

$$D_i = \frac{1}{6t} \left\langle (r_i(t) - r_i(0))^2 \right\rangle \tag{2}$$

where $r_i(t)$ and $r_i(0)$ are the positions of a specific molecule of component i at time t and time 0, respectively. There are some empirical correlations developed in the literature (Darken 1948; Hertz 1977; Adamson 1960; Friedman and Mills 1986; Mills and Friedman 1987) on the relationship of $D_{12} = f(D_1, D_2, x_1)$. However, in principle D_{12} and (D_1, D_2) are fundamentally