CO_2/HCs混合物宽区域黏度模型的热力学研究

宋渤,田远思,王晓坡,刘志刚

西安交通大学热流科学与工程教育部重点实验室,西安 710049

摘要　基于Vesovic-Wakeham理论,建立CO_2/HCs二元混合物黏度预测模型,对CO_2/CH_4,CO_2/C_2H_6,CO_2/C_3H_8,CO_2/*n*-C_4H_{10}和CO_2/iso-C_4H_{10}这5种重要CO_2/HCs二元体系的黏度进行了预测,温度范围为273.15~973.15 K,压力范围为0.1~200 MPa,最大黏度预测值达140 μPa·s。与大量文献实验数据的比较表明,所预测的黏度计算值具有较高的精度,可以满足工程应用的实际要求。

关键词　Vesovic-Wakeham理论;黏度;CO_2/HCs;二元混合物

中图分类号　TQ021　　**文献标志码**　A　　**doi**　10.3981/j.issn.1000-7857.2014.27.002

Viscosity Molding of CO_2/HCs Fluid Mixtures in Wide Thermodynamic Ranges

SONG Bo, TIAN Yuansi, WANG Xiaopo, LIU Zhigang

Key Laboratory of Thermo-Fluid Science and Engineering, Ministry of Education; Xi´an Jiaotong University, Xi´an 710049, China

Abstract　The CO_2/HCs fluids are widely discussed in the engineering and scientific studies. The viscosity, as one of the most important transport properties, plays a key role in the applications of CO_2/HCs mixtures in different fields. The theoretical approaches are effective to supplement the experimental viscosity data in wide thermodynamic ranges. In this paper, viscosity models are built for CO_2/HCs binary mixtures based on the Vesovic-Wakeham theory. The viscosity correlations and the potential parameters of pure species are selected from literature and utilized in the constructions of models. The viscosities of five industrially important CO_2/HCs binary systems are predicted in the temperature range from 273.15 K to 973.15 K and at the pressure up to 200 MPa. The studied systems are CO_2/CH_4, CO_2/C_2H_6, CO_2/C_3H_8, CO_2/*n*-C_4H_{10} and CO_2/iso-C_4H_{10}. The calculated values are compared with a large amount of experimental viscosity data over a wide temperature-pressure range. The extensive analysis shows that the calculated viscosity values of the present work could be used with confidence in different industrial applications.

Keywords　Vesovic-Wakeham theory; viscosity; CO_2/HCs; binary mixtures

二氧化碳/轻烃混合物(CO_2/HCs)在工程生产和科学研究中得到了广泛的应用[1,2]。CO_2/HCs混合物是一类优势互补的替代制冷剂,CO_2可以抑制HCs类物质的可燃性,二者混合还可以降低CO_2较高的运行压力。天然气储层中注入CO_2,能够促进天然气的增产回收,并且是一种碳储存的有效途径。同时,研究典型的CO_2/HCs二元体系间作用,可以进一步揭示流体微观运动与宏观表象的相互关系。

黏度是流体最重要的迁移性质之一,对于CO_2/HCs混合物的研究和应用,黏度是不可或缺的基础数据。目前国内外对CO_2/HCs混合物质的热力学性质进行了大量的理论和实验研究[3~6],而对迁移性质研究的较少,亟待开展相关的工作。对于混合物的黏度而言,实验测量手段无法完全满足实际所需,这就需要利用理论预测方法弥补实验的不足,准确、大量地获得混合物的黏度数据。

收稿日期:2014-04-18;修回日期:2014-05-23

基金项目:国家自然科学基金项目(51376149);《科技导报》博士生创新研究资助计划项目(kjdb2012002)

作者简介:宋渤,博士研究生,研究方向为流体热物性,电子信箱:ckssvva@163.com;王晓坡(通信作者),副教授,研究方向为流体热物性,电子信箱:wangxp@mail.xjtu.edu.cn

引用格式:宋渤, 田远思, 王晓坡, 等. CO_2/HCs混合物宽区域黏度模型的热力学研究[J]. 科技导报, 2014, 32(27): 19-22.

Vesovic 等[7~9]通过改进分子硬球理论，建立了适用于稠密流体的黏度模型，能够有效预测从低密度区至超临界区的黏度。文献[10]采用Vesovic-Wakeham理论（VW理论），计算获得了多种HFC类混合制冷剂的黏度值。本文对CO_2/HCs二元体系进行系统研究，以建立不同分子间的黏度预测模型。

1 黏度预测模型

根据硬球理论模型，一定的温度和压力下，组分1和组分2构成的二元混合物的黏度表达式[11]为

$$\eta_{\mathrm{mix}}(\rho,T)=\frac{H_{11}Y_2^2-2H_{12}Y_1Y_2+H_{22}Y_1^2}{H_{11}H_{22}-H_{12}^2}+K_{\mathrm{mix}} \tag{1}$$

$$Y_1=x_1\left(1+\frac{1}{2}x_1\alpha_{11}\bar{\chi}_{11}\rho+\frac{m_2}{m_1+m_2}x_2\alpha_{12}\bar{\chi}_{12}\rho\right) \tag{2}$$

$$Y_2=x_2\left(1+\frac{1}{2}x_2\alpha_{22}\bar{\chi}_{22}\rho+\frac{m_1}{m_1+m_2}x_1\alpha_{12}\bar{\chi}_{12}\rho\right) \tag{3}$$

$$H_{11}=\frac{x_1^2\bar{\chi}_{11}}{\eta_1^0}+\frac{x_1x_2\bar{\chi}_{12}}{2\eta_{12}^0A_{12}^*}\frac{m_1m_2}{(m_1+m_2)^2}\left(\frac{20}{3}+\frac{4m_2}{m_1}A_{12}^*\right) \tag{4}$$

$$H_{22}=\frac{x_2^2\bar{\chi}_{22}}{\eta_2^0}+\frac{x_1x_2\bar{\chi}_{12}}{2\eta_{12}^0A_{12}^*}\frac{m_1m_2}{(m_1+m_2)^2}\left(\frac{20}{3}+\frac{4m_1}{m_2}A_{12}^*\right) \tag{5}$$

$$H_{12}=-\frac{x_1x_2\bar{\chi}_{12}}{2\eta_{12}^0A_{12}^*}\frac{m_1m_2}{(m_1+m_2)^2}\left(\frac{20}{3}-4A_{12}^*\right) \tag{6}$$

$$K_{\mathrm{mix}}=\frac{3}{\pi}\rho^2\left(x_1^2\bar{\chi}_{11}\alpha_{11}^2\eta_1^0+2x_1x_2\bar{\chi}_{12}\alpha_{12}^2\eta_{12}^0+x_2^2\bar{\chi}_{22}\alpha_{22}^2\eta_2^0\right) \tag{7}$$

其中，ρ为密度，T为温度，x为物质的量分数，m为分子质量，η^0为零密度下的黏度，$A^*=\Omega^*(2,2)/\Omega^*(1,1)$，是碰撞积分$\Omega^*$的函数，由对比态理论计算[12]。

在式(2)~式(7)中，参数α_{12}和$\bar{\chi}_{12}$代表了流体压力对混合物黏度的作用，在VW理论[7~9]中

$$\bar{\chi}_{12}(\rho,T)=1+\frac{2}{5}\left[x_1(\bar{\chi}_1-1)+x_2(\bar{\chi}_2-1)\right]+\frac{\frac{6}{5}(\bar{\chi}_1-1)^{1/3}(\bar{\chi}_2-1)^{1/3}\left[x_1(\bar{\chi}_1-1)^{2/3}+x_2(\bar{\chi}_2-1)^{2/3}\right]}{(\bar{\chi}_1-1)^{1/3}+(\bar{\chi}_2-1)^{1/3}} \tag{8}$$

$$\alpha_{12}=\frac{1}{8}\left(\alpha_{11}^{1/3}+\alpha_{22}^{1/3}\right)^3 \tag{9}$$

对于某一组分i，

$$\bar{\chi}_{ii}(\rho,T)=1+2x_i(\bar{\chi}_i-1) \tag{10}$$

$$\frac{\eta_i}{\eta_i^0\alpha_{ii}\rho^*}=\frac{2}{\sqrt{\beta}}+1=3.1954 \tag{11}$$

其中，$1/\beta=1/4+3/\pi$。ρ^*为流体的转换密度，当流体密度$\rho<\rho^*$时，

$$\bar{\chi}_i=\frac{2}{\frac{\eta_i-\rho\alpha_{ii}\eta_i^0}{\eta_i^0}+\left[\left(\frac{\eta_i-\rho\alpha_{ii}\eta_i^0}{\eta_i^0}\right)^2-\frac{4\rho^2\alpha_{ii}^2}{\beta}\right]^{1/2}} \tag{12}$$

当流体密度$\rho>\rho^*$时，

$$\bar{\chi}_i=\frac{2}{\frac{\eta_i-\rho\alpha_{ii}\eta_i^0}{\eta_i^0}-\left[\left(\frac{\eta_i-\rho\alpha_{ii}\eta_i^0}{\eta_i^0}\right)^2-\frac{4\rho^2\alpha_{ii}^2}{\beta}\right]^{1/2}} \tag{13}$$

对于特定温度T，

$$\frac{\mathrm{d}\eta_i}{\mathrm{d}\rho^*}=\frac{\eta_i}{\rho^*} \tag{14}$$

通过纯质的黏度关联式可以获得对应的转换密度ρ^*，再结合纯质的势能参数，预测不同物质的量之比下二元混合物的黏度。

2 结果与讨论

利用VW理论预测CO_2/HCs二元体系的黏度，计算过程中需要用到纯质的黏度关联式η，为了将VW理论有效运用于CO_2/HCs混合物，采用表达式[13]：

$$\eta=\eta_0\left(1+N_A\sigma^3\rho B_\eta^*\right)+D_\eta \tag{15}$$

$$\eta_0=\frac{5}{16}\left(\frac{mkT}{\pi}\right)^{1/2}\frac{f_\eta}{\sigma^2\Omega^*(2,2)} \tag{16}$$

$$\Omega^*(2,2)=\exp\sum_{i=0}^{6}a_i\left(\ln T^*\right)^i \tag{17}$$

$$f_\eta=\sum_{i=0}^{4}d_i\left(\ln T^*\right)^i \tag{18}$$

$$B_\eta^*=\sum_{i=0}^{6}b_i\left(T^*\right)^{-i} \tag{19}$$

$$D_\eta=(1+aT)^2\frac{b_1\rho+b_2\rho^2}{1+c_1\rho+c_2\rho^2} \tag{20}$$

其中，N_A为阿伏伽德罗常量，k为玻耳兹曼常数，对比温度$T^*=T/\varepsilon$，σ和ε分别为硬球半径和势阱深度。此外，式(17)~式(19)中还包含多项系数：$a_0=4.369\times10^{-1}$，$a_1=-4.505\times10^{-1}$，$a_2=5.326\times10^{-2}$，$a_3=3.519\times10^{-2}$，$a_4=-1.751\times10^{-2}$，$a_5=2.773\times10^{-3}$，$a_6=-1.529\times10^{-4}$；$d_0=1.001$，$d_1=1.843\times10^{-3}$，$d_2=1.793\times10^{-3}$，$d_3=-6.604\times10^{-4}$，$d_4=5.818\times10^{-5}$；$b_0=-0.2201$，$b_1=2.075$，$b_2=5.512$，$b_3=-13.91$，$b_4=10.82$，$b_5=-4.263$，$b_6=0.5245$。对于不同物质，方程(20)中拟合参数的具体取值见表1。

表1 方程(20)中系数的值

Table 1 Coefficients of equation (20)

物质	a/K^{-1}	b_1/(μPa·s·dm^3·mol^{-1})	b_2/(μPa·s·dm^6·mol^{-2})	c_1/(dm^3·mol^{-1})	c_2/(dm^6·mol^{-2})
CO_2	-1.751×10^{-5}	−0.7070	0.1908	0.0635	-2.874×10^{-3}
CH_4	-3.034×10^{-4}	−0.1042	0.1201	0.0898	-3.033×10^{-3}
C_2H_6	1.712×10^{-4}	0.6993	0.0675	0.0152	-3.206×10^{-3}
C_3H_8	-4.485×10^{-4}	0.3317	0.3775	−0.0452	-4.802×10^{-4}
n-C_4H_{10}	-3.797×10^{-4}	1.072	0.1977	−0.1524	6.887×10^{-3}
iso-C_4H_{10}	-4.856×10^{-4}	1.863	0.2157	−0.1314	5.033×10^{-3}

混合物中不同分子间的势能参数由相同分子间参数[13]计算得到,遵循Lorentz-Berthelot混合法则,有

$$\sigma_{12}=(\sigma_1+\sigma_2)/2 \tag{21}$$

$$\varepsilon_{12}=(\varepsilon_1\varepsilon_2)^{1/2} \tag{22}$$

预测所采用的CO_2/HCs二元体系势能参数如表2所示。

表2　CO_2/HCs混合物势能参数

Table 2　Potential parameters for CO_2/HCs mixtures

物质	σ/nm	ε/K
CO_2/CH_4	0.3796	181.63
CO_2/C_2H_6	0.4086	237.42
CO_2/C_3H_8	0.4261	286.95
CO_2/n-C_4H_{10}	0.4375	332.97
CO_2/iso-C_4H_{10}	0.4407	323.25

本文计算值与文献实验值的偏差分布如图1所示,Jackson[14]和Kestin等[15]分别测量了CO_2/CH_4常压下的黏度,温度为25~200°C;Kestin等[16]测量了30°C时CO_2/CH_4的黏度值,最高压力为2.5 MPa。除去个别实验点,理论值和实验结果的相对偏差均小于±2.5%。基于毛细管法,Dewitt等[17]获得了CO_2/CH_4混合物在3种配比下的黏度,温度范围为50~200°C,压力范围为3.4~68 MPa。中低密度时,本文计算值与Dewitt和Thodos实验值吻合较好,绝大多数偏差不超过±5%,随着密度的增加,两者的偏差也随之增大,最大偏差达到了9%以上,这是由于理论值和实验值分别采用了不同的状态方程,在计算混合物高密度时存在一定的差异。

Hendl等[18]测量了CO_2/C_2H_6不同组分下的黏度,并拟合了相应的黏度关联式,温度由室温至633 K,密度范围为0.010–0.057 mol·L^{-1}。在测量范围内,本文计算结果和关联式吻合较好,对于选取的75组数据,相对偏差介于−0.83%~−2.4%。Abe等[19]采用振动盘黏度计分别测量了常压下CO_2/C_2H_6、CO_2/C_3H_8和CO_2/n-C_4H_{10}的黏度,实验温度由25℃到195℃。除个别实验点外,本文结果与Abe等实验数据的相对偏差均不大于−3%。

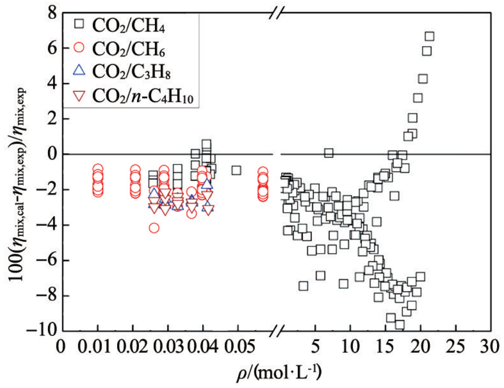
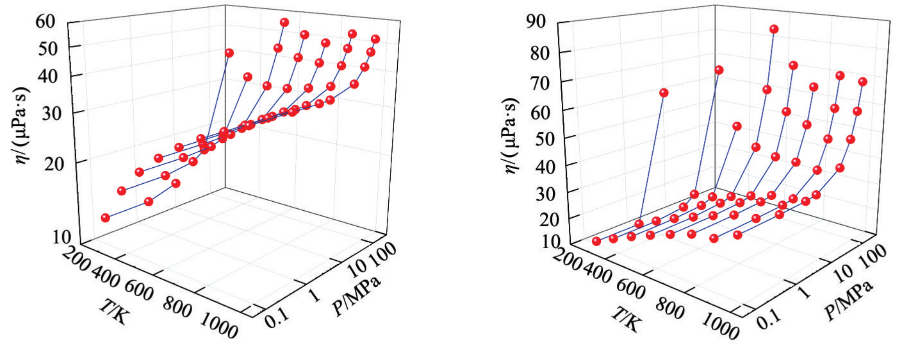


图1　CO_2/HCs二元混合物黏度偏差比较

Fig. 1　Deviations of the values calculated in this work from the experimental viscosity data for CO_2/HCs mixtures

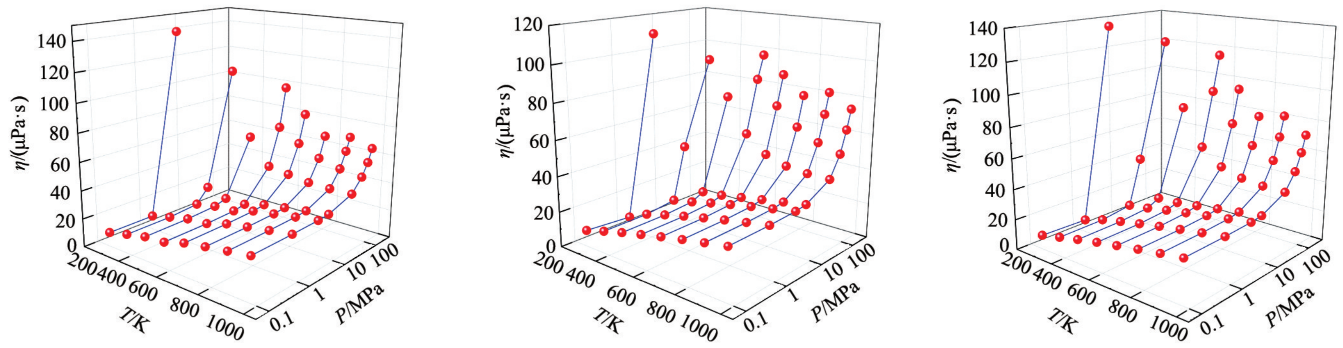
影响黏度计算值的因素主要有纯质黏度、势能参数和状态方程。纯质黏度决定了计算值的温度和压力范围,对预测精度也有一定的影响,本文采用的关联式选自文献[13]。纯质的硬球半径和势阱深度同样来自文献[13],由Lorentz-Berthelot法则得到混合物的相应参数,引起的误差可以忽略不计。纯质和混合物的密度由美国NIST热物性软件REFPROP 8.0[20]计算,状态方程对精度的影响较小。综合考虑上述各类因素,结合与文献值的比较,CO_2/HCs混合物黏度预测结果的不确定度估计为±5%,能够满足实际应用的要求。计算值温度范围由273.15~973.15 K,最低压力为0.1 MPa,最高压力随着温度的增加而增大:小于300 K时为5 MPa,300~500 K时为50 MPa,500~800 K时为150 MPa,大于800 K时为200 MPa。物质的量之比相同时,5种CO_2/HCs混合物的黏度预测结果如图2所示。



(a) CO_2/CH_4　　(b) CO_2/C_2H_6

图2　等摩尔CO_2/HCs混合物黏度

Fig. 2　Viscosity of CO_2/HCs mixtures at equimolar



(c) CO_2/C_3H_8　　(d) $CO_2/n-C_4H_{10}$　　(e) $CO_2/iso-C_4H_{10}$

图2　等物质的量CO_2/HCs混合物黏度(续)

Fig. 2　Viscosity of CO_2/HCs mixtures under equimolar condition (continued)

3　结论

应用Vesovic-Wakeham理论,研究了不同物质的量之比下CO_2/CH_4、CO_2/C_2H_6、CO_2/C_3H_8、$CO_2/n-C_4H_{10}$、$CO_2/iso-C_4H_{10}$这5种CO_2/HCs二元体系的黏度,计算结果的温度范围为273.15～973.15 K,压力范围为0.1～200 MPa,与实验数据比较表明,CO_2/HCs混合物黏度预测值具有较高的精度。

参考文献(References)

[1] 张英芝, 杨正明, 唐立根, 等. 特低渗油藏注CO_2驱油微观机制[J]. 科技导报, 2012, 30(35): 29-32.
Zhang Yingzhi, Yang Zhengming, Tang Ligen, et al. Microscopic mechanism of CO_2 flooding in extra- low permeability reservoir[J]. Science & Technology Review, 2012, 30(35): 29-32.

[2] 王杰, 谭保国, 吕广忠. 一种通过数值模拟手段划分CO_2驱替相带的新方法——以高89块油藏为例[J]. 科技导报, 2013, 31(9): 46-49.
Wang Jie, Tan Baoguo, Lü Guangzhong. Numerical simulation for division of phase zone displacement: With Gao89 as an example[J]. Science & Technology Review, 2013, 31(9): 46-49.

[3] de la Cruz de Dios J, Bouchot C, Galicia Luna L A. New p-ρ-T measurements up to 70 MPa for the system CO_2 + propane between 298 and 343 K at near critical compositions[J]. Fluid Phase Equilibria, 2003, 210(2): 175-197.

[4] Tsuji T, Tanaka S, Hiaki T. P-V-T-x relationship for $CO_2+C_4H_{10}$ and $CO_2+iC_4H_{10}$ binary gas mixtures and the partial molar volume of C_4H_{10} and iC_4H_{10} at 360.00 K[J]. Journal of Supercritical Fluids, 2004, 29(3): 215-220.

[5] Kim J H, Kim M S. Vapor-liquid equilibria for the carbon dioxide + propane system over a temperature range from 253.15 to 323.15 K[J]. Fluid Phase Equilibria, 2005, 238(1): 13-19.

[6] Feng X J, Liu Q, Zhou M X, et al. Gaseous pvTx properties of mixtures of carbon dioxide and propane with the burnett isochoric method[J]. Journal of Chemical and Engineering Data, 2010, 55(9): 3400-3409.

[7] Vesovic V, Wakeham W A. The prediction of the viscosity of dense gas mixtures[J]. International Journal of Thermophysics, 1989, 10(1): 125-132.

[8] Vesovic V. Predicting the viscosity of natural gas[J]. International Journal of Thermophysics, 2001, 22(2): 415-426.

[9] de Wijn A S, Riesco N, Jackson G, et al. Viscosity of liquid mixtures: The Vesovic- Wakeham method[J].Journal of Chemical Physics, 2012, 136(7): 074514.

[10] 宋渤, 王晓坡, 刘志刚. HFC类二元混合制冷剂气相黏度预测[J]. 工程热物理学报, 2012, 33(6): 929-933.
Song Bo, Wang Xiaopo, Liu Zhigang. Prediction of gaseous viscosity of binary HFC refrigerant mixtures[J]. Journal of Engineering Thermophysics, 2012, 33(6): 929-933.

[11] Di Pippo R, Dorfman J R, Kestin J, et al. Composition dependence of the viscosity of dense gas mixtures[J]. Physica A, 1977, 86(2): 205-223.

[12] Maitland G C, Rigby M, Smith E B, et al. Intermolecular forces: Their origin and determination[M]. Oxford: Clarendon Press, 1981.

[13] Najafi B, Ghayeb Y, Parsafar G A. New correlation functions for viscosity calculation of gases over wide temperature and pressure ranges[J]. International Journal of Thermophysics, 2000, 21(5): 1011-1031.

[14] Jackson M W. Viscosities of the binary gas mixtures, methane-carbon dioxide and ethylene-argon[J]. Journal of Physical Chemistry, 1956, 60 (6): 789-791.

[15] Kestin J, Ro S T. The viscosity of nine binary and two ternary mixtures of gases at low density[J]. Berichte der Bunsengesellschaft für physikalische Chemie, 1974, 78(1): 20-24.

[16] Kestin J, Yata J. Viscosity and diffusion coefficient of six binary mixtures[J]. Journal of Chemical Physics, 1968, 49(11): 4780-4791.

[17] Dewitt K J, Thodos G. Viscosities of binary mixtures in the dense gaseous state: The methane- carbon dioxide system[J]. Canadian Journal of Chemical Engineering, 1966, 44(3): 148-151.

[18] Hendl S, Vogel E. Temperature and initial density dependence of viscosity of binary mixtures: Carbon dioxide - ethane[J]. High Temperature - High pressures, 1993, 25(3): 279-289.

[19] Abe Y, Kestin J, Khalifa H E, et al. The viscosity and diffusion coefficients of the mixtures of light hydrocarbons with other polyatomic gases[J]. Berichte der Bunsengesellschaft für physikalische Chemie, 1979, 83(3): 271-276.

[20] Lemmon E W, Huber M L, McLinden M O. NIST standard reference database 23, Reference fluid thermodynamic and transport properties database (REFPROP), version 8.0[C]. Gaithersburg: National Institute of Standards and Technology, 2007.

(责任编辑　刘志远)