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High-Pressure Cylindrical Acoustic Resonance Diffusion Measurements of Methane in Liquid Hydrocarbons[1]

S. O. Colgate,[2,3] V. E. House,[2] V. Thieu,[2]
K. Zachery,[2] J. Hornick,[2] and J. Shalosky[2]

A novel cylindrical acoustic resonance method for the measurement of gas diffusion into liquids at high pressures is described. The measurements were performed in a vertically oriented cylindrical acoustic resonator containing both the liquid solvent and gaseous diffusant while under high-precision isothermal and isobaric control. Individual resonance modes of the liquid column, the gas column, and the two-phase coupled fluid are resolved in the fast Fourier transform acoustic-resonance spectrum (FFT-ARS). High-resolution acoustic spectra measured at frequent time intervals reveal the changes which accompany the diffusion of gas into the liquid phase. One change, namely, the growth in length of the liquid column, results in a systematic shift to higher frequencies of axial modes in the gas column. The temporal behavior of this moving boundary, together with quantitative measurement of the flow to the gas column required to sustain the constant pressure, permits determination of the gas-into-liquid diffusion coefficient. Diffusion coefficients were determined from the change in frequency as a function of time of axial resonance modes in the gas-phase virtual cylinder as the surface of the underlying liquid phase advanced due to gas absorption. Measurements of the systems methane/*n*-octane, methane/*n*-nonane, and methane/*n*-decane were performed as a function of temperature at a pressure of 250 psia. Comparisons is made to results obtained elsewhere and by other methods but at the same temperatures and pressure.

KEY WORDS: acoustic resonance spectroscopy; diffusion kinetics; high pressure; methane; liquid hydrocarbons.

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[2] Department of Chemistry, University of Florida, Gainsville, Florida 32611-7200, U.S.A.

[3] To whom correspondence should be addressed.

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1. INTRODUCTION

Acoustic resonance techniques applied to the measurement of themophysical properties and phase behavior are well established in this and other laboratories [1–3]. For an acoustically stimulated fluid contained in a cavity resonator of well-defined geometry, these measurements depend on either the calculated speed of sound from a single resonant frequency or the identification of a discontinuity in a resonant-frequency track measured as a function of temperature or pressure. All precision acoustic measurements take advantage of the extreme sensitivity of the speed of sound relative to the condition or state of the fluid under observation. Typically, spherical resonators are employed for high-accuracy measurements due to the possibility for substantial elimination of viscous effects at the resonator walls by considering only pure radial resonance modes. For multiphase work, however, spherical resonators are impractical due to complicated geometric perturbations imposed on the resonance frequency modes. For multiphase acoustic measurements, vertically oriented cylindrical resonators offer distinct advantages in that each phase can be assumed to constitute its own virtual cylindrical resonator, and the sets of resonance modes derived from the individual phases can be discerned in a single acoustic spectrum. In the case of gas/liquid diffusion kinetics, one can monitor the frequency change over time of a suitable resonant mode measured in either the gas-phase or the liquid-phase virtual cylinder to meter the process advancement.

Solution of the differential equations for the Fickian diffusion of gases into liquids confined in a cylinder yields

$$\frac{C_t}{C_s} = 1 - \frac{8}{\pi^2} \sum_{n = \text{odd}} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D}{4L_t^2} \right) t \qquad (1)$$

where C_t is the concentration at time t, C_s the saturation concentration, L_t the liquid length at time t, and D the diffusion coefficient. Thus if one knows the reduced concentration, C_t/C_s, and the liquid-column length at any time t, the diffusion coefficient can be determined numerically. The theory of normal-mode acoustic resonance in a lossless fluid confined to a cylinder of length l and diameter d gives [4]

$$\text{frequency} = \frac{c}{2} \left(\left(\frac{n_z}{l} \right)^2 + \left(\frac{\alpha_{mn}}{d} \right)^2 \right)^{1/2} \qquad (2)$$

where c is the speed of sound, n_z an integer, and α_{mn} tabulated eigenvalue (namely the nth zero of $dJ_m(\pi\alpha)/d\alpha = 0$). For $\alpha_{mn} = 0$, the column length of the phase may be calculated directly from a single resonance-mode frequency and speed-of-sound determination. The speed of sound may be determined from observed modes for which $n = 0$. Consider an initially evacuated vertically positioned cylindrical-cavity resonator partially filled with liquid prior to introducing the diffusing gas at time zero. The diffusion process is carried out under isothermal and isobaric conditions. As the gas diffuses into the liquid, the liquid-column length will increase (gas-column length decrease). At least initially, and over the entirety of gas uptake for many systems, the evolution of the properties of the liquid phase will exhibit Henry's law behavior. Thus one can calculate the reduced

$$\frac{C_t}{C_s} = \frac{f_t - f_0}{f_s - f_0} \tag{3}$$

concentration directly from resonance frequency data ($\alpha_{mn} = 0$) gathered over time from the relation where f_t is a resonance frequency at any time during the process, f_0 is the frequency at time 0, and f_s is the frequency at saturation. Knowing the overall length of the resonator, the speed of sound in the gas phase and identifying the value of n corresponding to the resonance mode of interest, the liquid-column length can be calculated by difference at any time t from Eq. (2).

2. THE CYLINDRICAL ACOUSTIC CAVITY RESONATOR SYSTEM

The cylindrical-cavity acoustic resonator system (CACRS) was designed for maximum versatility, accuracy, and precision with regard to $PVTc$ (c = speed of sound) measurement and control. Figure 1 is a diagram of the CACRS. The cylindrical resonator communicates with a sealed calibrated bellows assembly through an isolation valve. The entire working fluid volume of the resonator system resides in an air bath operated by a custom digital thermal-control system. The standard deviation of temperature as measured with a four-wire resistance thermometer in the bath from the programmed set point was typically no greater than 0.001 K. A custom-design digital pressure controller maintained set-point pressure to ±0.02 psia. For this system, the extreme sensitivity of the digital Bourdon (Heise) pressure gauge to variations in room temperature necessitated its placement inside the temperature-control bath. All control elements were monitored with digitally interfaced high-precision (6.05-digit) multimeters. The cylindrical resonator was precision-machined with flat circular piezoelectric acoustic transmission and with reception transducers located at the cylinder ends. Acoustic input to the resonator was supplied by a computer-interfaced frequency synthesizer/function generator. Acoustic output was electrically isolated to eliminate spurious noise and was gain-boosted with a filterable low-noise preamplifier. This output signal was fed into a high-speed digitizer, which in turn was interfaced to the same computer used to

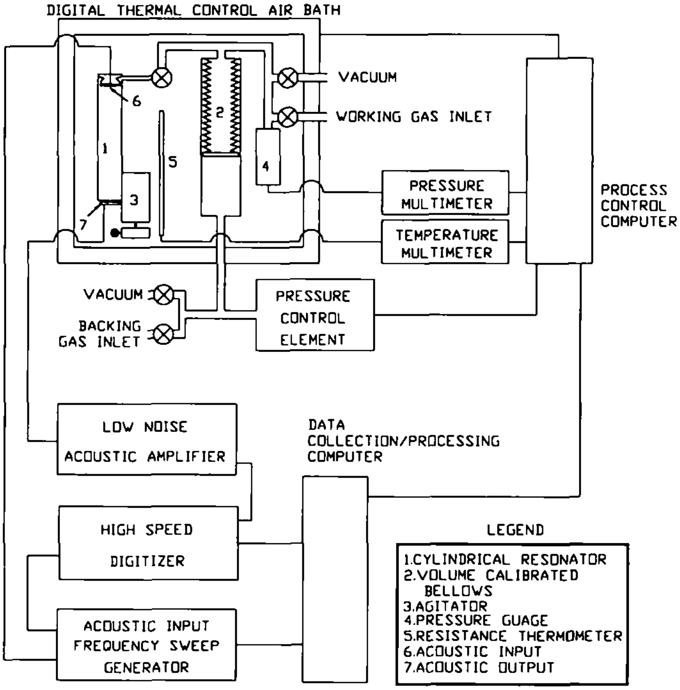

Fig. 1. Schematic diagram of the apparatus.

control the input signal. Thus in normal operation, synchronization of the input and output signal was both computer-controlled and monitored.

A series of working-gas and backing-gas isolation and leak valves allowed for easy system evacuation and gas loading. The resonator was easily removable for liquid loading. The resonator was mounted in the air bath on vibration dampers, which served the dual purpose of aiding in the elimination of mixing currents during diffusion measurements caused by mechanical sources, as well as allowing for some degree of freedom of motion for shaking to achieve saturation. Shaking was provided by a small electric motor which spun an eccentrically weighted wheel. The motor was attached directly to the resonator body and could be controlled either digitally or manually. The total resonator volume was 5.33 ml (6.35 cm long, 1.03 cm in diameter).

3. EXPERIMENTS

Diffusion kinetics of methane (Scott Specialty Gases; 99.99% purity) into *n*-octane (Aldrich; 99 + %), *n*-nonane (Aldrich; 99 + %), and *n*-decane

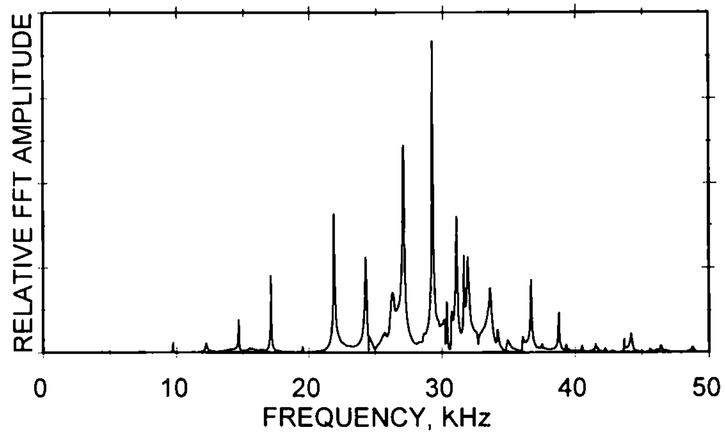

Fig. 2. Typical two-phase acoustic resonance spectrum.

(Alfa; 99 + %) were measured at temperatures of 7.55, 17.90, 28.25, and 38.60°C at a pressure of 250 psia. A typical diffusion run proceeded as follows. The cylindrical resonator was first loaded with about 1 ml of the hydrocarbon liquid and evacuated before the isolation valve was closed which separates the resonator from the remainder of the working volume. Methane gas was then introduced and sealed into this working volume and the system was allowed to equilibrate to the desired temperature and pressure. After the equilibration period, acoustic data acquisition was begun simultaneously with the opening of the isolation valve. Data gathered included acoustic spectra over the frequency range of 0 Hz to 50 kHz (resolution of 0.76 Hz) and time in seconds (resolution of 0.1 s). A typical run lasted 12 h, with the final 3 h consisting of resonator shaking on a 50% duty cycle. Shaking was performed to facilitate facile saturation of the liquid phase with methane. The nonshaking period of the duty cycle allowed for any accumulated liquid to drain from the walls of the resonator. During a run, 200 total spectra were gathered evenly spaced over time. Thus 150 spectra were captured during the diffusion process and 50 spectra were gathered during the shaking portion of the run. Figure 2 is a typical acoustic resonance spectrum gathered during a run. Since in this system acoustic excitation was introduced at the top of the resonator, the large acoustic impedance presented by the gas–liquid interface caused the principal resonant modes observed to be those along the gas-phase virtual cylinder axis [i.e., $\alpha_{mn} = 0$ in Eq. (2)]. By identifying any two of these modes, the value of n_z in Eq. (2) can be determined. Typically modes corresponding to n_z of 6, 7, or 8 were the most prominent and

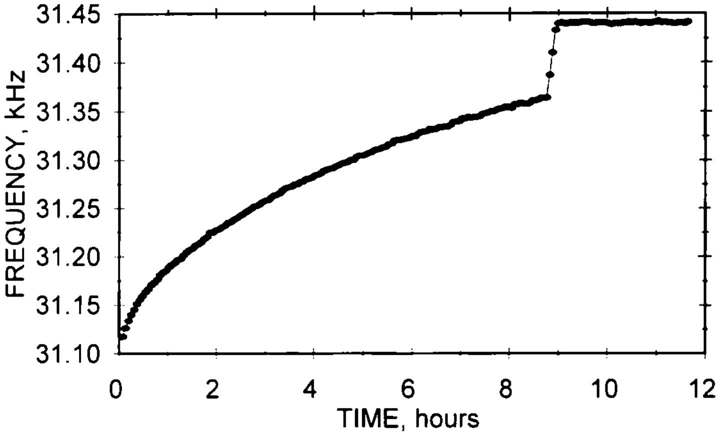

Fig. 3. Typical resonance frequency track versus time for a diffusion run.

were used for diffusion coefficient determination. Figure 3 is a track of a typical resonance mode as a function of time during one of the diffusion runs.

4. CALCULATIONS

Diffusion coefficients were calculated numerically by the Newton–Raphson method from Eq. (1). Liquid-column length was determined from methane speed-of-sound calculations using the AGA8 equation of state and included correction for the vapor pressure of the liquid phase. The saturation frequency was determined by averaging the frequency values over the last portion of the frequency track where no additional gas uptake could be observed after shaking. Due to unavoidable Joule effects on resonance frequencies observed at startup, the value for f_0 was determined by assuming the diffusion coefficient to be independent of concentration and

Table I. Acoustically Measured Diffusion Coefficients ($cm^2 \cdot s^{-1}$)

Temperature (°C)	*n*-Octane	*n*-Nonane	*n*-Decane
7.55	5.4×10^{-5}	4.4×10^{-5}	3.7×10^{-5}
17.9	6.2×10^{-5}	4.9×10^{-5}	4.2×10^{-5}
28.25	7.1×10^{-5}	5.7×10^{-5}	5.0×10^{-5}
38.6	8.5×10^{-5}	6.9×10^{-5}	6.2×10^{-5}

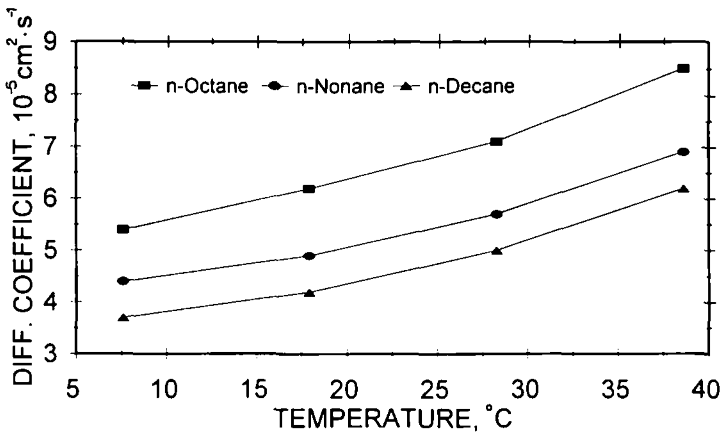

Fig. 4. Graph of acoustically determined diffusion coefficients.

thus constant over time; by means of a Simplex method the standard deviation of the averaged diffusion coefficient, calculated over nonshaking acquisitions, was minimized with regard to variations of the starting frequency and starting time. Results from all runs are listed in Table I and shown graphically in Fig. 4.

5. DISCUSSION

It is apparent from Fig. 4 that the acoustic diffusion coefficients are self consistent reflecting expected trends, namely increased diffusion rates at higher temperature and lower carbon number. Using an optical interferometric method, Killie and co-workers [5] determined the diffusion coefficient for the methane/*n*-octane system at 28.25°C and 250 psia to be $6.3 \times 10^{-5}\ \mathrm{cm^2 \cdot s^{-1}} \pm 0.3 \times 10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$, which is 11% lower than the value of $7.1 \times 10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$ obtained with the acoustic technique. Typical minimum standard deviations of the calculated diffusion coefficients were of the order of $\pm 0.2 \times 10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$. The lower diffusion rate obtained from the optical method may reflect that method's measurement of the diffusion coefficient near infinite dilution, while the acoustic method weights the calculation toward more concentrated solutions. The standard minimized deviations calculated for the acoustic technique are probably elevated from the assumption of zero concentration dependence of the diffusion coefficient. Further calculations on the current data are under way to attempt to expose this dependence.

Improvements of the technique are planned and involve the installation of a sensitive bellows positioning indicator, which with calibration will allow for the determination of gas volume uptake and thus solution component activities and Henry's law constants. Installation of a cylindrical piezoelectric transducer cylinder wall will allow for direct speed-of-sound determination and thus eliminate the need for calculated equation of state values.

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4. See, for example, P. M. Morse, in *Vibration and Sound* (McGraw-Hill, New York, 1948), p. 399.
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