

THE CALCULATION OF HIGH-PRESSURE VISCOSITY FOR REFRIGERANT MIXTURES

IZRAČUN VISKOZNOSTI PRI VISOKIH TLAKIH ZA ZMESI HLADIL

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Abstract

This paper features a mathematical model for computing the viscosity in the fluid domain for a hydrofluorocarbon mixture with the help of statistical thermodynamics. The viscosity of HFC-134a (1,1,1,2-Tetrafluoroethane) and HFC-125 (Pentafluoroethane) mixtures was calculated as an example of hydrofluorocarbon mixtures. To calculate the thermodynamic properties of a real fluid, the models were applied based on the Lennard-Jones intermolecular potential. The analytical results obtained via statistical thermodynamics are compared with the experimental data and show relatively good agreement.

Povzetek

V članku je prikazan matematični model izračuna viskoznosti v plinastem področju za mešanico fluoroo-gljikovodikov s pomočjo statistične termodinamike. V predstavljenem članku smo izračunali viskoznost za zmes hladil HFC-134a (1,1,1,2-tetrafluoroetane) in HFC-125 (Pentafluoroetane) kot primer fluoriranih ogljikovodikov. Za izračun termodinamičnih lastnosti realne tekočine so bili uporabljeni modeli na podlagi Lennard-Jonesovega intermolekularnega potenciala. Analitični rezultati, pridobljeni s statistično mehaniko, so primerljani z eksperimentalnimi podatki in kažejo razmeroma dobro ujemanje.

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1 INTRODUCTION

The computation of thermo-mechanical properties in the high-pressure range is vital for a large number of fluids that are essential to energy technology. Some great, even insurmountable problems remain in identifying analytical expressions for the transport characteristics of fluids at high pressures. Using super-computers and the methods of molecular dynamics, it is possible to follow each molecule in the system of particles. One drawback of numerical methods, however, is that analytical records of functions are unfortunately lost.

For more than half of century, chlorofluorocarbons (CFCs) have been used as working fluids in refrigeration, heat pump and air conditioning applications. These compounds are very stable, non-toxic and non-flammable and, therefore are regarded as safe refrigerants. For several decades chlorine-fluorine-hydrocarbons were considered harmless refrigerants. Most CFCs have been replaced by hydrofluorocarbons (HFCs) which have a similar molecular structure but do not contain chlorine atoms. For example, one of the most important CFCs, R12, has been already replaced by 1,1,1,2-tetrafluoroethane (R134a) in several applications. Refrigerants 134a and R125 are alternative refrigerants, which are suitable as substitutes for R22 and R502.

2 CALCULATION OF VISCOSITY BY STATISTICAL MECHANICS

Accurate knowledge of the nonequilibrium or transport properties of pure gases and liquids is essential for the optimum design of different items of chemical process plants, for the determination of intermolecular potential energy functions, and for the development of accurate theories of transport properties in dense fluids. Transport coefficients describe the process of relaxation to equilibrium from a state perturbed by the application of temperature, pressure, density, velocity, or composition gradients. The theoretical description of these phenomena constitutes that part of nonequilibrium statistical mechanics known as kinetic theory. From the semi-classical kinetic theory for polyatomic fluids the coefficients of thermal conductivity, shear viscosity and bulk viscosity can be expressed:

$$\lambda = \frac{2k^2T}{3m} [A, A], \quad \eta = \frac{1}{10} kT [B, B], \quad \kappa_s = kT [\Gamma, \Gamma] \quad (2.1)$$

where A , B and Γ are complex vector, tensor and the scalar functions, [1,2,3]. The detailed description of the physical origin of bulk viscosity is explained in the literature, [2]. It arises in dense polyatomic gases and liquids. The transport properties for pure gases are represented as sums of terms for the temperature-dependent dilute-gas contributions and terms for the temperature- and density-dependent residual contributions. Contributions for the critical enhancement are not included in these background functions. From the Boltzmann equation, for mono-atomic dilute gases, transport properties not far from the Maxwellian can be calculated, [1-3]. This means that transport phenomena are treated with small temperature or velocity gradients of the molecules. On this basis, the dynamic viscosity for single-component gas can be expressed:

$$\eta_0 = \frac{5kT}{8\Omega^{(2,2)}} \left(1 + \frac{3}{49} \left(\frac{\Omega^{(2,3)}}{\Omega^{(2,2)}} - \frac{7}{2} \right)^2 \right) \quad (2.2)$$

where, and $\Omega(l,s)$ is the transport collision integral. With the Lennard-Jones intermolecular potential, it is almost impossible to obtain collision integrals analytically. Because of the difficulty of calculating these integrals, their values are usually taken from published tables. To make computerized calculations more convenient and to improve on the accuracy obtainable by linear interpolation of the tables., the empirical formulation of Neufeld [5] et al. was used, obtained on the basis of numerical simulations and interpolation procedure.

$$\Omega^{(l,s)*} = \frac{A}{T^{*B}} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)} + RT^{*B} \sin(ST^{*W} - P) \quad (2.3)$$

This equation contains 12 adjustable parameters and is developed for 16 collision integrals. The dilute gas viscosity is obtained from kinetic theory assuming that a Lennard-Jones (LJ) potential applies, and using the expression:

$$\eta_0(T) = 26.69579 \cdot 10^{-1} \frac{\sqrt{MT}}{\Omega^{(2,2)*} \sigma^2}, \quad (2.4)$$

where η is in Pa s, M is the molecular mass in gmol⁻¹, T is in K, $\Omega(2,2)$ is a collision integral and σ is the Lennard-Jones parameter. In this paper, the Chung-Lee-Starling model (CLS) will be presented, [6]. Equations for the viscosity are developed based on kinetic gas theories and correlated with the experimental data. The low-pressure transport properties are extended to fluids at high densities by introducing empirically correlated, density dependent functions. These correlations use acentric factor ω , dimensionless dipole moment μ_r and an empirically determined association parameters to characterize the molecular structure effect of polyatomic molecules κ , the polar effect and the hydrogen bonding effect. In this paper, new constants for fluids are determined.

The dilute gas dynamic viscosity for the CLS model is written as:

$$\eta_0(T) = 26.69579 \cdot 10^{-1} \frac{\sqrt{MT}}{\Omega^{(2,2)*} \sigma^2} F_c \quad (2.5)$$

The factor F_c has been empirically found to be [6]:

$$F_c = 1 - 0.2756\omega + 0.059035\mu_r^4 + \kappa \quad (2.6)$$

where ω is the acentric factor, μ_r relative dipole moment and κ is a correction factor for hydrogen-bonding effect of associating substances such as alcohols, ethers, acids, and water.

For dense fluids, Eq. (5) is extended to account for the effects of temperature and pressure by developing an empirically correlated function of density and temperature as shown below:

$$\eta = \eta_k + \eta_p \quad (2.7)$$

$$\eta_k = \eta_0 \left(\frac{1}{G_2} + A_6 Y \right) \quad (2.8)$$

$$\eta_p = \left[36.344 \cdot 10^{-6} - (MT_c)^5 / V_c^{2/3} \right] A_7 Y^2 G_2 \exp(A_8 + A_9 / T^* + A_{10} / T^{*2}) \quad (2.8)$$

$$Y = \rho V_c / 6, G_1 = \frac{1.0 - 0.5Y}{(1.0 - Y)^3} \quad (2.9)$$

$$T_c = \frac{1.2593\epsilon}{k_B}, V_c = (0.809\sigma(A))^3 \quad (2.10)$$

$$G_2 = \frac{\{A_1(1 - \exp(-A_4 Y)) + A_2 G_1 \exp(A_5 Y) + A_3 G_1\}}{(A_1 A_4 + A_2 + A_3)} \quad (2.11)$$

The constants A1-A10 are linear functions of the acentric factor, the reduced dipole moment, and the association factor

$$A_i = a_0(i) + a_1(i)\omega + a_2(i)\mu_r^4 + a_3(i)\kappa, i=1,10 \quad (2.12)$$

where the coefficients a_0 , a_1 , a_2 , and a_3 are presented in the work of Chung et al., [6].

For the determination of viscosity for fluid mixtures, a purely analytical model has been used, [2]. According to this theory, the viscosity of dense fluid mixtures containing N components can be written in the form:

$$\eta = - \frac{\begin{vmatrix} H_{11} & \cdots & H_{1N} & \psi_1 \\ \vdots & & \vdots & \vdots \\ H_{N1} & & H_{NN} & \psi_N \\ \psi_1 & & \psi_N & 0 \end{vmatrix}}{\begin{vmatrix} H_{11} & \cdots & H_{1N} \\ \vdots & & \vdots \\ H_{N1} & \cdots & H_{NN} \end{vmatrix}} \quad (2.13)$$

$$H_{ii} = \frac{\psi_i^2}{\eta_i} + \sum_{\substack{j=1 \\ j \neq i}}^N \frac{\psi_i \psi_j}{2\eta_{ij} A_{ij}^*} \frac{M_i M_j}{(M_i + M_j)^2} \left(\frac{20}{3} + \frac{4M_j}{M_i} A_{ij}^* \right) \quad (2.14)$$

$$H_{ij} (j \neq i) = - \frac{\psi_i \psi_j}{2\eta_{ij} A_{ij}^*} \frac{M_i M_j}{(M_i + M_j)^2} \left(\frac{20}{3} - 4A_{ij}^* \right) \quad (2.15)$$

where ρ is the molar density, ψ_i and ψ_j are mole fractions of species i and j , and M_i and M_j are their molecular masses. A_{ij}^* is a weak function of intermolecular potential for i - j interactions. The symbol η_i represents the viscosity of pure component i , and η_{ij} represents the viscosity of i - j interaction. We have developed the new equation for η_{ij} :

$$\eta_{ij} = \sqrt{\eta_i \eta_j} \quad (2.16)$$

3 RESULTS AND DISCUSSION

Figures 1-11 show the deviation of the results for ternary mixture R125+R134a in the real gas region between the analytical computation (CLS-Chung-Lee-Starling model) and experimental results, [7-9]. Table 1 shows the most important data for analytical calculation. The results for all transport properties obtained with the CLS model show relatively good agreement.

Table 1: The important constants for analytical calculation for R125 and R-134a

| | R-134a | R-125 |
|-------------------|------------|-------------|
| ε (J) | 410.04E-23 | 337.678E-23 |
| σ (m) | 4.76E-10 | 5.005E-10 |
| ω (-) | 0.32684 | 0.3061 |
| μ_r (-) | 0.15 | 0.6 |
| κ (-) | 0 | 0 |

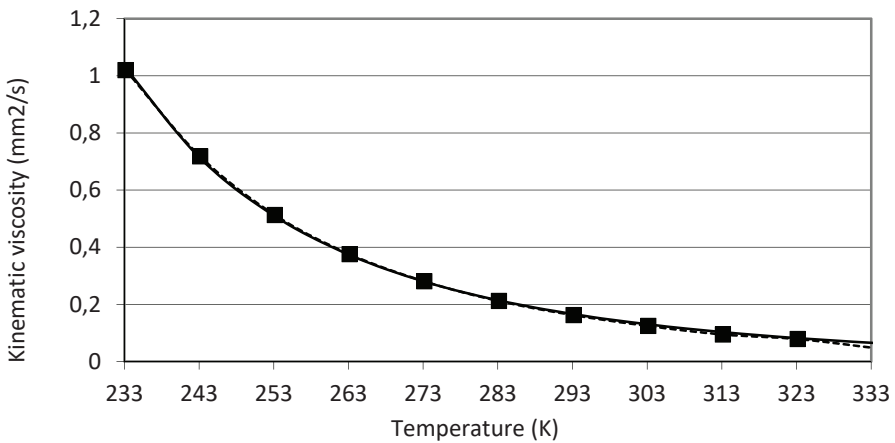


Figure 1: Kinematic viscosity for R125 in saturated gas region

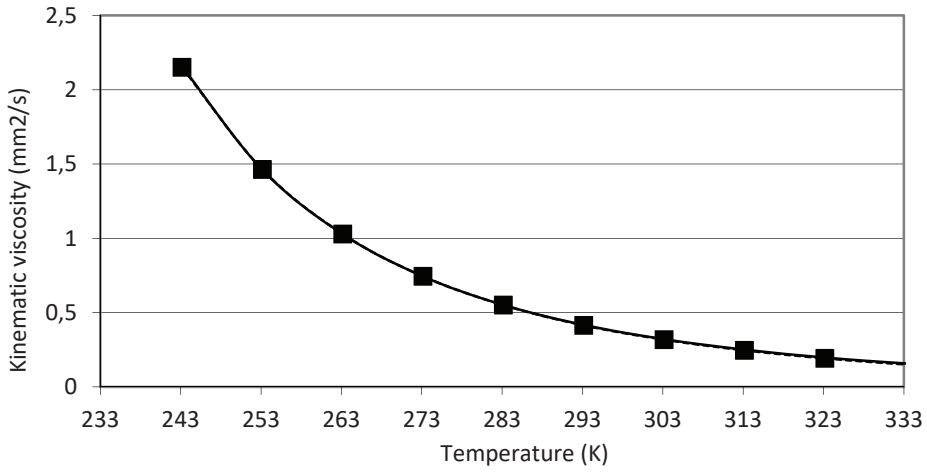


Figure 2: Kinenatic viscosity for R134a in saturated gas region

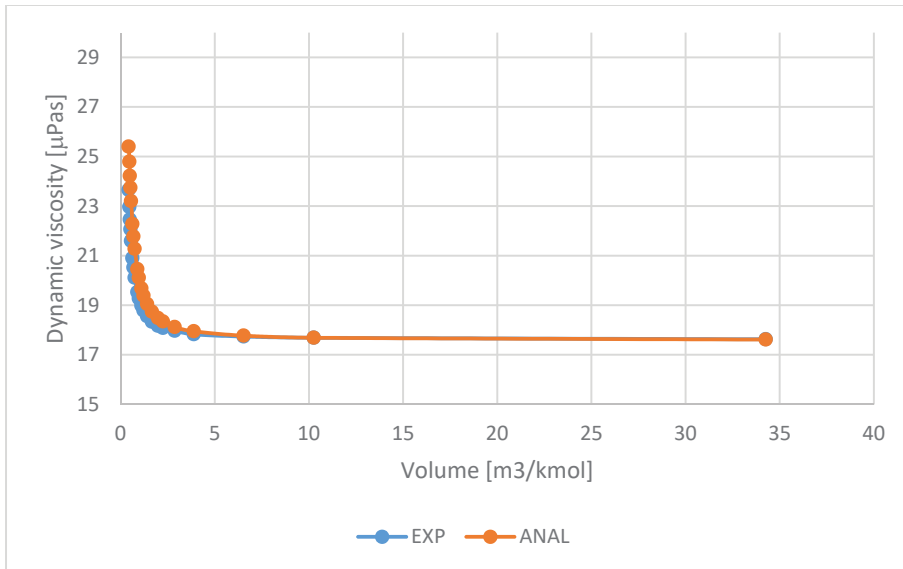


Figure 3: Viscosity for mixture of R125+R134a at 423 K and 75.1% of R125

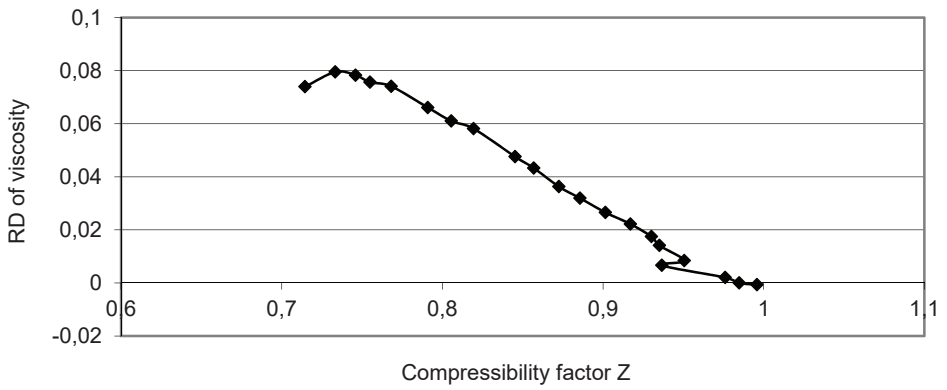


Figure 4: Compressibility factor for mixture of R125+R134a at 423 K and 75.1% of R125

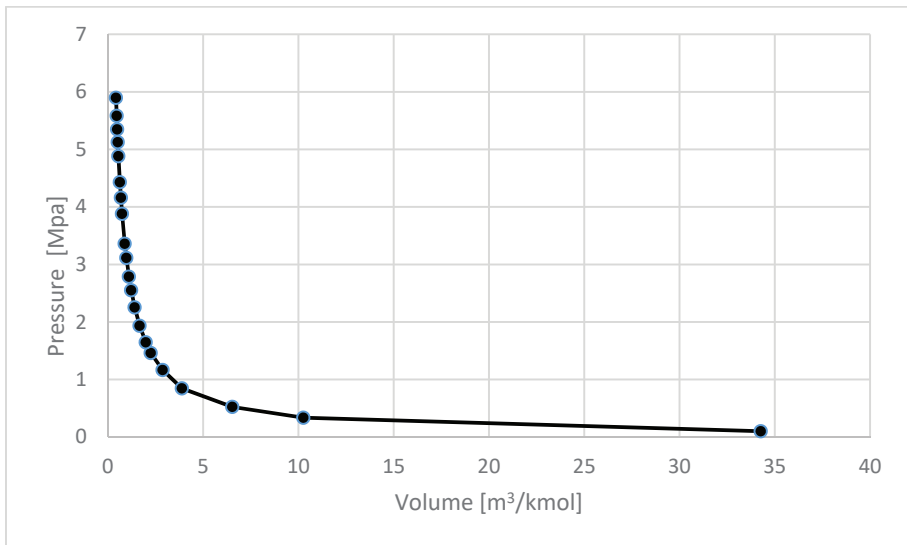


Figure 5: Pressure-volume diagram for mixture of R125+R134a at 423 K and 75.1% of R125

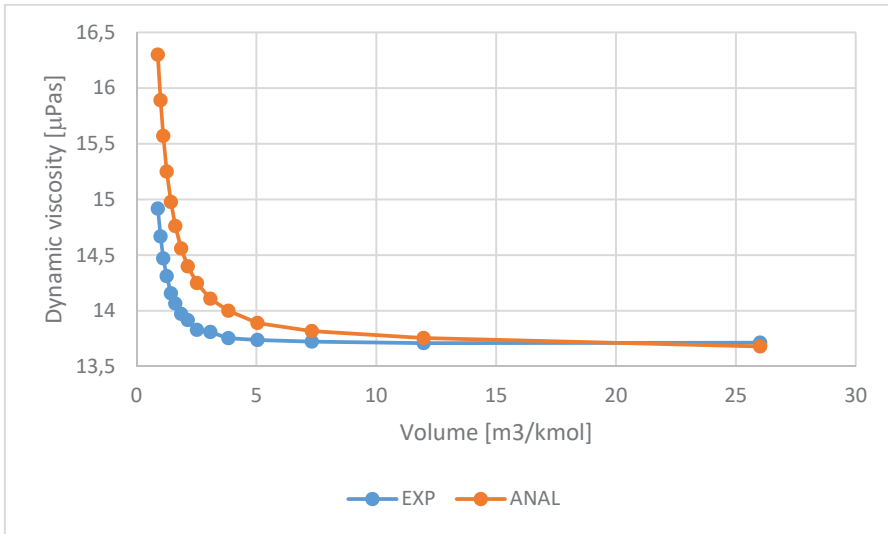


Figure 6: Viscosity for mixture of R125+R134a at 323 K and 75.1% of R125

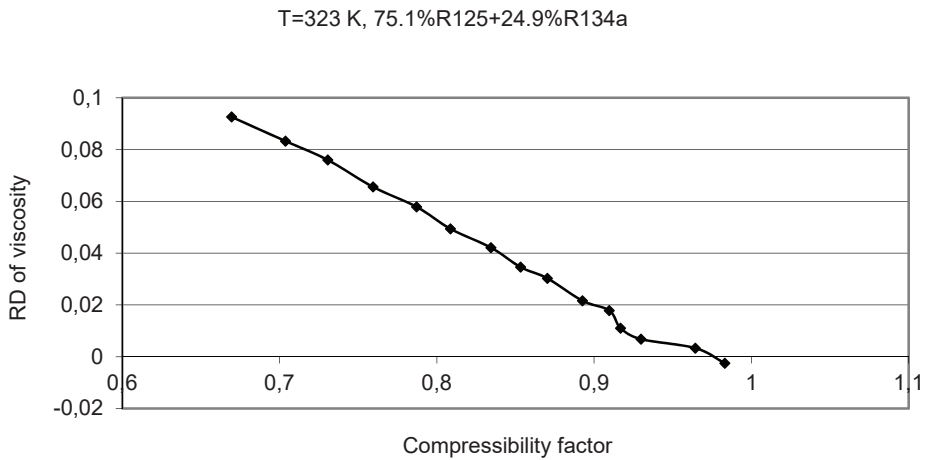


Figure 7: Compressibility factor for mixture of R125+R134a at 323 K and 75.1% of R125

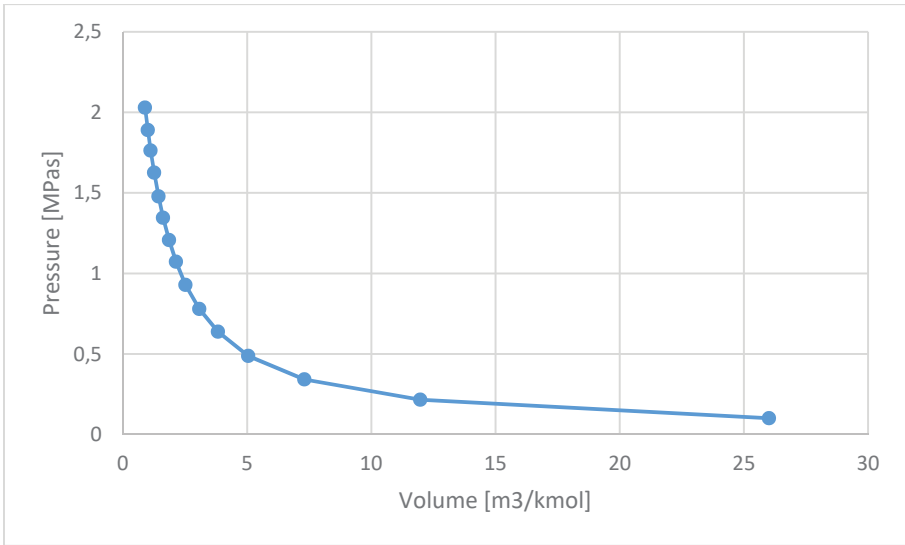


Figure 8: Pressure-volume diagram for mixture of R125+R134a at 423 K and 75.1% of R125

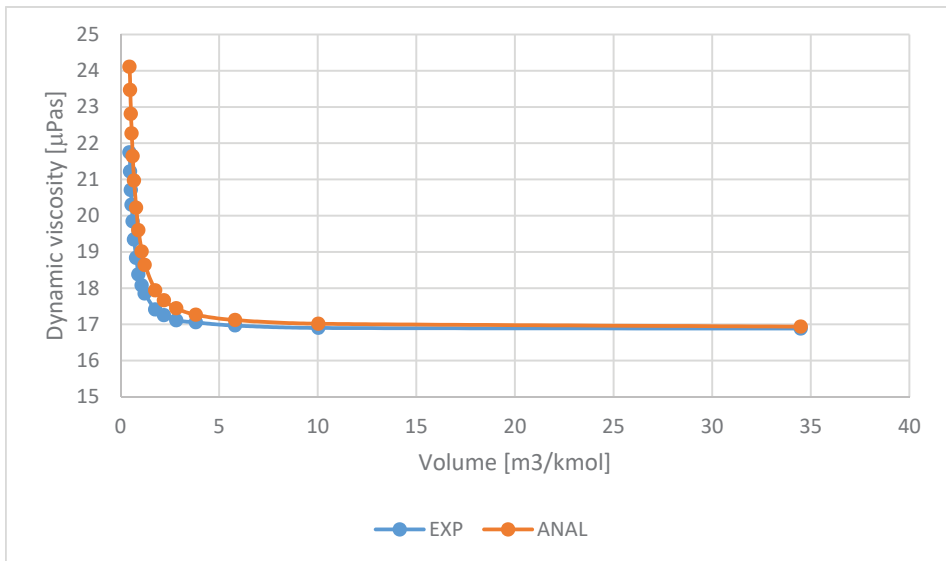


Figure 9: Viscosity for mixture of R125+R134a at 423 K and 75.1% of R125 and 25.1% of R125

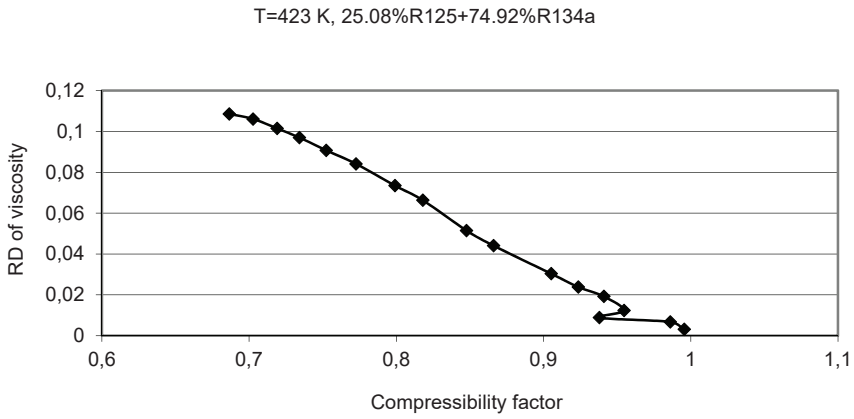


Figure 10: Compressibility factor for mixture of R125+R134a at 423 K and 25.1% of R125

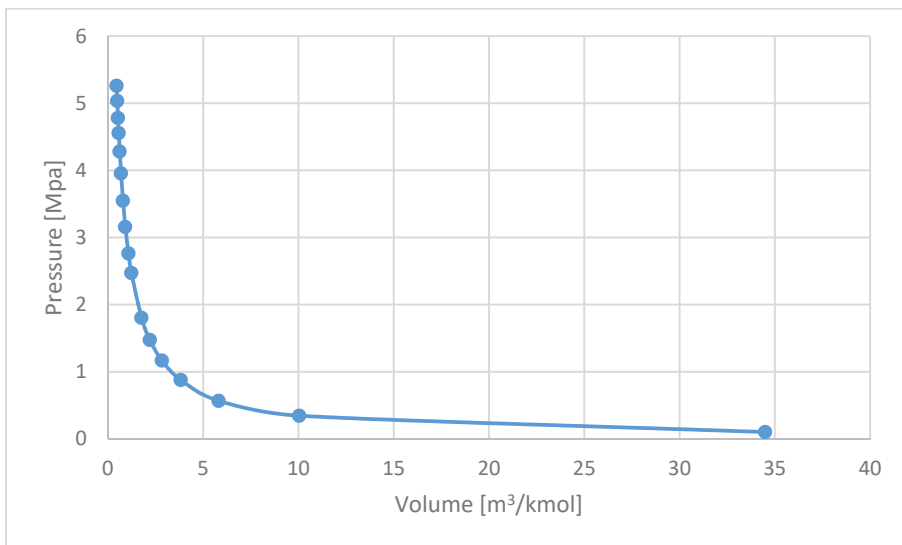


Figure 11: Compressibility factor for mixture of R125+R134a at 423 K and 25.1% of R125

References

- [1] **J. Millat, J.H. Dymond:** *C.A. Nieto de Castro, Transport Properties of Fluids*, Cambridge, University Press, 1996
- [2] **J.H. Ferziger, H.G. Kaper:** *Mathematical Theory of Transport Processes in Gasses*, North-Holland Publishing Company, London, 1972
- [3] **F.R.W.McCourt, J.J. Beenakker, W.E. Köhler, I. Kuscer:** *Nonequilibrium Phenomena in Polyatomic gases*, Clarendon Press, London, 1990
- [4] **S. Chapman, T.G. Cowling:** *The Mathematical Theory of Non-Uniform Gases*, Third Edition, Cambridge, University Press, 1970
- [5] **P.D. Neufeld, A.R. Janzen, R.A. Aziz:** *Empirical Equations to Calculate 16 of the Transport Collision Integrals for the Lennard-Jones (12-6) Potential*, The Journal of Chemical Physics, Vol.57, No.2, pp. 1100-1102
- [6] **T.-H. Chung, L.L. Lee, K.E. Starling:** *Applications of Kinetic Gas Theories and Multiparameter Correlation for Prediction of Dilute Gas Viscosity and Thermal Conductivity*, Ind. Eng. Chem. Res., Vol. 27, No. 4, pp. 671-659, 1988
- [7] **N. Shibasaki-Kitajawa, M. Takahashi, C. Yokoyama:** *Viscosity of Gaseous HFC-134a Under High Pressures*, International Journal of Thermophysics, Vol.19, No. 5, pp.:1285-1295, 1998
- [8] **M. Takahashi, N. Shibasaki-Kitajawa, C. Yokoyama:** *Viscosity of Gaseous HFC-125 Under High Pressures*, International Journal of Thermophysics, Vol.20, No. 2, pp.:445-453, 1999
- [9] **C. Yokoyama, T. Nishino, M. Takahashi:** *Viscosity of Gaseous Mixtures of HFC-125+HFC-134a under Pressure*, Fluid Phase Equilibria, Vol. 174, pp. 231-240, 2000