

Measurement and modelling of mass diffusion coefficients for application in carbon dioxide storage and enhanced oil recovery

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Several very important processes involve the injection of light gases into fluid-saturated porous rocks located deep underground. These processes include geological storage of anthropogenic carbon dioxide and enhanced/improved oil recovery by injection of carbon dioxide or other light gases. The most promising options for geological storage of CO₂ involve injection into either a deep saline aquifer or a depleted oil or gas field. In these cases, injected CO₂ will invade pore space that was previously saturated with brine and/or hydrocarbon fluids, interfaces will form between these phases, and at least some of the CO₂ will, over time, dissolve into the pore fluids. The initial non-equilibrium composition of the phases provides the driving force for dissolution of CO₂, while mass diffusion coefficients play a role in controlling the rate at which this process proceeds. It is important to recognize that injected CO₂ is unlikely to be chemically pure and impurities will generally have different solubility behavior and different diffusion coefficients. A similar situation exists in CO₂-enhanced oil recovery wherein CO₂ is injected into an oil reservoir with the intention of mobilizing oil that would otherwise remain behind. In miscible flooding, the CO₂ dissolves in the oil creating a low-viscosity phase that can flow much more easily to the production wells. The miscibility behavior of oil and CO₂ depends upon temperature, pressure and the oil composition and, typically, a minimum miscibility pressure exists below which oil and CO₂ are only partially miscible. Even when CO₂ flooding is carried out under partially-miscible conditions, dissolution of CO₂ can greatly decrease the viscosity of the oil and lower its interfacial tension with brine, thereby improving both the production rate and cumulative recovery of oil. Other gases can also be used to stimulate oil production, for example by boosting reservoir pressure and sweeping hydrocarbons towards production wells. A detailed scientific understanding of interfacial mass transfer in these processes requires knowledge of the relevant diffusion coefficients and it can be challenging to estimate these reliably under the high-pressure and high-temperature (HPHT) conditions prevalent deep underground. This contribution addresses the measurement and modelling of the diffusion coefficients of CO₂, and other gases, in both brines and liquid hydrocarbons under HPHT conditions.

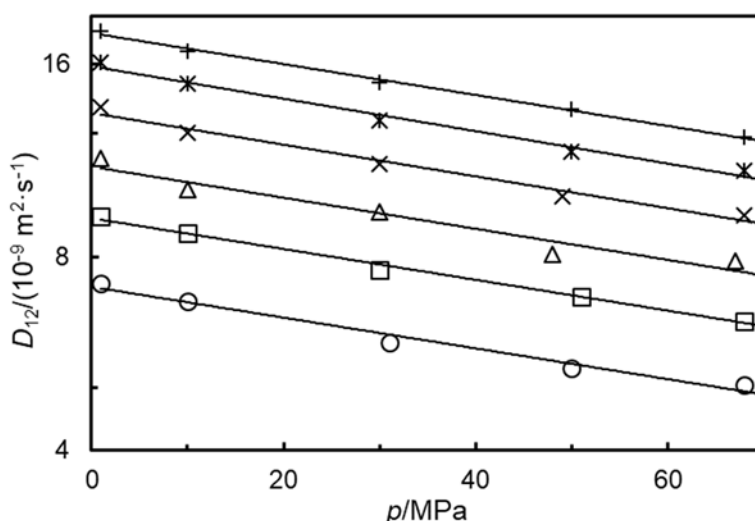


Figure 1. Mutual diffusion coefficients D_{12} of CO₂ at infinite dilution in heptane as a function of pressure p at various temperatures: O, $T = 298$ K; □, $T = 323$ K; △, $T = 348$ K; ×, $T = 373$ K; *, $T = 398$ K; +, $T = 423$ K.

In this work, measurements were carried out by the Taylor dispersion method [1, 2] to determine the mutual diffusion coefficient for CO₂ in water or hydrocarbon at effectively infinite dilution. Measurements were carried out for CO₂ in water, hexane, heptane, octane, decane, dodecane, hexadecane, cyclohexane, squalane and toluene at temperatures between 298 K and 423 K with pressures up to 69 MPa. Measurements of CO₂ diffusivity in different brines were also carried out by ¹³C pulsed-field gradient NMR.

The diffusion coefficients of CO₂ in aqueous media at infinite dilution were found to be almost independent of pressure over the range investigated and the results could be correlated with the Stokes-Einstein equation incorporating a weakly-temperature-dependent hydrodynamic radius. On the other hand, the diffusion coefficients of CO₂ in hydrocarbons were strongly dependent upon both temperature and pressure, as exemplified in Fig. 1 for the (CO₂ + heptane) system. In this case, new theory was developed to model the data. The results of both the experimental and modelling work will be discussed in detail.

References

- [1] C. Secuianu, G. C. Maitland, J. P. M. Trusler, W. A. Wakeham: *Mutual diffusion coefficients of aqueous KCl at high pressures measured by the Taylor dispersion method* J. Chem. Eng. Data **56**, 4840-4848 (2011).
- [2] S. P. Cadogan, G. C. Maitland, J. P. M. Trusler: *Diffusion coefficients of CO₂ and N₂ in water at temperatures between 298.15 K and 423.15 K at pressures up to 45 MPa*. J. Chem. Eng. Data **59**, 519-525 (2014).

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