J. Chem. Eng. Data **1980**, *25*, 57–59

Dynamic Viscosity of Ternary Mixtures of CCl_2F_2 (R-12), $CHClF_2$ (R-22), and $C_2Cl_2F_4$ (R-114) Vapors

Bhagwant Singh and M. A. Tirunarayanan*

Department of Mechanical Engineering, Indian Institute of Science, Bangalore 560012, India

The viscosities of ternary mixtures of R-12, R-22, and R-114 vapors were determined at ambient temperature and pressure within ±1% by using an oscillating disk viscometer. The empirical viscosity obtained by Wilke's equation compares very well with the experimental results obtained with this viscometer. In the case of this ternary vapor mixture, as long as the molar fraction ratio of R-12 to R-114 is maintained at approximately $2^{1/2}$ (=inverse ratio of their molecular weights) the viscosity of the ternary mixture at ambient temperature and pressure remains constant irrespective of the percentage of R-22 present in the mixture.

Viscosity plays an important role in explaining physical and physicochemical phenomena and also in solving many chemical engineering problems involving mass, momentum, and heat transfer and the design of related equipment. In recent years, the practice has been to use the mixture of components to improve the performance of the systems. Therefore, information on the viscosity of multicomponent mixtures is important for numerous tasks in industrial practice and the development of industrial processes. An exhaustive survey of the published literature shows that no attempts have been made to measure the viscosity of the ternary mixtures of R-12, R-22, and R-114 vapors. However, Srichand, Tirunarayanan, and Ramachandran (*6*) have made an attempt to measure the viscosity of the binary mixtures of R-12 and R-22 at ambient temperatures and pressures. Singh (*5*) has also measured the viscosity of binary mixtures resulting from R-12, R-22, and R-114 at the ambient temperatures and pressures by using the same oscillating disk viscometer as used by Gururaja, Tirunarayanan, and Ramachandran (*1*). After suitable modifications, the viscometer was used to measure the viscosity of the ternary mixtures at ambient temperature and pressure. The following equations derived according to Newell's theory (*4*) were used for evaluating the viscosity of vapor mixtures.

$$C_N = \left[\frac{2I}{\pi \rho b R^4}\left(\frac{\Delta}{\theta} - \Delta_0\right) + a\frac{\Delta}{\theta} \right]\beta^2 + \left[f\frac{3\Delta^2 - 1}{\theta^2} \right]\beta^4 + \left[\frac{h\Delta(\Delta^2 - 1)}{\theta} \right]\beta^6 \quad (1)$$

$$\mu = 2\pi\rho b^2/\beta^2 T_{p_0} \quad (2)$$

Experimental Section

The oscillating disk viscometer employed in the present investigation was the same as described by Srichand et al. (*6*). Here it is sufficient to say that great care was taken in ensuring good parallelism of the fixed plates and the oscillating disk and in attaining equality of the upper and lower separations. The characteristics of the suspension system are given in Table I.

The gas mixture for investigation was prepared by using a simple float balance, designed by Srichand, Tirunarayanan, and Ramachandran (*7*), giving accuracy in the determination of the mass of the components to within ±0.1 g. The prepared mixture was allowed to remain in the cylinder for about 2 weeks to ensure thorough mixing by diffusion. After 2 weeks, experiments were performed for the determination of the viscosity.

Table I. The Suspension System

Dimensions	
radius of the disk, R	3.5450 cm
thickness of the disk, d	0.1234 cm
total gap, D	0.2998 cm
upper separation, b_1	0.0882 cm
lower separation, b_2	0.0882 cm
diameter of the suspension wire	0.0023 in.
(material: 87 pt-13 Rh alloy, stress relieved)	
Characteristics	
harmonic mean sepn	0.0882 cm
moment of inertia of the suspension system	74.1894 g-cm^2
period of oscillation under vacuum, T_0	22.80 s
damping decrement under vacuum, Δ_0	0.0001
Lamp and Scale Arrangement	
dist of scale from the mirror	200.6 cm

The temperature of the vapor mixture was measured with two calibrated copper–constantan thermocouples; the emf developed was measured with a precision L and N potentiometer of accuracy 0.01 mV. The pressure of the vapor mixture in the oscillating disk viscometer was kept slightly above atmospheric and was measured by a manometer. The absolute pressure of the vapor mixture was measured within 0.12%. The density of the gas mixture was estimated from the known values of pressure, temperature, and percentage combination. The rest of the procedure for the measurement of the viscosity is the same as described by Srichand et al. (*6*).

Calibration of the Viscometer

The instrument was calibrated experimentally; 99.9% pure nitrogen was used for calibration, as an accurate value of viscosity at 25 °C can be computed from the empirical correlation (*3*).

$$\mu_{25} = (177.86 + 107.19\rho + 749.6\rho^2 - 434.0\rho^3)\ \mu\text{P} \quad (3)$$

The temperature correction from ref 3 is 0.455 μP/°C, and the standard deviation of this fit is 0.14 μP. Also the following values are used: viscosity corrected to 27.2 °C, 178.99 μP; temperature inside the viscometer, 27.2 °C; pressure in the viscometer, 15.6 psia; period of oscillation in gas, T_p, 22.82 s; damping decrement in gas, Δ = 0.027 12, a = 0.6666, f = 0.0222, h = 0.008 46. Putting the relevant quantities in eq 1 and neglecting Δ^3, we obtained the calibrated instrument constant as C_N = 1.096 39. The theoretical value of the instrument constant, C_N', of the oscillating disk viscometer was evaluated by using the equation given by Iwasaki and Kestin (*2*) and was found to be 1.096 12. The theoretical value, C_N', is smaller than the experimental value, C_N, as is to be expected since the theory of the instrument leaves out the effects of the drag of the mirror and the stem.

Test Results and Discussion

Viscosity values of ternary vapor mixtures of R-12, R-22, and R-114 are presented in Table II at the temperature and pressure

0021-9568/80/1725-0057$01.00/0

Table II. Viscosity of Mixtures of R-12, R-22, and R-114 Vapors

	molar fraction						viscosity × 10^6, P		
no.	R-12 x_1, %	R-22 x_2, %	R-114 x_3, %	temp, °C	density ρ_m, g/cm^3	damping decrement, Δ	present investigation (exptl)	Wilke's (*8*) eq (empirical)	% dev of exptl data
1	4.88	60.29	33.83	27.2	0.005 065	0.018 72	123.41	123.50	−0.07
2	8.13	68.73	23.14	27.1	0.004 870	0.018 86	124.35	124.46	−0.09
3	16.42	62.98	20.60	27.2	0.004 719	0.019 01	125.30	125.39	−0.07
4	22.07	61.64	16.29	27.2	0.004 646	0.019 09	125.85	125.89	−0.03
5	36.31	52.62	11.07	27.1	0.004 588	0.019 18	126.47	126.49	−0.02
6	42.33	49.74	7.93	27.3	0.004 642	0.019 19	126.50	126.48	+0.02
7	55.37	41.76	2.87	27.2	0.004 652	0.019 24	126.83	126.81	+0.02
8	51.69	21.44	26.87	27.3	0.005 471	0.018 64	122.88	122.90	−0.02
9	52.72	10.72	36.56	27.2	0.005 838	0.018 41	121.34	121.31	+0.02
10	56.44	07.64	35.92	27.2	0.005 870	0.018 39	121.23	121.26	−0.02

actually maintained in the present investigation: (1) the empirically determined viscosity of mixtures by use of Wilke's equation (*8*) and (2) the viscosity of mixtures experimentally determined in the present investigation. It may be noted that empirical viscosity of mixtures compares very well with the experimental viscosity obtained in the present investigation. The agreement is within ±0.1% with the present experiment results. No experimental data are available in the literature for this combination. An interesting observation was made during this experimentation. Wilke's (*8*) equation for a ternary mixture is

$$\mu_m = \frac{\mu_1}{1 + (x_2/x_1)\phi_{12} + (x_3/x_1)\phi_{13}} + \frac{\mu_2}{1 + (x_3/x_2)\phi_{23} + (x_1/x_2)\phi_{21}} + \frac{\mu_3}{1 + (x_1/x_3)\phi_{31} + (x_2/x_3)\phi_{32}} \tag{4}$$

where subscript 1 refers to R-12, 2 refers to R-22, and 3 refers to R-114. Let

$$F_1 = 1 + (x_2/x_1)\phi_{12} + (x_3/x_1)\phi_{13} \tag{5}$$

$$F_2 = 1 + (x_1/x_3)\phi_{31} + (x_2/x_3)\phi_{32} \tag{6}$$

The value of ϕ_{ij} is calculated from

$$\phi_{ij} = \frac{[1 + (\mu_i/\mu_j)^{1/2}(M_j/M_i)^{1/4}]^2}{2(2^{1/2})(1 + M_i/M_j)^{1/2}} \tag{7}$$

Now, if the percentage of R-22, x_2, is fixed at a certain value, e.g., 90%, then because $x_1 + x_2 + x_3 = 100$, $x_1 + x_3 = 10$. Hence x_1 and x_3 can take various values such that $x_1 + x_3 = 10$: $x_1 = 1$, $x_3 = 9$, $x_1/x_3 = 1/9$; $x_1 = 2$, $x_3 = 8$, $x_1/x_3 = 1/4$; $x_1 = 3$, $x_3 = 7$, $x_1/x_3 = 3/7$; $x_1 = 9$, $x_3 = 1$, $x_1/x_3 = 9$. In all cases, $x_1 + x_2 + x_3 = 100$ with x_2 fixed at 90%. If F_1 is calculated for all the various values of x_1/x_3 as a parameter with a fixed value of x_2, a set of values for F_1 is obtained. If these values of F_1 are plotted against x_1/x_3 on semilog paper as shown in Figure 1, curve A_1 is obtained. If this procedure is repeated for F_2 for the same value of x_2, a set of values for F_2 is obtained. If these values of F_2 are plotted on the same graph against x_1/x_3, curve A_2 is obtained. These two curves, A_1 and A_2, intersect at some point.

If, now, x_2 is held fixed at 80%, then $x_1 + x_3 = 20$ and if F_1 and F_2 are calculated as indicated above and plotted on the graph, curves B_1 and B_2 are obtained. The intersection of B_1 and B_2 is at the same value of x_1/x_3 as that of A_1 and A_2. This is true for all percentages of R-22, say, 70%, 60%, 50%, etc. as long as the above procedure is followed. Figure 1 shows that all such curves intersect at the value of $x_1/x_3 = 1.414 = 2^{1/2}$. This ratio is the inverse ratio (170.936/120.925 = 1.414) of the molecular weights of individual gases R-12 and R-114.

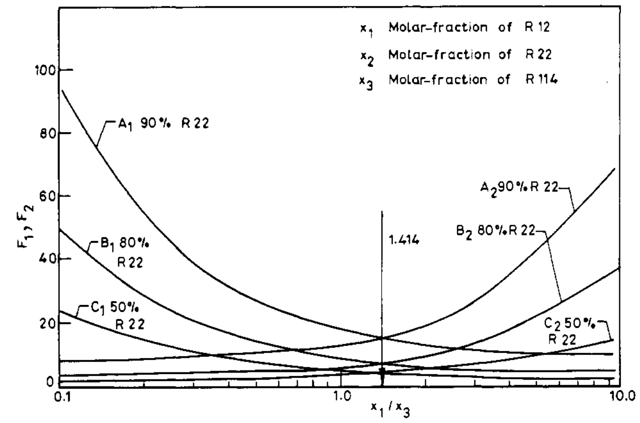

Figure 1. Variation of F_1 and F_2 with x_1/x_3 for constant values of x_2 for the mixture of R-12, R-22, and R-114 vapors.

The viscosity of the mixture is now calculated with x_1/x_3 (R-12 to R-114) held fixed at 1.414 and varying x_2 such that $x_1 + x_2 + x_3 = 100$. The viscosity of all mixtures which had x_1/x_3 in the ratio 1.414 was the same irrespective of the percentage of R-22 present in the mixture.

Conclusions

The viscosity values obtained from Wilke's equation for the ternary vapor mixtures of R-12, R-22, and R-114 agree within 0.1% with the experimental data obtained in the present investigation.

When molar fraction ratio of R-12 to R-114 is about $2^{1/2}$ in a ternary mixture of R-12, R-22, and R-114, the viscosity of this mixture at ambient temperature and pressure remains constant irrespective of the percentage of R-22 in the mixture.

Glossary

a	constant in eq 1
A_1, A_2	curves in Figure 1, plots of F_1 and F_2 against x_1/x_3 for the same percentage of R-22 (x_2 = 90%)
b_1	upper separation, cm
b_2	lower separation, cm
b	harmonic mean separation, $2b_1b_2/b_1 + b_2$, cm
B_1, B_2	curves in Figure 1, plots of F_1 and F_2 against x_1/x_3 for the same percentage of R-22 (80%)
C_1, C_2	curves in Figure 1, plots of F_1 and F_2 against x_1/x_3 for the same percentage of R-22 (50%)
C_N	experimental calibration constant
C_N'	theoretical calibration constant
f	constant in eq 1
F_1, F_2	functions given by eq 5 and 6, respectively

h	constant in eq 1
I	moment of inertia of the suspension system, g-cm^2
L	distance of the scale from the mirror, cm
M_i, M_j	molecular weights
R	radius of the disk, cm
T_{p_0}	period of oscillation of the disk under vacuum, s
x_1, x_2, x_3	molar fractions of vapors in the mixture
β	dimensionless harmonic mean separation, b/δ
δ	boundary layer thickness, cm
Δ_0	damping decrement under vacuum
Δ	damping decrement in the gas
μ, μ_1, μ_2, μ_3	dynamic viscosity, μP
ρ	density of the fluid, g/cm^3
θ	ratio of periods of oscillation in the gas and in vacuum, T_1/T_{p_0}
ϕ_{12}, ϕ_{13}, ϕ_{21}, ϕ_{23}, ϕ_{31}, ϕ_{32}	constants in eq 4

Literature Cited

(1) Gururaja, G. J., Tirunarayanan, M. A., Ramachandran, A., *J. Chem. Eng. Data*, **12**, 562 (1967).
(2) Iwasaki, H., Kestin, J., *Physics*, **29**, 1345 (1963).
(3) Kestin, J., Leidenfrost, W., *Physica* (*Utrecht*), **25**, 1033 (1959).
(4) Newell, G. F., *Z. Angew. Math. Phys.*, **10**, 160 (1959).
(5) Singh, B., M.Sc. Thesis, Indian Institute of Science, June 1974.
(6) Srichand, M., Tirunarayanan, M. A., Ramachandran, A., *ASHRAE J.*, **12**, 61 (1970).
(7) Srichand, M., Tirunarayanan, M. A., Ramachandran, A., *J. Sci. Instrum.*, **2**, 539 (1969).
(8) Wilke, C. R., *J. Chem. Phys.*, **18**, 517 (1950).

Received for review November 10, 1978. Accepted August 9, 1979.

Infinite Dilution Henry's Constants of Light Hydrocarbons in *n*-Hexadecane, *n*-Octadecane, and 2,2,4,4,6,8,8-Heptamethylnonane by Inert Gas Stripping

D. Richon and H. Renon*

Centre Réacteurs et Processus, Equipe de Recherche Associée au CNRS No. 768, Ecole des Mines, 75006 Paris, France

The inert gas stripping method described in previous papers has been extended to accurate measurements of Henry's constants. The results show the very strong influence of branching of the molecule of solvent on solubility. Determinations of limiting Henry's constants were carried out for C_1 to C_4 hydrocarbons in *n*-hexadecane and 2,2,4,4,6,8,8-heptamethylnonane at 298.15 K and in *n*-octadecane at 323.15 K. Comparisons of results in *n*-hexadecane and *n*-octadecane are made with published results.

Solubilities of gases characterized by Henry's constants are useful data for oil recovery or transportation problems.

Oil is a complex mixture of many hydrocarbons. Among them are normal or branched molecules. Effect of branching is very important on most thermodynamical properties. It must be carefully investigated. The results of the present investigation show that the solubility of light hydrocarbons is several times greater in branched than in normal hexadecane.

A fast and accurate method is required to investigate numerous solvents. For this purpose, the gas stripping method is particularly convenient but a special equilibrium cell should be used.

Chemicals

Methane, ethane, *n*-propane, and *n*-butane were supplied by L'Air Liquide, the stated purities are respectively 99.95, 99.9, 99.5, and 99%. *n*-Hexadecane was obtained from Merck, *n*-octadecane from Fluka, and 2,2,4,4,6,8,8-heptamethylnonane from Sigma. These three components have a purity of not less than 99% and have been used without further purification.

Apparatus and Procedure

The apparatus and procedure were described in a previous paper (*4*, *6*). Only one part of the apparatus, the equilibrium cell, is changed. The new cell appears on Figure 1. The volume of vapor phase, V_G, above liquid mixture in the cell has been reduced as suggested by Richon et al. (*6*) and the collector has been modified to obtain a simple geometrical shape for the vapor space. The liquid level in the cell should be not lower than 1 cm from the top of the cell. As a consequence, it is necessary to place two baffles in the glass cell body to achieve efficient stirring of liquid phase. Equilibrium between liquid and vapor phase is reached only with these special conditions of cell design. Several parameters such as length and number of capillaries, position of baffles, and speed of magnetic stirring have been investigated.

Henry's constant is given by the equation

$$H_i^{\infty} = -\frac{1}{t} \ln \frac{S_i}{(S_i)_{t=0}} \frac{RTN}{D + \dfrac{V_G}{t} \ln \dfrac{S_i}{(S_i)_{t=0}}}$$

It is a simplification of Duhem and Vidal's (*2*) equation when the corrective term accounting for the variation of the total gas flow rate due to the vaporization of solute is neglected.

Results and Discussion

Measurements for methane to *n*-butane in *n*-hexadecane and *n*-octadecane have been performed in order to test the new apparatus, while new Henry's constants of the new solvent 2,2,4,4,6,8,8-heptamethylnonane give information on the branching effect of the solvent in solute–solvent interaction. The results are reported in Table I.

For both *n*-hexadecane and *n*-octadecane, Henry's constants of methane obtained by gas stripping are lower than those obtained by the chromatographic retention time method (*3*, *7*) while Henry's constants of ethane to *n*-butane are in good agreement. In order to explain the discrepancy between the two methods, especially for methane, we compared our results to those of Cukor (*1*) obtained by the static method. Henry's constants of Cukor interpolated at 298.15 K are approximately

0021-9568/80/1725-0059$01.00/0