Supporting Information

Speed of Sound Measurements of Binary Mixtures of 1,1-Difluoroethylene (R-1132a) + Propane and Derived Speed of Sound of Pure R-1132a

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Estimating dispersion effect

Lin and Trusler[1] provide a framework for estimating the effect of dispersion on speed of sound measurements. The relative dispersion in the speed of sound (c/c_0 – 1) can be estimated by,

$$\left(\frac{c}{c_0}-1\right)=\left[1-\left(\frac{(\gamma-1)\Delta}{1-\Delta}\right)\frac{(f/f_0)^2}{1+(f/f_0)^2}\right]^{1/2} \qquad \text{(S1)}$$

where $\gamma = C_p/C_v$ and $\Delta = C_{vib}/C_p$. C_p is the isobaric heat capacity, C_v is the isochoric heat capacity, and C_{vib}, is the vibrational heat capacity. f is the frequency at which the measurement was performed and f_0 is the zero-frequency given by,

$$f_0=\left[2\pi(1-\Delta)\tau_{11}\right]^{-1} \qquad (2)$$

where τ_{11} is the molecular relaxation time. τ_{11} is defined by,

$$\tau_{11}^{-1}=(\bar{v}/\lambda)P_{11}^{*} \qquad (3)$$

where $\bar{v}$ is the average molecular speed defined by,

$$\bar{v}=(8kT/\pi M)^{1/2} \qquad (4)$$

where k is the Boltzmann constant, T is the temperature, and M is the molar mass. λ is the mean free path defined by,

$$\lambda=\left[\sqrt{2}\pi\sigma^2 n\right]^{-1} \qquad (5)$$

where σ is the molecular diameter (calculated using the method of Chung et al.[2]) and n is the number density. P_{11}^{*} is the vibration translation transition probability. To determine the vibration transition probability the vibrational relaxation time in the gas phase must be known. Currently no vibrational relaxation time data is available for R-1132a. Therefore, to estimate the impact of dispersion on the R-1132a measurements P_{11}^{*} for carbon dioxide[1], defined by equation 6, was used for this estimate.

$$P_{11}^{*} = 9.46 \cdot 10^{-6} \exp\left(T / 252K\right) \tag{6}$$

It is important to note that the relative impact of dispersion on R-1132a speed of sound measurements provided here are conservative. Demirdesen et al.[3] found that dispersion for R-1132a was negligible comparative to the results reported by Estrada-Alexanders and Trusler[4] for carbon dioxide. Both studies analyzed the influence of dispersion using resonator-type speed of sound instruments to measure the excess experimental half-widths, which is the sum of boundary layer and bulk sound absorption terms. Estrada-Alexanders and Trusler showed that for carbon dioxide that the effects of dispersion could increase measurement uncertainties up to 10% whereas Demirdesen et al. found no apparent effect of dispersion for R-1132a measurements. In our measurements we observed that at least a single short path echo was observable when loading pure R-1132a, which does not allow for a dual-path pulse-echo analysis. Measurements for R-1132a utilizing a single echo at a greater uncertainty could have been achieved[5] but this capability was not utilized for any measurements in this study. However, when loading carbon dioxide, no echoes were visible rendering any speed of sound measurements impossible. The relaxation time was calculated to account for the inclusion of propane in the mixture using the following relationship,

$$\frac{1}{\tau} = \frac{x}{\tau_{11}} + \frac{(1-x)}{\tau_{12}} \tag{7}$$

where τ is the relaxation time of the mixture, τ_{11} is the relaxation time of pure R-1132a, and τ_{12} is the relaxation time associated with unlike collisions (between R-1132a and propane molecules).

Lin and Trusler assumed that $\tau_{11}/\ \tau_{12}$ was approximately 400 across all temperatures and pressures. Given that dispersion is less severe in R-1132a relative to carbon dioxide a value of 100 was used for the ratio $\tau_{11}/\ \tau_{12}$. The estimated effect of dispersion on the speed of sound is plotted in figure S1. Figure S1 shows that the effect of dispersion decreases with increased pressure and concentration of propane, which is the same trend observed experimentally. Figure S1 shows that relative to the measured speed of sound dispersion effects are on the order of 10^{-5} or 0.001% of the measured speed of sound value. Given a typical uncertainty of our speed of sound measurements is between 0.04% to 0.2% of the measured speed of sound value we conclude that dispersion has a negligible impact on our measurements.

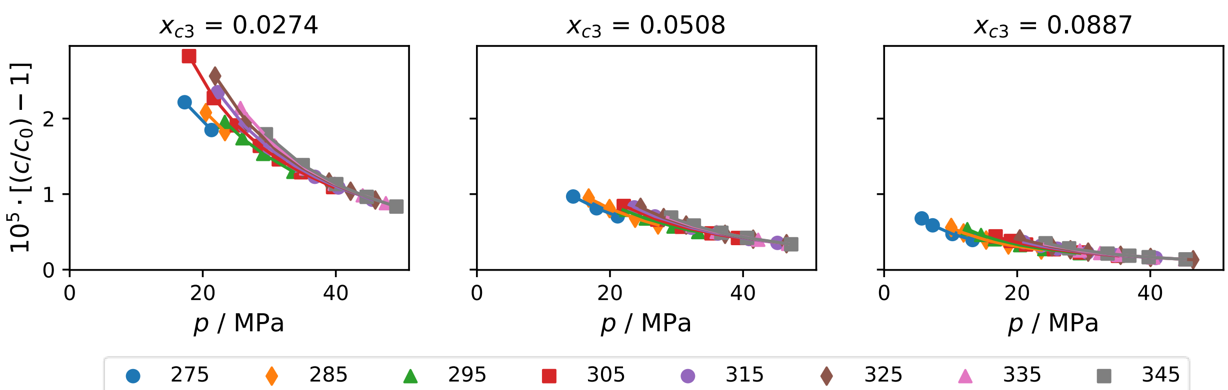

Figure S1. Relative impact of dispersion on speed of sound measurements on mixtures of R-1132a and propane as a function of pressure.

References

1. C.-W. Lin, J.P.M. Trusler, J. Chem. Eng. Data 59, 4099 (2014) doi:https://doi.org/10.1021/je5007407

2. T.H. Chung, M. Ajlan, L.L. Lee, K.E. Starling, Ind. Eng. Chem. Res. 27 (4), 671 (1988) doi:https://doi.org/10.1021/ie00076a024

3. D. Demirdesen, C. Wedler, R.E. Low, J.P.M. Trusler, Int. J. Thermophys. 44, 90 (2023) doi:https://doi.org/10.1007/s10765-023-03198-y

4. Estrada-Alexanders, J.P.M. Trusler, J. Chem. Thermodyn. 30 (12), 1589 (1998) doi:https://doi.org/10.1006/jcht.1998.0428

5. D. Menegazzo, A.J. Rowane, L. Fedele, S. Bobbo, G. Lombardo, M.O. McLinden, In 26th IIR International Congress of Refrigeration, (Paris, France, 2023)