J. Chem. Eng. Data **2008,** *53,* 303–306

Viscosity of Binary Mixtures of Carbon Monoxide and Helium

D. J. Richardson,[†] G. Mason,[†] B. A. Buffham,[†] K. Hellgardt,[‡] I. W. Cumming,[†] and P. A. Russell*,[§]

Loughborough University Loughborough, Leicestershire LE11 3TU, UK, Imperial College, London SW7 2AZ, UK, and University of Teesside, Middlesbrough, Tees Valley TS1 3BA, UK

Perturbation viscometry has been used to measure the viscosity of carbon monoxide−helium mixtures relative to the viscosity of carbon monoxide for points covering the full composition range at 25 °C and 0.11 MPa (abs). The viscosity versus composition curve is shown to have a maximum at around 9 % carbon monoxide. The results obtained agree, to within the uncertainty of the curve predictions from Chapman−Enskog using the parameters determined by the theory of corresponding states.

Introduction

Maxima in binary viscosity composition curves have been predicted, for example, using Chapman−Enskog theory, and observed experimentally for many years. Two papers[1,2] have been published that give equations to predict the presence of a maximum in terms of thermal properties of the gases and their molecular masses. Carbon monoxide−helium is one mixture where a maximum is predicted but there are no extant experimental data verifying its existence.

One set of experimental viscosities for both pure components and two mixture compositions at five temperatures between (25 and 200) °C has been produced.[3] The data reported[3] have only four different compositions and are insufficient to confirm the presence of a maximum. In recent years, several authors have made predictions of the properties of helium−carbon monoxide mixtures, including the viscosity.[4–6] These authors only published predictions and comparisons for the two specific mixture compositions measured experimentally[3] and do not report the position of any maximum in the curve.

Here, we report values of the mixture viscosity relative to the viscosity of carbon monoxide at room temperature for binary mixtures covering the full composition range obtained using perturbation viscometry.[7] This study came about following an observation made while investigating the sorption of CO on a catalyst material. The method has been described in detail previously.[8] The apparatus being used is shown in simplified form in Figure 1. It is essentially a perturbation viscometer with a packed bed of catalyst installed upstream of the delay lines. A helium carrier is initially passed through both sides of the apparatus, then one side is perturbed by a small continuous flow of carbon monoxide. The pressure difference upstream of the measuring capillaries is continuously recorded and registers all changes in flow and viscosity in the measuring capillaries. The delay lines are lengths of empty tubing and serve to separate changes in the pressure signal due to flow or composition changes. Figure 2 is the pressure record obtained. The negative peak is the sorption of the carbon monoxide onto the catalyst bed. The step change in the trace (B) is due to the change in viscosity caused by the composition as the carbon monoxide reached the measuring capillary. The bump in the pressure trace on the front edge of the step change at B is indicative that a maximum in the viscosity−composition curve close to the helium end of the composition range has been traversed. This result was compared with a viscosity curve predicted using the method of Reichenberg.[9] Reichenberg's method was chosen because it has been reported to give reliable estimations[10,11] of viscosities of binary mixtures. A large discrepancy in both the size and position of the maximum was observed. In view of the lack of previously published data and to confirm the position and size of the maximum, further measurements were required.

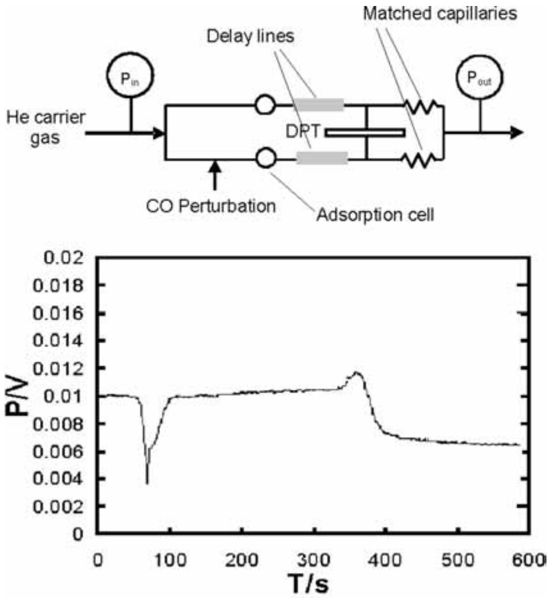

Figure 1. (a) Sketch of the experimental setup for an adsorption experiment where the differential pressure transducer (DPT) measures the pressure changes between the measurement and reference streams. (b) Gives the pressure response recorded DPT response ($P \cdot mV^{-1}$) with time ($T \cdot s^{-1}$) as a (13 % mole fraction) front of carbon monoxide passes through the system.

Experiments

The adsorption apparatus was simplified by removing the two catalyst beds to restore the apparatus to a more conventional perturbation viscometer design. The measurements were made

---

* Corresponding author. E-mail: p.russell@tees.ac.uk.

[†] Loughborough University Loughborough.

[‡] Imperial College.

[§] University of Teesside.

10.1021/je7004775 CCC: $40.75

using the perturbation viscometer operating with perturbations of increasing size up to the same size as the main carrier flow. In this way, measurements could be made for half of the composition range. This method was chosen in preference to the original version of the method (where the composition of the main flow is varied and only small perturbations are made to the composition) to minimize the use of carbon monoxide by running with pure helium as the carrier gas at all times and just using carbon monoxide for the perturbations. A small number of measurements were made using carbon monoxide as the main flow to complete the measurements across the composition range. The theory for large perturbations[12] was used to analyze the results.

The apparatus produces two independent measurements of the viscosity: one when adding the perturbation and a second when the perturbation flow is removed. This can be seen from the sample pressure record given in Figure 2. A pressure ratio can be defined for adding the perturbation flow (see eq 1) that relates the pressure change due to the increase in flow ($P_1 - P_0$) when adding the perturbation to the pressure change ($P_2 - P_1$) due to the change in viscosity due to the change in mixture composition. A similar but not equal ratio can be defined (see eq 2) for removing the perturbation flow.

$$R_{\mathrm{add}} = \frac{P_2 - P_1}{P_1 - P_0} \tag{1}$$

$$R_{\mathrm{rem}} = \frac{P_4 - P_3}{P_3 - P_2} \tag{2}$$

Equations 3 and 4 are, respectively, the equations required to convert the pressure ratios for adding and removing the perturbation flow to the viscosity ratio for the mixture viscosity relative to the viscosity of the carrier gas.

$$\frac{\mu_{\mathrm{mix}}}{\mu_1} = 1 + \frac{mR_{\mathrm{add}}}{(M + mC_{\mathrm{add}})} \tag{3}$$

$$\frac{\mu_{\mathrm{mix}}}{\mu_1} = 1 + \frac{R_{\mathrm{rem}}}{\left(\frac{M}{m} - R_{\mathrm{rem}}\right)} \tag{4}$$

where M is the flow of the carrier gas; m is the flow of the perturbation gas; and C_{add} is a very small correction factor to account for the small turndown in flow as the very large perturbations pass through the apparatus.[12] (Note eq 4 is slightly different from that given in ref 12 due to a typing mistake that has been found and corrected from the original paper.) The two viscosity ratios should be the same if the data are consistent.

To produce a complete set of data, measurements will be made from both ends of the composition range. Viscosity measurements from the component 1 end were relative to the viscosity of component 1. Similarly, viscosity measurements made from the component 2 end were relative to the viscosity of component 2. To rationalize the data so that all viscosities were relative to a single pure component, the pure component ratios from a literature source were required to convert the data measured relative to component 2 to be relative to component 1 (see eq 5).

$$\frac{\mu_{\mathrm{mix}}}{\mu_2} \cdot \frac{\mu_2}{\mu_1} = \frac{\mu_{\mathrm{mix}}}{\mu_1} \tag{5}$$

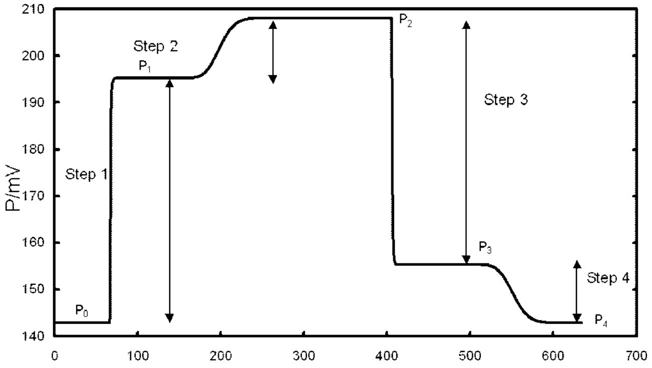

Figure 2. Transducer pressure difference ($P \cdot mV^{-1}$) reading versus time ($T \cdot s^{-1}$) for a typical viscosity experiment.

Table 1. New Mixture Viscosities (μ_{mix}) Relative to the Viscosity of Helium (μ_1) for the System Helium (1) + Argon (2) at 298 K and 0.11 MPa (abs) Measured Using Both Added (add) and Removed (rem) Perturbation Flows[a]

X_2	$\mu_{\mathrm{mix}} / \mu_{1,\mathrm{add}}$	$\mu_{\mathrm{mix}} / \mu_{1,\mathrm{rem}}$	diff	confidence limit (add)	confidence limit (rem)
		Argon Perturbation			
0.488	1.1715	1.1808	0.0093	0.001	0.0004
0.402	1.1791	1.1788	0.0003	0.001	0.0003
0.135	1.1224	1.1191	0.0033	0.001	0.001
0.287	1.1721	1.1739	0.0018	0.002	0.002
0.159	1.1363	1.1349	0.0014	0.002	0.001
0.063	1.0709	1.0700	0.0009	0.003	0.004
		Helium Perturbation			
0.932	1.1435	1.1438	0.0003	0.02	0.01
0.885	1.1485	1.1490	0.0005	0.02	0.02
0.814	1.1557	1.1554	0.0003	0.009	0.008
0.751	1.1622	1.1613	0.0009	0.006	0.003
0.695	1.1668	1.1674	0.0007	0.004	0.004
0.622	1.1724	1.1736	0.0012	0.003	0.005
0.539	1.1774	1.1784	0.0010	0.005	0.003
0.499	1.1794	1.1798	0.0004	0.003	0.003

[a] The difference (diff) between the ratios for adding and removing the flows is given as well as the confidence limits calculated by the propagation of error for each measurement.

Argon−Helium Measurements at 298 °C and 0.11 MPa (abs). To check that the apparatus was operating correctly, measurements were carried out first on the argon−helium system. This mixture has been studied in detail, and good quality data sets have been reported[13,14] at the temperature of interest. Measurements were made with gases supplied by BOC at “four nines” purity.

The results are given in Table 1 together with an estimate of the uncertainty calculated by propagation of error theory for each measurement and the difference of the add and remove perturbation results.

The data are plotted in Figure 3 together with the data measured by Kalelkar and Kestin[13] and Maitland and Smith[14] and two predicted data sets. The predicted data sets were obtained from two sources. The first was calculated from Chapman−Enskog theory using the parameters reported by Maitland et al.[15] obtained from the corresponding states theory. The second prediction was made using the Reichenberg method and the pure component viscosities reported by Kalelkar and Kestin.[13]

One data point is obviously spurious (add argon perturbation at helium mole fraction of 0.488). This is because the viscosity pressure step exceeded the linear range of the transducer. This affects both add and remove perturbations but in different ways. The error arises in the viscosity step for the addition of the flow but in the flow step when removing the flow. The flow step is 5 times bigger than the viscosity step; therefore, the error is much less significant in the flow step.

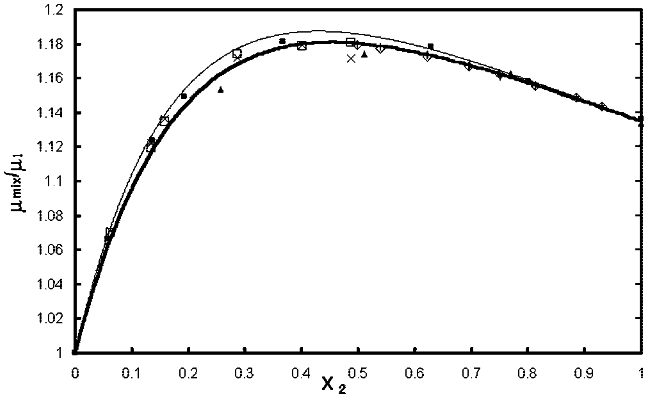

Figure 3. Plot of the mixture viscosity (μ_{mix}) relative to the viscosity of Helium (μ_1) versus argon mole fraction (X_2) for the system helium (1) + argon (2) at 298 K and 0.11 MPa (abs) where: ×, new data added argon perturbation; □, new data removed argon perturbation; ◇, new data added He perturbation; +, new data removed He perturbation; ■, experimental data of Kalelkar and Kestin et al. (1970); ▲, experimental data of Maitland and Smith (1973); —, Chapman−Enskog prediction; —, Reichenberg prediction.

We recommend that the add value for the point is not used in further calculations.

The average uncertainty in the results is 0.4 %, with a maximum uncertainty of 1.7 %. The uncertainty calculated by the error propagation theory is dependent on the size of the change in viscosity achieved for a given perturbation flow and explains the wide range of uncertainty. However, the small divergence between the paired results (average value 0.15 %) indicates that the uncertainty is probably less than that suggested by that calculated by error propagation. We would suggest that the divergence between the two independent measurements is the better estimate of the uncertainty in this data set and that 0.15 % should be taken as the uncertainty for this data set.

The claimed uncertainty of the new data is supported by the excellent agreement of the new data with that of Kalelkar and Kestin.[13] An accuracy of 0.1 % is claimed by Kalelkar and Kestin[13] for their measured pure component viscosities which translates to an error of 0.15 % in their viscosity ratios. All new points lie within the band of error for the Kalelkar and Kestin[13] data, bar the one spurious data point already identified above.

The two prediction methods both lie within 0.5 % of the new experimental data and can be said to represent the data well. Maitland et al.[14] claim an uncertainty in their results of 1 % which is the typical deviation of their data from the other two experimental sets. Indeed, two of the five points measured at 0.2568 and 0.5113 argon mole fraction, by Maitland et al.,[14] seem to systematically underestimate the viscosity ratio when compared with the other data sets and predictions. Therefore, we conclude that the new data and those of Kalelkar and Kestin[13] should be used in preference to those of Maitland et al.[14] Further, we have confirmed that the apparatus works correctly as a viscometer.

Table 2. New Mixture Viscosities (μ_{mix}) Relative to the Viscosity of Carbon Monoxide (μ_1) for the System Carbon Monoxide (1) + Helium (2) at 298 K and 0.11 MPa (abs) Measured Using Both Added (add) and Removed (rem) Perturbation Flows[a]

X_2	$\mu_{mix}/\mu_{2,add}$	$\mu_{mix}/\mu_{2,rem}$	diff	confidence limit (add)	confidence limit (rem)
		Carbon Monoxide Perturbation			
0.047	1.1232	1.1235	0.0003	0.01	0.03
0.074	1.1242	1.1246	0.0004	0.01	0.01
0.209	1.1156	1.1156	0.0001	0.06	0.08
0.310	1.1027	1.1032	0.0005	0.005	0.01
0.450	1.0802	1.0820	0.0018	0.003	0.003
0.120	1.1229	1.1229	0.0000	0.02	0.009
0.505	1.0704	1.0740	0.0036	0.003	0.002
0.019	1.1204	1.1204	0.0001	0.04	0.03
0.032	1.1217	1.1218	0.0001	0.03	0.03
0.137	1.1229	1.1228	0.0001	0.02	0.009
0.315	1.1016	1.1025	0.0009	0.005	0.01
0.359	1.0942	1.0966	0.0024	0.005	0.01
0.165	1.1204	1.1201	0.0003	0.02	0.009
		Helium Perturbation			
0.612	1.0553	1.0545	0.0008	0.003	0.004
0.501	1.0717	1.0722	0.0005	0.003	0.003
0.792	1.0279	1.0274	0.0005	0.005	0.004
0.896	1.0138	1.0133	0.0004	0.01	0.01
0.947	1.0053	1.0068	0.0014	0.04	0.04
0.752	1.0338	1.0342	0.0003	0.004	0.004
0.659	1.0480	1.0489	0.0009	0.004	0.002

[a] The difference (diff) between the ratios for adding and removing the flows is given as well as the confidence limits calculated by propagation of error for each measurement.

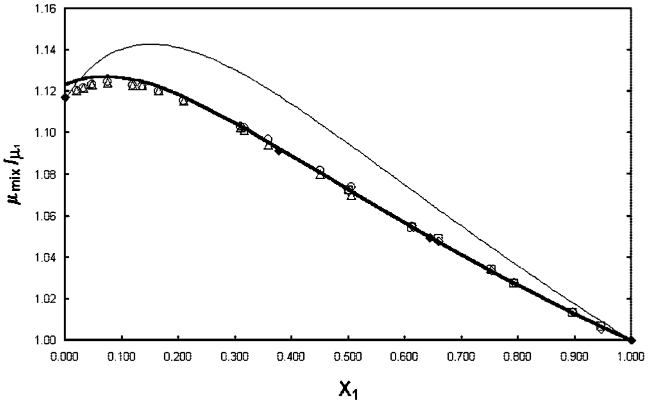

Figure 4. Plot of the mixture viscosity (μ_{mix}) relative to the viscosity of carbon monoxide (μ_1) versus carbon monoxide mole fraction (X_1) for the system carbon monoxide (1) + helium (2) at 298 K and 0.11 MPa (abs) where: ○, new data added CO perturbation; Δ, new data removed CO perturbation; ◇, new data added He perturbation; □, new data removed He perturbation; ♦, experimental data of Kestin et al. (1982); —, Chapman−Enskog prediction using parameters determined by Kestin et al. (1982); —, Reichenberg prediction.

Helium−Carbon Monoxide Mixtures at 25 °C and 1.1 bar Pressure. Measurements were again made with gases supplied by BOC at four nines purity. The results are given in Table 2 together with an estimate of the uncertainty calculated by the propagation of error theory for each measurement. The data are plotted in Figure 4 together with the data measured by Kestin et al.[3] and two predicted data sets. The predicted data sets were obtained from two sources. The first was calculated from Chapman−Enskog theory using the parameters reported by Maitland et al.[15] obtained from the corresponding states theory. The second prediction was made using the Reichenberg method and the pure component viscosities reported by Kestin et al.[3]

The average uncertainty in the results is 1.5 % with a maximum uncertainty of 4 %. However, the average divergence between the paired results is 0.1 %. This highlights the problem of using propagation of errors to calculate the uncertainty for this type of measurement. The uncertainty calculated by the error propagation theory is dependent on the size of the change in viscosity achieved for a given perturbation flow and explains the wide range of uncertainty. Many of the results have a low uncertainty of 0.3 %, but the average is distorted by the presence of a few values with a calculated error of 4 %. We would suggest that the divergence between the two independent measurements is the better estimate of the uncertainty in this data set. This is supported by the excellent agreement (within 0.2 %) with the data of Kestin et al.[3] who used the same apparatus as Kalelkar and Kestin[13] and claim an accuracy of 0.15 % for viscosity ratios.

The Chapman−Enskog theory and the parameters reported by Maitland et al.[15] are used to calculate the predicted viscosity−composition curve. It agrees to within 0.5 % with the two experimental data sets and is the best model for this system. The curve deviates from the experimental data at the helium end of the composition range. The prediction relies on the parameters presented by Maitland et al.[15] to calculate the absolute viscosities. The prediction is very good for the carbon monoxide result and agrees to within 0.1 % with the experimental value. However, the agreement of the predicted viscosity and experimental value at this temperature is less satisfactory at the helium end of the composition range. Because the same helium parameters are used to predict the intermediate viscosities, this may explain the systematic deviation as the prediction nears the helium end of the composition range. Maitland et al.[15] only claim an accuracy of 1 % for the predicted absolute viscosities that propagates to an error of 1.5 % in the ratio. This indicates that the deviation of the model from the experimental model is within the stated accuracy of said model.

The second predicted viscosity−composition curve produced by Reichenberg's method diverges from the experimental data by up to 6 %. This is not unexpected, as Poling[11] reported test cases for this model where deviations from experimental error varied from 2 % for nitrogen−carbon monoxide to 5 % for ammonia mixtures. We conclude that this model is not suitable for this mixture.

Conclusions

A detailed experimental data set has been produced at 298 K and 0.11 MPa (abs) for helium−carbon monoxide mixtures. The new data have been shown to be as good as the best extant literature data. A maximum has been identified in the viscosity−composition curve at 0.09 carbon monoxide mole fraction. Good agreement has been found between the Chapman−Enskog model using parameters determined by corresponding states theory, and we would suggest that this is the preferred method to predict viscosities for this mixture. Finally, it has been shown that the method of Reichenberg is unsuitable for predicting viscosities for helium−carbon monoxide mixtures.

Literature Cited

(1) Hirschfelder, J. O.; Taylor, M. H.; Kihara, T.; Rutherford, R. Viscosity of Two-Component Gaseous Mixtures. *Phys. Fluids* **1961**, *4*, 663–668.

(2) Shashkov, A. G.; Abramneko, T. N.; Boborneva, D. K. Concentration Dependence of the Viscosity for Binary Gas Mixtures. *J. Eng. Phys. Thermophys.* **1972**, *23*, 1535–1540.

(3) Kestin, J.; Ro, S. T.; Wakeham, W. A. The viscosity of carbon-monoxide and its mixtures with other gases in the temperature range 25C-200C. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 753–760.

(4) Gianturco, F. A.; Paesani, F.; Laranjeira, M. F.; Vassilenko, V.; Cunha, M. A.; Shashkov, A. G.; Zolotoukhina, A. F. Computed and measured transport coefficients for CO-He mixtures: testing a density functional approach. *Mol. Phys.* **1998**, *94*, 605–622.

(5) Haghighi, B.; Fathabadi, M.; Papari, M. M. Calculation of the transport properties of CO-noble gases mixtures at low density by the semi-empirical inversion method. *Fluid Phase Equilib.* **2002**, *203*, 205–225.

(6) Heck, E. L.; Dickinson, A. S. Transport properties of He-CO mixtures. *Mol. Phys.* **1997**, *91*, 31–45.

(7) Russell, P. A.; Heslop, M. J.; Mason, G.; Buffham, B. A. A novel thermostatted apparatus for the measurement of viscosity gradients for gas mixtures. *AIChE J.* **2003**, *49*, 1986–1994.

(8) Buffham, B. A.; Hellgardt, K.; Heslop, M. J.; Mason, G. Remote sensing of the flux responses of a gas-solid catalytic micro-reactor. *Chem. Eng. Sci.* **2000**, *55*, 1621–1632.

(9) Reichenberg, D. *The Estimation of the Viscosities of Gases and Gas Mixtures. Symposium on Transport Properties of Fluids and Fluid Mixtures, Their measurement, Estimation, Correlation and Use*; East Kilbride: Glasgow, Scotland, 1979.

(10) Monnery, W. D.; Svrcek, W. Y.; Mehrotra, A. K. Viscosity: A Critical Review of Practical Predictive and Correlative Methods. *Can. J. Chem. Eng.* **1995**, *73*, 3–40.

(11) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; Mcgraw Hill: New York, 2001.

(12) Russell, P. A.; Buffham, B. A.; Mason, G.; Heslop, M. J. The effect of very large perturbation flows on a perturbation viscometer. *Chem. Eng. Sci.* **2005**, *60*, 2943–2954.

(13) Kalelkar, A. S.; Kestin, J. Viscosity of He-Ar and He-Kr Binary gaseous mixtures in the Temperature Range 25–720 °C. *J. Chem. Phys* **1970**, *52* (8), 4248–4261.

(14) Maitland, G. C.; Smith, E. B. Viscosity of Binary Gas Mixtures at High Temperatures. *J. Chem. Soc. Faraday Trans.* **1973**, *70*, 1191–1211.

(15) Maitland, G. C.; Rigby, M.; Smith, E. B.; Wakeham, W. A. *Intermolecular forces;* Clarendon Press: Oxford, 1981.

Received for review August 23, 2007. Accepted October 19, 2007.

JE7004775