

Thermophysical Properties of 1,1,1,2-Tetrafluoroethane (CH₂FCF₃) Refrigerant–Oil Mixtures in the Saturated Liquid Phase with Lubricant Concentration in the Range (0 to 100) ppm

Maogang He,^{*,†} Ying Zhang,[†] Qiu Zhong,[†] Rong Xue,[†] Xinxin Zhang,[†] Zhigang Liu,[†] and Jiyou Fei[‡]

State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an 710049, PRC, and School of Mechanical Engineering, Dalian Jiaotong University, Dalian 116028, PRC

The kinematic viscosity, the specific heat capacity at constant pressure, the specific heat capacity at constant volume, and the surface tension of 1,1,1,2-tetrafluoroethane (R134a) refrigerant–oil mixtures in the saturated liquid phase were measured when the lubricant concentrations were (20, 50, 80, and 100) ppm. According to the experimental results, the effect of lubricant concentration on the above four thermophysical properties was analyzed, and the relational expressions describing the relation between these four thermophysical properties and temperature and lubricant concentration were also established.

1. Introduction

As a widely used refrigerant, the theoretical and experimental researches on the thermophysical properties of R134a date back to the early 1990s. Its thermophysical properties, mainly including *PVTx* property, critical property, specific heat capacity, surface tension, viscosity, and so on, have been researched in detail.^{1–4} All these thermophysical properties are widely used as fundamental data for designing the refrigeration cycle. In the practical refrigeration cycle, because of the addition of compressor lubricant, the actual thermophysical properties of R134a refrigerant–oil mixtures deviate from those of pure R134a, and the actual performance of the refrigeration cycle deviates from the designing performance accordingly. So, it is necessary to conduct targeted research on thermophysical properties of R134a refrigerant–oil mixtures and provide the thermophysical properties of R134a refrigerant–oil mixtures for designing a new refrigeration cycle and for improving the performance of the existing cycle. Taking the R134a refrigeration system using a falling film evaporator, for example, viscosity and surface tension are the key parameters for designing the liquid distributor and the pipe bundle arrangement of the falling film evaporator.

At present, the researches on R134a refrigerant–oil mixtures mainly concentrate on its flow characteristic in small pipelines and its heat transfer characteristic in different models.^{5–8} There are seldom descriptions on experimental research of its thermophysical properties. Only a small amount of literature covered theoretical prediction of oily refrigerant's thermophysical properties, and R134a refrigerant–oil mixtures were slightly involved.^{9–12}

Considering the fact mentioned above, a kind of commonly used lubricant which has a good match with R134a and whose brand is Solest 120 was chosen to conduct the experimental measurement in this work. Solest 120 is a kind of POE (polyol ester) lubricant which is specially designed for an HFC

Table 1. Physical Properties of Solest 120

physical properties	values	physical properties	values
viscosity at 313.15 K	12.77 mm ² ·s ⁻¹	pour point	240.15 K
viscosity at 373.15 K	1.27 mm ² ·s ⁻¹	flash point	524.15 K
viscosity index	90	ignition point	544.15 K
density	9.41 · 10 ⁻⁴ g·mm ⁻³	specific density	0.951

(hydrofluorocarbon) compressor, and it can be applied to R134a, R404, R407, R507, and so on. The main physical properties of Solest 120 are listed in the Table 1.

Four thermophysical properties of R134a refrigerant–oil mixtures in the saturated liquid phase, namely, the kinematic viscosity, the specific heat capacity at constant pressure, the specific heat capacity at constant volume, and the surface tension, were measured. The effect of lubricant concentration was analyzed. R134a used in this experiment is manufactured by Sinochem Modern Environmental Protection Chemicals (Xi'an) Co. Ltd., and its purity is 99 %.

2. Experimental section

2.1. Experimental Section for Kinematic Viscosity. In this study, the inclined-tube viscometer was adopted to measure kinematic viscosity of R134a refrigerant–oil mixtures. The measuring principle of the inclined-tube viscometer can be depicted by measuring the flowing parameter of the liquid column which flows at a uniform speed in a thin tube which has an obliquity, and the viscosity of the experimental liquid can be obtained. Refs 13 and 14 represent the measuring principle and the experimental apparatus in detail, so the measurement theory was depicted as follows briefly.

The measuring equation of the inclined-tube viscometer can be obtained from the equilibrium equation describing uniform flow of the liquid column which flows at a uniform speed in a thin tube which has an obliquity, and the measuring equation is written as:

$$u_0 = k_1 \sin \alpha + k_2(k_1 = \rho g R^2 / 8\eta = g R^2 / 8\nu, \\ k_2 = (\cos \theta_{c,b} - \cos \theta_{c,f}) \gamma R / 4l\eta) \quad (1)$$

Here, u_0 is the velocity of the liquid column from the practical measurement when the liquid column flows at a uniform speed,

* Corresponding author. Tel: +86-29-8266-3863. Fax: +86-29-8266-8789. E-mail address: mghe@mail.xjtu.edu.cn.

[†] Xi'an Jiaotong University.

[‡] Dalian Jiaotong University.

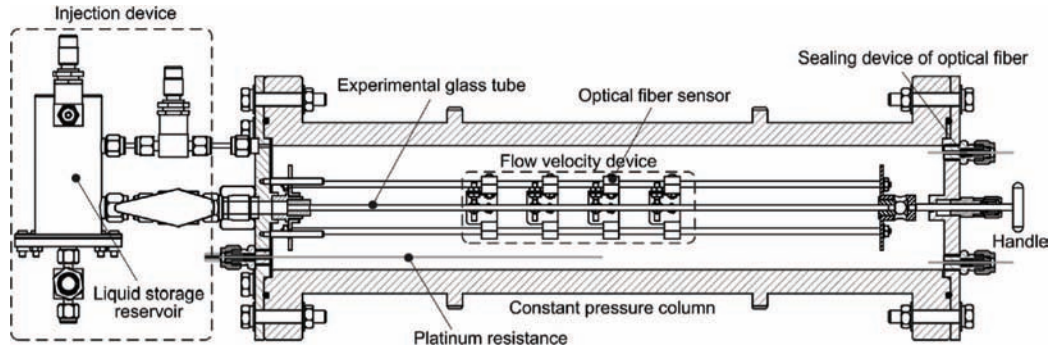


Figure 1. Experimental cell of viscosity.

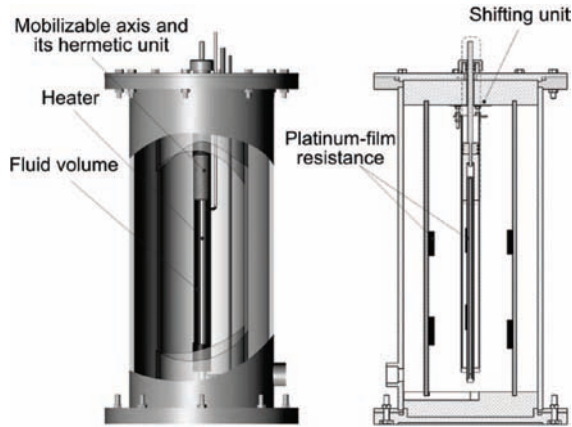


Figure 2. Changeable volume calorimeter.

$\text{mm}\cdot\text{s}^{-1}$; α is the angle between the direction of the thin tube and the horizontal direction, $^\circ$; ρ is the density of the experimental liquid, $\text{g}\cdot\text{mm}^{-3}$; R is the inside radius of the thin tube, mm ; $\theta_{c,b}$ is the contact angle of back meniscus, $^\circ$; $\theta_{c,f}$ is the contact angle of front meniscus, $^\circ$; γ is the surface tension acting on liquid, $\text{N}\cdot\text{mm}^{-1}$; and l is the length of the liquid column, mm .

From eq 1, a conclusion that can be safely reached is that when the tube has different inclination angles and the liquid column flows at a uniform speed, as long as the velocity of the liquid column and the value of the inclination angle are obtained, a linear curve can be fitted by the least-squares method. The rate of the slope of this curve is k_1 . Ultimately, the kinematic viscosity η and the dynamic viscosity η of the experimental liquid can be obtained. Accordingly, the equations for the dynamic viscosity coefficient and the kinematic viscosity coefficient can be depicted as follows.

$$\eta = \rho g R^2 / 8k_1, \quad \nu = g R^2 / 8k_1 \quad (2)$$

Figure 1 depicts the design diagram of the experimental cell of viscosity.

2.2. Experimental Section for Specific Heat Capacity. The changeable volume calorimeter was used to measure the specific heat capacity at constant pressure and the specific heat capacity at constant volume of R134a refrigerant–oil mixtures in the saturated liquid phase. The experimental system was established according to the traditional principle of the quasisteady state which is widely used in measurement of specific heat capacity, so it is unnecessary to depict the experimental system in detail. The name of “Changeable Volume” means that compared with the traditional calorimeter the fluid volume of the changeable volume calorimeter can be changed by a high-precision positioning platform. Also, when measuring the specific heat

capacity at constant pressure, the real-time changing of fluid volume can be achieved by a high-precision positioning platform, and the internal pressure in the fluid volume maintains a fixed value. When the specific heat capacity at constant volume is measured, the fluid volume maintains a certain fixed volume by fixing the positioning platform. Figure 2 depicts the design diagram of the changeable volume calorimeter.

2.3. Experimental Section for Surface Tension. The capillary rise method was adopted to measure the surface tension of R134a refrigerant–oil mixtures in the saturated liquid phase.¹⁵ To avoid the impact of capillary rise brought by experimental liquid in the vessel and eliminate the error brought by the unsharp liquid level, the differential capillary rise method (DCRM) was adopted in this experiment.

The equation for measuring surface tension adopted in DCRM is expressed as follows

$$\sigma = \frac{g(\rho' - \rho'')\Delta h}{2(1/r_1 - 1/r_2)} = \frac{1}{2}g a^2(\rho' - \rho'') \quad (3)$$

where σ is the surface tension, $\text{mN}\cdot\text{m}^{-1}$; ρ' is the density of saturated liquid, $\text{kg}\cdot\text{m}^{-3}$; ρ'' is the density of saturated gas, $\text{kg}\cdot\text{m}^{-3}$; Δh is the height difference, mm ; r_1 and r_2 are the inner diameters of two capillary tubes, mm ; and a is the capillary constant, mm .

2.4. Analysis of Experimental Uncertainty. According to the regulation of the experimental uncertainty given by the International Organization for Standardization, the compound uncertainty, U , describing the temperature, the pressure, and the viscosity can be calculated from the following equation

$$U = k \cdot u_c = k \sqrt{\sum (u_i)^2} \quad (4)$$

where u_i is the standard deviation of every error source; u_c is the compound standard deviation compounded by every error; k is the confidence coefficient and it is usually taken to be 2 or 3. When $k = 2$, the degree of confidence is 95%. When $k = 3$, the degree of confidence is 99%. In this study, the confidence coefficient of the compound uncertainty is taken to be 2.

In this work, the experimental uncertainties of viscosity, specific heat capacity, and surface tension are listed in the Table 2.

3. Result and Analysis

3.1. Kinematic Viscosity of R134a Refrigerant–Oil Mixtures. Table 3 lists the kinematic viscosity of R134a refrigerant–oil mixtures in the saturated liquid phase from (267.15 to 303.15) K when the lubricant concentrations are (20, 50, 80, and 100) ppm. Figure 3 depicts the kinematic viscosity's variation curve with temperature under the condition of these four lubricant concentrations.

Table 2. Experimental Uncertainties of Viscosity, Specific Heat Capacity, and Surface Tension

experimental system of viscosity	temperature	± 20.6 mK
	pressure	± 3.72 kPa
experimental system of specific heat capacity	viscosity	± 0.0013 mm ² ·s ⁻¹
	temperature	± 20.6 mK
experimental system of surface tension	pressure	± 3.72 kPa
	specific heat capacity	± 0.012 kJ·(kg·K) ⁻¹
experimental system of surface tension	temperature	± 10 mK
	pressure	± 3.72 kPa
	surface tension	± 0.2 mN·m ⁻¹

Table 3. Kinematic Viscosity ν of R134a Refrigerant–Oil Mixtures in the Saturated Liquid Phase

T/K	$\nu/\text{mm}^2\cdot\text{s}^{-1}$				
	0 ppm ^a	20 ppm	50 ppm	80 ppm	100 ppm
267.15	0.2191	0.2660	0.3431	0.4173	0.4687
269.15	0.2146	0.2591	0.3315	0.4009	0.4492
271.15	0.2101	0.2524	0.3201	0.3850	0.4303
273.15	0.2059	0.2453	0.3093	0.3698	0.4121
275.15	0.2017	0.2388	0.2986	0.3549	0.3943
277.15	0.1977	0.2324	0.2882	0.3404	0.3772
279.15	0.1938	0.2262	0.2780	0.3264	0.3606
281.15	0.1900	0.2201	0.2682	0.3129	0.3446
283.15	0.1863	0.2140	0.2587	0.2998	0.3292
285.15	0.1827	0.2081	0.2495	0.2872	0.3143
287.15	0.1792	0.2024	0.2405	0.2751	0.3001
289.15	0.1758	0.1967	0.2319	0.2634	0.2865
291.15	0.1725	0.1911	0.2235	0.2522	0.2734
293.15	0.1692	0.1857	0.2154	0.2414	0.2609
295.15	0.1661	0.1809	0.2073	0.2308	0.2489
297.15	0.1630	0.1757	0.1997	0.2210	0.2376
299.15	0.1600	0.1706	0.1924	0.2116	0.2269
301.15	0.1571	0.1655	0.1854	0.2026	0.2168
303.15	0.1542	0.1606	0.1786	0.1940	0.2072

^a Note: data of pure R134a are from NIST-REFPROP7.0.

These experimental results indicate that at the same temperature, with the increase in lubricant concentration, the kinematic viscosity of R134a refrigerant–oil mixtures in the saturated liquid phase significantly increases. The impact of lubricant on kinematic viscosity gradually decreases with the rise of temperature. In the low-temperature region, with the increase in lubricant concentration, the kinematic viscosity increases significantly. In contrast, in the high-temperature region, with the increase in lubricant concentration, it does not increase significantly.

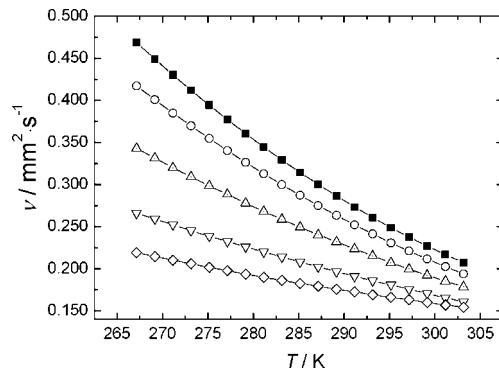
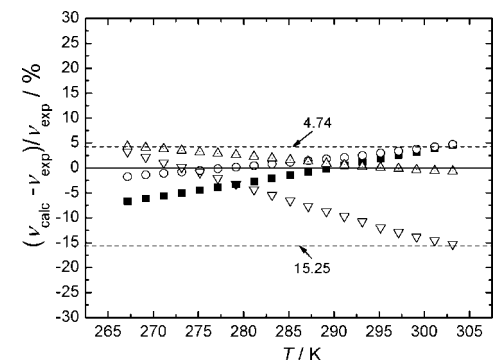
According to the principle of nonlinear regression which is usually used in the mathematical computation, the equation fitted by the experimental results expressing the relation between the kinematic viscosity ν and lubricant concentrations φ and temperature T can be gained and is listed as follows

$$\nu = (1 - 0.00238T + 1.14739 \cdot 10^{-5}T^2 - 2.99156 \cdot 10^{-8}T^3) \cdot \varphi^{0.02891} \quad (5)$$

where ν is kinematic viscosity, mm²·s⁻¹; φ is lubricant concentration, ppm; and T is temperature, K.

Figure 4 depicts the deviations between calculated kinematic viscosity according to eq 5 and the experimental results. When eq 5 is adopted to calculate the kinematic viscosity, the absolute average of relative deviations is 3.49 % compared with the experimental results.

3.2. Specific Heat Capacity at Constant Pressure of R134a Refrigerant–Oil Mixtures. Experimental researches indicate that R134a has a large volumetric expansion, and it cannot be

**Figure 3. Kinematic viscosity of R134a refrigerant–oil mixtures.****Figure 4. Deviations between calculated results and experimental results.****Table 4. Specific Heat Capacity at Constant Pressure c_p of R134a Refrigerant–Oil Mixtures**

T/K	$c_p/\text{kJ}\cdot(\text{kg}\cdot\text{K})^{-1}$				
	0 ppm ^a	20 ppm	50 ppm	80 ppm	100 ppm
267.15	1.3254	1.3201	1.3220	1.3267	1.3141
269.15	1.3304	1.3215	1.3298	1.3305	1.3186
271.15	1.3357	1.3246	1.3367	1.3342	1.3239
273.15	1.3410	1.3271	1.3411	1.3526	1.3338
275.15	1.3466	1.3314	1.3552	1.3543	1.3597
277.15	1.3523	1.3615	1.3515	1.3690	1.3535
279.15	1.3581	1.3674	1.3699	1.3667	1.3554
281.15	1.3641	1.3891	1.3803	1.3674	1.3753
283.15	1.3704	1.3866	1.3829	1.3710	1.3733
285.15	1.3768	1.3898	1.3876	1.3776	1.3692
287.15	1.3835	1.3888	1.3944	1.3872	1.4032
289.15	1.3903	1.4036	1.4033	1.3898	1.4052
291.15	1.3975	1.4042	1.4043	1.4154	1.4052
293.15	1.4049	1.4106	1.4275	1.4139	1.4032
295.15	1.4125	1.4212	1.4120	1.4122	1.4173
297.15	1.4205	1.4298	1.4260	1.4239	1.4263
299.15	1.4288	1.4345	1.4391	1.4382	1.4389
301.15	1.4375	1.4437	1.4420	1.4411	1.4421
303.15	1.4465	1.4551	1.4574	1.4531	1.4473

^a Note: data of pure R134a are from NIST-REFPROP7.0.

simply deemed that specific heat capacity at constant pressure is equal to specific heat capacity at constant volume when R134a is in the liquid state. So, separate research on these two specific heat capacities is required. Table 4 lists the specific heat capacity at constant pressure of R134a refrigerant–oil mixtures in the saturated liquid phase from (267.15 to 303.15) K when the lubricant concentrations are (20, 50, 80 and 100) ppm. Figure 5 depicts the distribution of R134a refrigerant–oil mixtures' experimental data points around the data curve of pure R134a.

These experimental results indicate that compared with the data of pure R134a there is no significant impact of lubricant on specific heat capacity at constant pressure of R134a refrigerant–oil mixtures in the saturated liquid phase when the

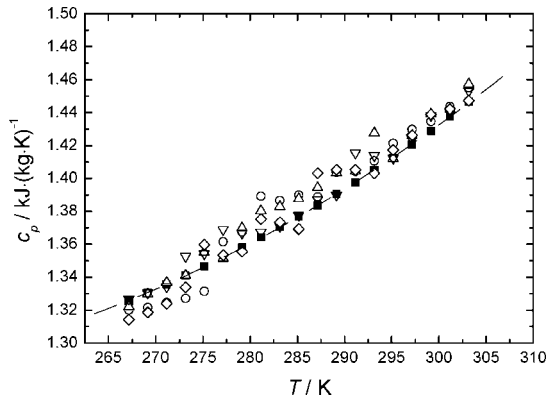


Figure 5. Specific heat capacity at constant pressure of R134a refrigerant–oil mixtures.

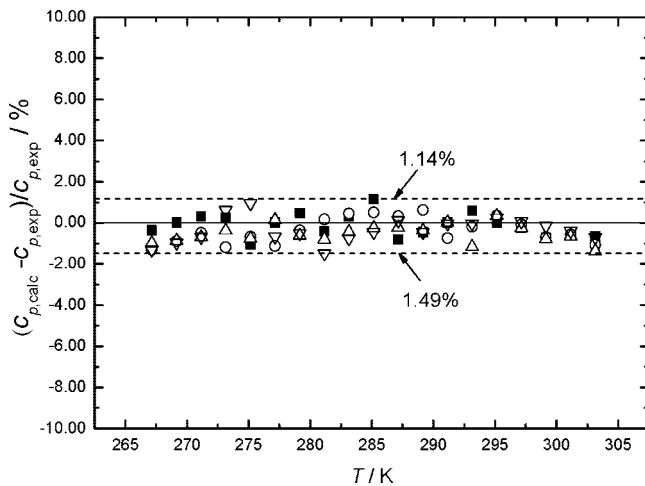


Figure 6. Deviations between calculated results and experimental results.

lubricant concentrations are (20, 50, 80, and 100) ppm. With the addition of lubricant, the specific heat capacity at constant pressure has a slight increase which is less than 2 % compared with that of pure R134a.

The equation fitted by the experimental results expresses the relation between the specific heat capacity at constant pressure and lubricant concentrations and temperature as follows

$$c_p = (1 - 0.01296T + 9.22995 \cdot 10^{-5}T^2 - 1.47896 \cdot 10^{-7}T^3) \cdot \varphi^{0.02891} \quad (6)$$

where c_p is specific heat capacity at constant pressure, $\text{kJ} \cdot (\text{kg} \cdot \text{K})^{-1}$; φ is lubricant concentration, ppm; and T is temperature, K.

Figure 6 depicts the deviations between calculated specific heat capacity at constant pressure according to eq 6 and experimental results. When eq 6 is adopted to calculate specific heat capacity at constant pressure, the absolute average of relative deviations is 0.53 % compared with the experimental results.

3.3. Specific Heat Capacity at Constant Volume of R134a Refrigerant–Oil Mixtures. Table 5 lists the specific heat capacities at constant volume of R134a refrigerant–oil mixtures in the saturated liquid phase from (267.15 to 303.15) K when the lubricant concentrations are (20, 50, 80, and 100) ppm. Figure 7 depicts the distribution of R134a refrigerant–oil mixtures' experimental data points around the data curve of pure R134a.

These experimental results indicate that compared with the data of pure R134a there is no significant impact of lubricant

Table 5. Specific Heat Capacity at Constant Volume c_v of R134a Refrigerant–Oil Mixtures

T/K	$c_v / \text{kJ} \cdot (\text{kg} \cdot \text{K})^{-1}$				
	0 ppm ^a	20 ppm	50 ppm	80 ppm	100 ppm
267.15	0.8717	0.8695	0.8681	0.8730	0.8701
269.15	0.8742	0.8601	0.8684	0.8789	0.8732
271.15	0.8766	0.8621	0.8534	0.8560	0.8810
273.15	0.8791	0.8631	0.8576	0.8569	0.8991
275.15	0.8816	0.8594	0.8755	0.8692	0.9021
277.15	0.8841	0.8763	0.8854	0.8605	0.8894
279.15	0.8866	0.8738	0.8776	0.8709	0.8809
281.15	0.8892	0.8720	0.8618	0.8804	0.8965
283.15	0.8918	0.8806	0.8682	0.8890	0.8763
285.15	0.8944	0.8899	0.8767	0.8966	0.8803
287.15	0.8970	0.9000	0.8873	0.9034	0.8885
289.15	0.8996	0.9102	0.9000	0.9092	0.9001
291.15	0.9023	0.9213	0.9149	0.9141	0.9175
293.15	0.9050	0.9129	0.9319	0.9181	0.9083
295.15	0.9077	0.9112	0.9201	0.9134	0.9101
297.15	0.9105	0.9163	0.9221	0.9137	0.9145
299.15	0.9133	0.9201	0.9287	0.9186	0.9205
301.15	0.9161	0.9223	0.9265	0.9211	0.9234
303.15	0.9189	0.9243	0.9276	0.9234	0.9245

^a Note: data of pure R134a are from NIST-REFPROP7.0.

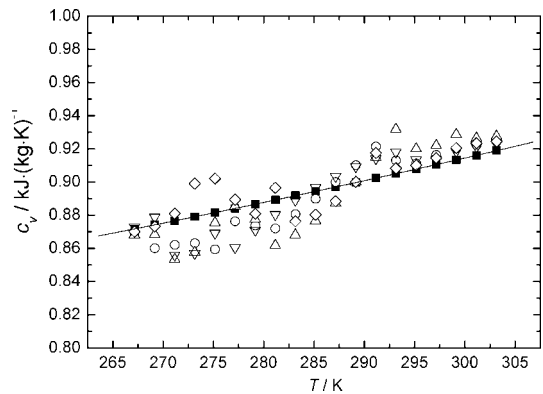


Figure 7. Specific heat capacity at constant volume of R134a refrigerant–oil mixtures.

on specific heat capacity at constant volume of R134a refrigerant–oil mixtures in the saturated liquid phase when the lubricant concentrations are (20, 50, 80, and 100) ppm. With the addition of lubricant, the specific heat capacity at constant volume has a slight decrease which is less than 2.97 % compared with that of pure R134a.

The equation fitted by the experimental results expresses the relation between the specific heat capacity at constant volume and lubricant concentration and temperature as follows

$$c_v = (1 + 0.0463T + 3.41858 \cdot 10^{-4}T^2 + 6.22228 \cdot 10^{-7}T^3) \cdot \varphi^{5.46813 \cdot 10^{-3}} \quad (7)$$

where c_v is specific heat capacity at constant volume, $\text{kJ} \cdot (\text{kg} \cdot \text{K})^{-1}$; φ is lubricant concentration, ppm; and T is temperature, K.

Figure 8 depicts the deviations between calculated specific heat capacity at constant volume according to eq 7 and the experimental results. When eq 7 is adopted to calculate specific heat capacity at constant volume, the absolute average of relative deviations is 3.29 % compared with the experimental results.

3.4. Surface Tension of R134a Refrigerant–Oil Mixtures. Table 6 lists the surface tensions of R134a refrigerant–oil mixtures in the saturated liquid phase from (273.15 to 293.15) K when the lubricant concentrations are (20, 50, 80, and 100) ppm. Figure 9 depicts the surface tension's variation curve with

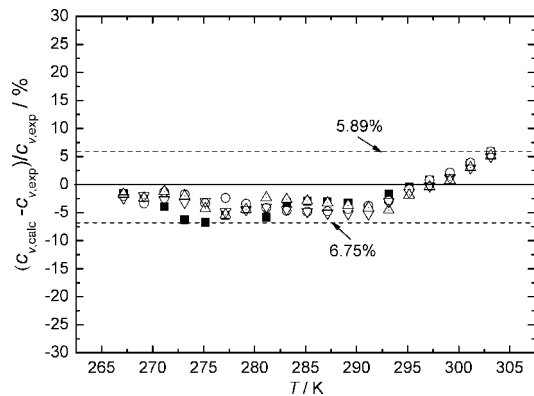


Figure 8. Deviations between calculated results and experimental results.

Table 6. Surface Tension σ of R134a Refrigerant–Oil Mixtures in the Saturated Liquid Phase

T/K	$\sigma/\text{mN}\cdot\text{m}^{-1}$				
	0 ppm ^a	20 ppm	50 ppm	80 ppm	100 ppm
273.15	11.84	11.88	11.94	12.00	12.04
275.15	11.50	11.55	11.62	11.69	11.74
277.15	11.15	11.21	11.30	11.39	11.45
279.15	10.82	10.88	10.99	11.09	11.15
281.15	10.47	10.55	10.67	10.78	10.86
283.15	10.12	10.21	10.34	10.48	10.57
285.15	9.78	9.88	10.02	10.17	10.27
287.15	9.44	9.54	9.71	9.87	9.97
289.15	9.09	9.21	9.39	9.56	9.68
291.15	8.75	8.88	9.07	9.26	9.39
293.15	8.41	8.54	8.75	8.95	9.09

^a Note: data of pure R134a are from NIST-REFPROP7.0.

temperature under the condition of these four lubricant concentrations.

These experimental results indicate that at the same temperature, with the increase in lubricant concentration, the surface tension of the R134a refrigerant–oil mixture in the saturated liquid phase significantly increases. The lubricant's influence on surface tension gradually increases with the increase of temperature. In the low-temperature region, with the increase in lubricant concentration, surface tension does not increase significantly. In contrast, in the high-temperature region, with the increase in lubricant concentration, it increases significantly.

The equation fitted by the experimental results expresses the relation between the surface tension and the variation of lubricant concentrations and temperature as follows

$$\sigma = (1 + 0.37753T - 1.83345 \cdot 10^{-3}T^2 + 2.14433 \cdot 10^{-6}T^3) \cdot \varphi^{0.43038} \quad (8)$$

where σ is surface tension, $\text{mN}\cdot\text{m}^{-1}$; φ is lubricant concentration, ppm; and T is temperature, K.

Figure 10 depicts the deviations between calculated surface tension according to eq 8 and experimental results. When eq 8 is adopted to calculate surface tension, the absolute average of relative deviations is 0.43 % compared with the experimental results.

4. Conclusions

In this work, the kinematic viscosity, the specific heat capacity at constant pressure, the specific heat capacity at constant volume, and the surface tension of R134a refrigerant–oil mixtures in the saturated liquid phase were measured when the lubricant concentrations were (20, 50, 80, and 100) ppm. The main conclusions can be drawn as follows.

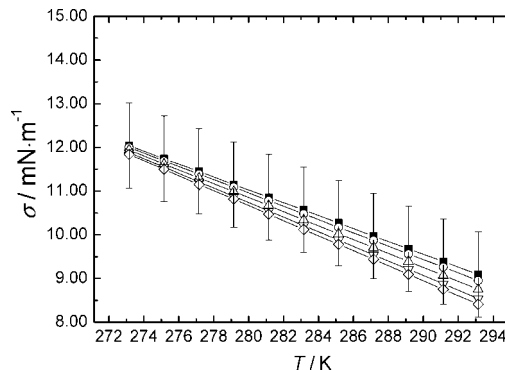


Figure 9. Surface tension of R134a refrigerant–oil mixtures.

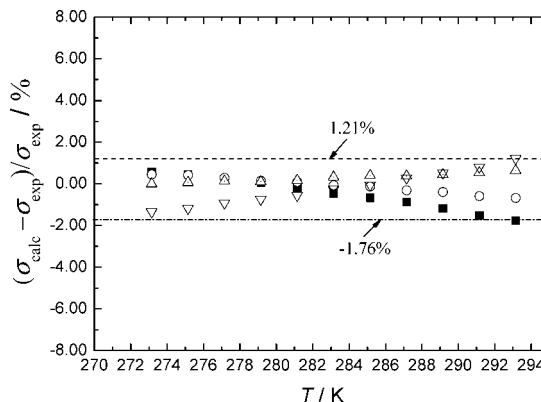


Figure 10. Deviations between calculated results and experimental results.

First, with the addition of lubricant, there is a significant impact on kinematic viscosity of the R134a refrigerant–oil mixture in the saturated liquid phase. With the increase in lubricant concentration, kinematic viscosity of R134a refrigerant–oil mixtures in the saturated liquid phase significantly increases, and the impact of lubricant on kinematic viscosity gradually decreases with the increase of temperature.

Second, with the addition of lubricant, there is no significant impact on specific heat capacity at constant pressure and on specific heat capacity at constant volume of R134a refrigerant–oil mixtures in the saturated liquid phase. With the addition of lubricant, the specific heat capacity at constant pressure of R134a refrigerant–oil mixtures in the saturated liquid phase slightly increases while the specific heat capacity at constant volume slightly decreases. But there is no evident regularity of the lubricant's impact that can be found.

Third, with the addition of lubricant, there is a significant impact on surface tension of R134a refrigerant–oil mixtures in the saturated liquid phase. With the increase in lubricant concentration, surface tension of R134a refrigerant–oil mixtures in the saturated liquid phase significantly increases, and the impact of lubricant on the surface tension gradually increases with the increase of temperature.

Lastly, the relational expressions describing the relation between the above four thermophysical properties and temperature and lubricant concentration were established. The relation expressions can be applicable under the condition of the lubricant concentration from (0 to 100) ppm.

When conducting the design calculation of refrigeration system using R134a as its refrigerant, the impacts of lubricant on viscosity and surface tension of R134a should be well considered. If there is no extreme need, the impacts of lubricant

on specific heat capacity at constant pressure and specific heat capacity at constant volume of R134a can be neglected.

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