采用PR方程的液相制冷剂摩擦理论黏度模型

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摘要：在对14种制冷剂(R152a、R123、R141b、R11、R12、R125、R22、R32、R143a、R227ea、R236ea、R236fa、R245ca、R245fa)的液相黏度实验数据进行收集的基础上，将摩擦理论与工程上常用的PR方程相结合，建立了这14种制冷剂的液相黏度模型，并通过最小二乘法回归得到了模型中的各系数.结果表明，在拟合范围内，这14种制冷剂的稀薄气体黏度计算值与文献值的绝对平均偏差在1%以内，各制冷剂液相黏度计算值与实验值的绝对平均偏差在0.31%～1.92%之间，能够满足实际工程需要.

关键词：摩擦理论；黏度模型；制冷剂；液相
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PR Equation of State Based Friction Theory Viscosity Model for Liquid Refrigerants

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Abstract: The experimental liquid viscosity data of 14 pure refrigerants (R152a, R123, R141b, R11, R12, R125, R22, R32, R143a, R227ea, R236ea, R236fa, R245ca, and R245fa) are collected, and then a liquid viscosity model of the refrigerants is established using the friction theory in conjunction with the Peng-Robinson (PR) equation of state. The coefficients of the viscosity model are obtained using the least square method. The results show that all the average absolute deviations between the viscosity values calculated and the data in literature for the refrigerants in the dilute gas phase are less than 1%. In addition, all the average absolute deviations between the measurements and the viscosity values calculated with the present model for the refrigerants in the liquid phase are 0.31% - 1.92%.

Keywords: friction theory; viscosity model; refrigerant; liquid phase

黏度是流体的一个基本物性数据.在制冷系统的优化设计过程中，制冷剂的黏度具有十分重要的作用.许多学者提出了多种制冷剂黏度的预测方法，如对比态法[1]、硬球理论[2]、修正的Chapman-Enskog理论[3]等.对比态法需要有较宽范围且具有较高精度的黏度实验数据的流体作为参考流体，硬球理论和修正的Chapman-Enskog理论虽然有严格的理论基础，但应用比较困难，在液相区精度不高.

近年来，Quiñones-Cisneros等提出了一个基于摩擦理论的黏度模型[4]，并成功地应用于醇类、烷烃类及天然气等多种物质[5-6].本文作者曾对该模型进行了详细研究，并利用制冷剂的专用状态方程——Span-Wagner方程建立了一个含有18个参数、5种替代制冷剂(R134a、R125、R152a、R32、R143a)的摩擦理论黏度模型[7]，该模型基本覆盖了从气相到液相的整个热力学区域(不包括临界区)，但该模型比较复杂且参数较多，实际应用时计算烦琐.鉴于在实际工程应用设计中经常用到液相制冷剂的黏度，本

收稿日期：2009-10-10. 作者简介：王晓坡(1979－)，男，讲师，博士. 基金项目：国家自然科学基金重点资助项目(50836004)；全国优秀博士学位论文作者专项资金资助项目(200540).

文将摩擦理论与工程上常用的 PR 方程相结合，建立了 14 种制冷剂的液相黏度模型，该模型仅含有 7 个参数，且结果表明能满足实际工程的需要.

1　摩擦理论黏度模型简介

关于摩擦理论黏度模型的详细阐述可参考文献[4]，在此只作简单介绍. 在摩擦理论黏度模型中，流体的黏度 η 分为稀薄气体黏度项 η_0 和剩余摩擦黏度项 η_f，即

$$\eta = \eta_0 + \eta_f \tag{1}$$

其中

$$\eta_0 = d_1 T^{0.25} + d_2 T^{2/3} \tag{2}$$

参与拟合的稀薄气体黏度数据取自文献[8]，拟合得到的系数 d_1、d_2 列于表 1. 在本文所拟合的制冷剂温度范围内，稀薄气体黏度计算值与文献值的绝对平均偏差都在 1%以内.

表 1　稀薄气体黏度拟合得到的式(2)各系数

物质	d_1	d_2
R152a	−0.002 321 63	0.000 442 365
R123	−0.001 473 72	0.000 382 648
R141b	−0.002 314 99	0.000 420 767
R11	−0.002 555 85	0.000 466 088
R12	−0.002 509 90	0.000 498 359
R125	−0.002 298 89	0.000 502 409
R22	−0.002 525 27	0.000 518 365
R32	−0.002 529 43	0.000 518 484
R143a	−0.002 113 90	0.000 447 033
R227ea	−0.002 371 22	0.000 480 638
R236ea	−0.002 513 19	0.000 478 364
R236fa	−0.002 444 17	0.000 473 380
R245ca	−0.002 501 17	0.000 459 720
R245fa	−0.002 448 94	0.000 459 072

对于 η_f，本文采用多项式摩擦黏度模型，其表达式为

$$\eta_f = k_r P_r + k_a P_a + k_{rr} P_r^2 \tag{3}$$

式中：P_r 和 P_a 分别为 van der Waals 斥力项和引力项；k_r、k_a、k_{rr} 为与温度有关的摩擦系数

$$k_r = \{a_1 \exp(\Gamma - 1) + a_2[\exp(2\Gamma - 2) - 1] + a_3[\exp(3\Gamma - 3) - 1]\}/P_c \tag{4}$$

$$k_a = \{b_1 \exp(\Gamma - 1) + b_2[\exp(2\Gamma - 2) - 1] + b_3[\exp(3\Gamma - 3) - 1]\}/P_c \tag{5}$$

$$k_{rr} = c_4[\exp(4\Gamma) - 1]/P_c^2 \tag{6}$$

$$\Gamma = T_c/T \tag{7}$$

2　制冷剂黏度模型及结果分析

本文将摩擦理论与 PR 方程相结合建立了 14 种制冷剂的液相黏度模型，这 14 种制冷剂包括 R152a、R123、R141b、R11、R12、R125、R22、R32、R143a、R227ea、R236ea、R236fa、R245ca、R245fa 等. 作者首先收集了近期发表的这 14 种制冷剂的液相黏度实验数据作为原始数据[9-23].

PR 方程是目前工程应用最广泛的立方型状态方程[24]，表达式为

$$P = \frac{RT}{vb} - \frac{a(T)}{v(v+b) + b(v-b)} \tag{8}$$

其中

$$a = 0.457\ 24\alpha R^2\ T^2/p_c \tag{8a}$$

$$b = 0.077\ 80RT_c/p_c \tag{8b}$$

$$\alpha = [1 + k(1 - T_r^{0.5})]^2 \tag{8c}$$

$$k = 0.374\ 64 + 1.542\ 26\omega - 0.269\ 92\omega^2 \tag{8d}$$

将摩擦理论与 PR 方程联系起来，即

$$P = P_r + P_a \tag{9}$$

其中

$$P_r = RT/(v-b) \tag{10}$$

$$P_a = -a/(v(v+b) + b(v-b)) \tag{11}$$

求解 PR 方程所需要的基本参数如临界温度 T_c、临界压力 P_c、偏心因子 ω 等均取自文献[8]. 将式(3)～(11)联合，利用最小二乘法从原始数据回归得到式(4)～(6)中各系数的值，见表 2.

参与回归的各制冷剂的温度、压力范围及制冷剂黏度模型计算值与实验值的绝对平均偏差 S_{AAD} 和最大偏差 S_{AMD} 列于表 3. 从表 3 可以看出，在拟合范围内，绝对平均偏差都在 2%以内. 图 1、2 分别表示用本文回归得到的模型预测各制冷剂黏度时与实验数据的偏差随温度、压力的变化(为了清楚地表示计算值与实验数据的偏差，在图中作者将 14 种制冷剂分为 2 个组，第 1 组包括 R152a、R123、R141b、R11、R12、R125，第 2 组包括 R22、R32、R143a、R227ea、R236ea、R236fa、R245ca、R245fa). 从图中可以看出，偏差随温度、压力没有明显的单调变化趋势. 对于制冷剂 R125，偏差较大的 2 个点(偏差分别为 21.64%、18.36%)对应的温度、压力分别为 T_1 = 330 K、P_1 = 2.957 9 MPa，T_2 = 335 K、P_2 = 3.848 MPa. 产生较大偏差的原因可能是这 2 个点接近

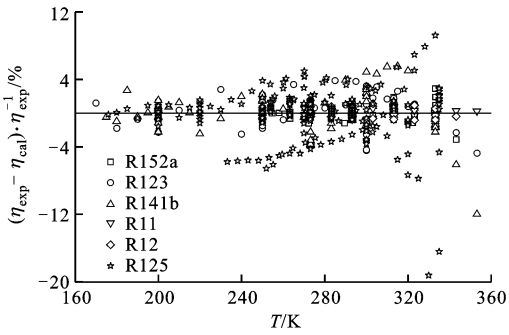
R125 的临界点(T_c、P_c 分别为 339.17 K、3.617 7 MPa),而 PR 方程在计算临界点附近的比热容时误差较大,同时在临界区液相黏度的测量结果偏差也较大.

表 2 式(4)~(6)中各系数的计算值 mPa·s

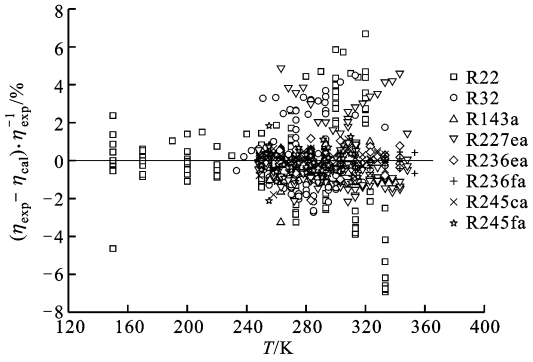
物质	a_1	a_2	a_3	b_1	b_2	b_3	c_4
R152a	−0.108 142	2.901 58	−2.977 47	−12.146 3	2.340 38	−7.085 44	−0.078 614 3
R123	0.217 337	−1.960 08	1.680 11	2.991 78	−0.809 591	2.096 38	0.017 575 9
R141b	0.800 041	−1.310 33	1.438 43	6.725 22	−2.280 19	3.585 38	0.034 373 7
R11	0.613 039	−4.168 83	4.702 91	9.274 05	−1.406 86	6.084 57	0.048 545 3
R12	0.394 529	−1.371 88	1.633 71	5.348 83	−1.693 43	3.380 71	0.029 128
R125	0.394 923	0.572 803	0.173 151	4.889 18	−1.346 85	2.169 18	0.026 264
R22	−0.022 055 4	2.040 51	−1.971 97	−3.583 89	0.076 294 2	−2.390 9	−0.019 896 9
R32	−0.319 945	4.121 5	−4.637 11	−38.265 8	11.351 3	−21.219 3	−0.264 846
R143a	0.109 427	1.322 02	−0.753 282	2.327 01	0.161 143	0.392 1	0.016 780 4
R227ea	−1.304 84	−22.140 5	18.473 7	−30.501 3	15.731 9	−12.110 5	−0.179 599
R236ea	−1.864 12	73.129 4	−66.280 4	22.512 4	−26.842 5	0.002 973 03	0.209 039
R236fa	0.067 625 7	128.784	−110.026	68.135	−50.969 1	11.596 5	0.484 57
R245ca	−7.961 78	−9.276 8	−8.938 11	−51.645 4	3.255 83	−15.623 6	−0.159 756
R245fa	−34.585 7	−72.722 2	−11.387 9	−383.499	79.068 5	−146.661	−1.789 85

表 3 各制冷剂的黏度偏差计算结果

物质	T/K	P/MPa	S_{AAD}/%	S_{AMD}/%
R152a	254~343	饱和状态~17.7	0.61	3.15
R123	170~353	饱和状态~33.61	1.59	4.75
R141b	175~353	饱和状态~30.18	1.79	11.99
R11	273~353	饱和状态~18.9	0.28	1.29
R12	273~343	饱和状态~15.1	0.34	1.10
R125	176~335	饱和状态~44.39	1.58	21.64
R22	190~333	饱和状态~31.46	1.92	6.92
R32	233~333	饱和状态~15.55	1.23	4.49
R143a	254~323	饱和状态~10.07	0.29	3.26
R227ea	248~348	饱和状态	1.25	4.60
R236ea	262~343	饱和状态	0.48	1.16
R236fa	262~353	饱和状态	0.33	1.05
R245ca	248~333	饱和状态	0.31	1.80
R245fa	250~315	饱和状态	0.59	2.12

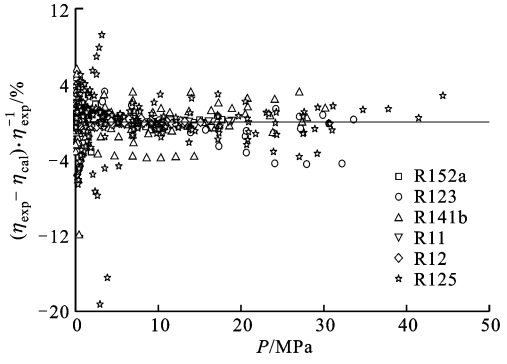


(a)第 1 组制冷剂

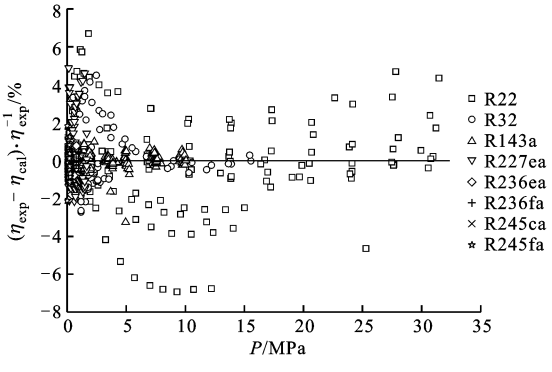


(b)第 2 组制冷剂

图 1　各制冷剂拟合的黏度偏差随温度的变化



(a)第 1 组制冷剂



(b)第 2 组制冷剂

图 2　各制冷剂拟合的黏度偏差随压力的变化

3　结　论

本文将摩擦理论与 PR 方程相结合建立了 14 种制冷剂的液相黏度模型，用最小二乘法回归得到了模型中稀薄气体黏度及剩余摩擦黏度各方程中的系数. 在回归的温度、压力范围内，制冷剂黏度模型计算值与实验值的绝对平均偏差都在 2% 以内，表明摩擦理论与 PR 方程结合所建立的黏度模型可以较好地预测制冷剂的液相黏度，能够满足实际工程的需要.

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