Solubility Measurements of 1,1,1,2-Tetrafluoroethane (R134a) and of Propane in Squalane at Temperatures from (325 to 400) K and Pressures from (0.1 to 1) MPa

Hui Hong,[†,‡] Maoqiong Gong,*,[†] and Jianfeng Wu[†]

Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, P.O. Box 2711, Beijing 100080, China, and Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

Solubility data for two binary systems, R134a (**1**) + squalane (**3**) and propane (**2**) + squalane (**3**), are presented in this paper. The solubility data were measured using the isochoric method with gas recirculation at temperatures from (325 to 400) K and pressures from (0.1 to 1.0) MPa. The uncertainty of the measured solubility data is less than 2.0 %. The experimental results were correlated with the Soave−Redlich−Kwong equation of state using the van der Waals mixing rule. The absolute mean deviation and maximum deviation of measured pressures from the correlated results are 0.68 % and 2.8 % for the R134a + squalane system, respectively. For the propane + squalane system, the absolute mean deviation and maximum deviation of measured pressures from the correlated results are 1.0 % and 4.0 %, respectively. Comparison of the present data with other literature data is also made.

Introduction

Phase behavior measurements for refrigerant and lubricant mixtures are very important both for the design of refrigeration systems and for the selection of proper lubricants for compressors. The solubility of refrigerants in oil significantly changes the oil viscosity and in turn the lubrication characteristics. In addition, the different solubility of different components in lubricant oil can change the circulating composition from the initial charged mixed refrigerants. This is one of the most important reasons for the composition shift for multicomponent mixed-refrigerant Joule−Thomson cryocoolers.[1,2]

In fact, actual lubricant oils are mixtures of various compounds with very high boiling points. The detail compositions for both the mineral oil and the synthetic oil are complicated and usually not available. Therefore, no vapor pressure data and critical parameters data are available for those lubricant oils. Hence, it is difficult to predict the thermodynamic performance of the blend of the oil and refrigerants. In fact, long-chain alkanes are the main composition of mineral oil. Squalane is a good lubricant in some applications. With known critical parameters,[3] it is easy to predict its properties by the equation of state. So, from a simplification point of view, squalane was selected as a mineral oil in this study. Only a few publications are available for the solubility measurements of refrigerants in squalane. Most of these solubility measurements are focused on alkanes and squalane systems.[4−8] Chappelow,[4] Diana,[6] and Aalto[7] measured the phase equilibria of the squalane + propane system, but the pressure range was below 0.1 MPa and above 1 MPa. No R134a + squalane phase equilibria data have been reported. In this paper, we reported the solubility measurements of R134a and propane in squalane, with a temperature range of (325 to 400) K and a pressure range of (0.1 to 1) MPa.

Experimental Section

Chemicals. Squalane was supplied by the KeHua Company. According to the manufacturer, the molar fraction was 98 %. R134a and propane were supplied by Atofina with a molar fraction of 99.9 %. All chemicals were used directly without further purification.

Apparatus and Procedure. The experimental measurements were conducted with an isochoric apparatus, the principle of which is similar to those described by Cukor and Prausnitz,[9] Baruah et al.,[10] and Wahlstrom.[11] That is, the mass of gas absorbed in a known quantity of squalane was calculated from the pressure change in the equilibrium cell with known volume and measured temperature.

The schematic diagram of the experimental apparatus is shown in Figure 1. The stainless steel equilibrium cell (A) with a measured volume of 329.2 mL was placed in a liquid-bath thermostat (B). The temperature of the liquid-bath thermostat could be controlled to vary from (300 to 450) K within a fluctuation of 0.1 K at any required temperature. A kind of silicon oil with high thermal conductivity was charged in the bath as the heat-transfer liquid. A self-made magnetic gas pump (D)[12] was used to circulate the gas to accelerate the equilibrium process. The circulating gas passed through two coil heat exchangers (C1 and C2), which were merged in the liquid bath. A gas bottle (E) with measured volume was used to supply gas to the equilibrium cell. The magnetic gas pump and the gas bottle were in a room with constant temperature.

The pure squalane was first degassed and then injected into the pre-evacuated equilibrium cell. The mass of the charged squalane was measured with a precise balance (Satorius BS 4000S) with an uncertainty of 0.01 g. After that, the liquid-bath thermostat with the equilibrium cell was heated to the highest measurement temperature and the total system with the magnetic pump and connecting pipes was evacuated by a vacuum pump. Then, the interconnecting valve was opened, and the gas in the gas bottle was charged into the system to a certain given pressure. The pump was then turned on to circulate the

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* Corresponding author. E-mail: gongmq@cl.cryo.ac.cn. Phone: +86 10 82543728. Fax: +86 10 62627843.

[†] Technical Institute of Physics and Chemistry.

[‡] Graduate School of the Chinese Academy of Sciences.

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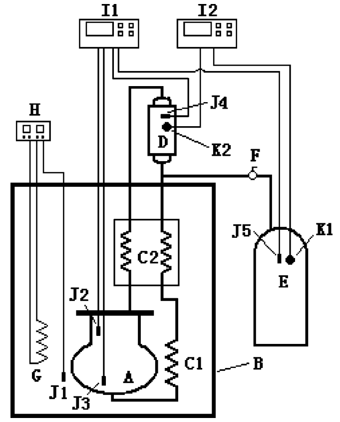

Figure 1. Schematic diagram of the experimental apparatus: A, equilibrium cell; B, liquid-bath thermostat; C1 and C2, heat exchangers; D, magnetic gas pump; E, gas bottle; F, valve; G, electric heater; H, temperature controller; I1 and I2, pressure and temperature indicator; J1−J5, platinum resistance thermometers; K1 and K2, pressure transducers.

gas passing from the top of the equilibrium cell through the heat exchangers and back into the bottom of the cell, to accelerate the equilibrium process. The progress of equilibrium was indicated by the pressure decrease of the equilibrium cell. When the cell pressure did not decrease and the fluctuation of pressure was less than 0.2 kPa within half an hour, equilibrium was reached. Then, the parameters of pressures and temperatures at the equilibrium state were recorded. The above process was repeated at different temperatures and/or at different initial charged pressures to obtain the solubility at different conditions.

Parameters, Measurements, and Uncertainties. Two platinum resistance thermometers were placed inside the equilibrium cell to measure the temperatures of the gas phase and the liquid phase. The temperature differences between the two thermometers were within 0.1 K under all equilibrium conditions. Another platinum resistance thermometer was placed inside the gas bottle to measure its temperature. The uncertainties for all temperature measurements were better than ±0.1 K over the entire temperature range. All the platinum resistance thermometers were calibrated by the Cryogenic Metrology Station of the Chinese Academy of Sciences.

One pressure transducer was used to measure the pressure of the equilibrium cell with a range of (0 to 1.5) MPa. Another pressure transducer was used to measure the pressure of the gas bottle with a range of (0 to 2.0) MPa. The uncertainties of both pressure transducers were within 0.04 %, and the total pressure measurement uncertainties were (600 and 800) Pa, respectively. Both transducers were calibrated before the measurements.

The volumes of the equilibrium cell, gas pump, gas bottle, and connecting pipes were measured with distilled water, which was weighed using the above precise balance with an uncertainty of 0.01 g. The density of the twice-distilled water was calculated by Refprop 7.0.[13] The uncertainty of the measured solubility data was less than 2.0 %.

Validation of the Experimental Facility. Prior to measuring the gas solubility, pure R134a was injected into the equilibrium cell to measure its saturated temperature and pressure, which were compared with the calculated results of Refprop 7.0. Table 1 shows the comparison results. The relative deviations between the measured and calculated data are within 0.3 %. The maximum deviation of pressure is 1.6 kPa. The results indicate that the experimental facility works reasonably well. The verification of this facility was also conducted by comparison of the solubility measurements with the literature data, which will be presented in the following section.

Table 1. Comparison of Measured Saturated Pressures and Calculated Pressures of R134a

T	P_{exptl}	$P_{Refprop}$	$P_{Refprop} - P_{exptl}$	$100(P_{Refprop} - P_{exptl})/P_{exptl}$
K	kPa	kPa	kPa	
304.0	788.5	789.2	0.7	0. 09
300.0	704.4	702.8	−1.6	−0.23
295.4	612.0	612.5	0.5	0.08

Table 2. Mole Fraction Solubility of R134a (1) in Squalane (3)

T	P	x_1	T	P	x_1
K	kPa		K	kPa	
400.1	74.5	0.0115	350.1	55.2	0.0126
400.1	150.9	0.0236	350.0	114.2	0.0255
400.0	277.0	0.0427	349.9	208.8	0.0462
400.0	463.9	0.0714	350.0	356.6	0.0767
400.0	542.4	0.0837	349.9	412.4	0.0906
400.1	675.2	0.1030	350.1	530.3	0.1144
375.1	65.4	0.0120	325.1	45.5	0.0133
375.1	132.4	0.0245	324.9	94.4	0.0268
375.0	245.3	0.0442	325.0	172.9	0.0487
374.9	413.7	0.0737	325.1	291.2	0.0810
375.0	482.9	0.0866	325.0	336.5	0.0957
375.1	617.6	0.1093	325.0	430.9	0.1213

Calculation of the Gas Solubility. The amount of gas fed into the equilibrium cell and gas pump was calculated according to the measured temperature and pressure change of the gas bottle. The amount of absorbed gas was calculated from the pressure change in the equilibrium cell and gas pump. The solubility calculation procedure was the same as that by Wahlstrom,[11] and the detailed equation can be expressed as follows:

$$n_r = \frac{\left[\dfrac{V_{bottle}}{V_r^v(T_{beg},P_{beg})} - \dfrac{V_{bottle}}{V_r^v(T_{end},P_{end})} - \dfrac{V_{pump}}{V_r^v(T_{pump},P)} + \dfrac{V_{s,cell} - V_{cell}}{V_r^v(T,P)}\right]}{\left[1 - \dfrac{V_{abs,gas}}{V_r^v(T,P)}\right]} \tag{1}$$

where n_r is the moles of refrigerant (**1**, **2**) in squalane (**3**). V_{bottle}, V_{cell}, and V_{pump} are the volumes of the gas bottle, the equilibrium cell, and the gas pump, respectively. $V_{s,cell}$ is the volume of squalane in the cell, calculated from its mass and density.[14] The molar volume V_r^v of the vapor-phase refrigerant is calculated with Refprop7.0, where T and P are the equilibrium conditions of cell. T_{beg}, P_{beg} and T_{end}, P_{end} are the conditions of the gas bottle before and after gas injection. T_{pump} is the temperature of the gas pump at the equilibrium state. The molar volume $V_{abs,gas}$ of the absorbed refrigerant in squalane is the liquid molar volume of the gas at equilibrium conditions T and P, if liquid refrigerant exists during these conditions; otherwise, $V_{abs,gas}$ is the liquid molar volume at the bubble point at equilibrium temperature T, if T is below the critical temperature. The partial molar volume in the liquid phase at infinite dilution according to O'Connell[15] will be used as $V_{abs,gas}$ when T is higher than the critical temperature.

Results and Correlations

The experimental solubility data for the R134a (1) + squalane (3) and propane (2) + squalane (3) systems are summarized in Tables 2 and 3. The solubility data were correlated with the

Table 3. Mole Fraction Solubility of Propane (2) in Squalane (3)

T/K	P/kPa	x_2	T/K	P/kPa	x_2
400.1	92.9	0.0371	353.1	508.7	0.2883
400.1	119.2	0.0478	353.2	735.9	0.3852
400.0	155.3	0.0616	350.1	55.9	0.0406
399.9	307.4	0.1203	350.0	71.7	0.0523
399.9	490.3	0.1743	349.9	93.1	0.0673
400.1	639.1	0.2217	349.9	184.2	0.1304
400.0	823.9	0.2683	349.9	290.9	0.1893
400.1	1260.1	0.3728	350.1	380.1	0.2392
374.9	73.8	0.0388	350.1	490.7	0.2893
374.9	95.4	0.0499	350.0	699.2	0.3868
375.1	123.8	0.0643	325.0	38.9	0.0425
375.1	244.1	0.1252	325.1	50.2	0.0546
375.1	389.3	0.1813	324.9	65.0	0.0702
375.1	506.4	0.2302	324.9	127.8	0.1354
375.1	653.7	0.2784	325.1	202.7	0.1959
375.0	941.5	0.3735	325.1	261.3	0.2471
353.2	304.7	0.1882	325.0	337.8	0.2978
353.2	395.1	0.2383	325.0	477.0	0.3953

SRK equation of state using the classical van der Waals mixing rule, which can be expressed as:

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b)} \tag{2}$$

$$\text{with } a(T) = a(T_c)\alpha(T) = 0.42748\frac{R^2 T_c^{\,2}\alpha(T)}{P_c} \tag{3}$$

$$b = 0.08664\frac{RT_c}{P_c} \tag{4}$$

$$\alpha(T) = [1 + (0.48 + 1.574\varpi - 0.176\varpi^2)(1 - T_r^{\,0.5})]^2 \tag{5}$$

$$T_r = \frac{T}{T_c} \tag{6}$$

where T_c and P_c are the critical temperature and pressure and ϖ is the acentric factor.

The van der Waals mixing rules are applied as follows:

$$a = \sum_{i=1}^{2}\sum_{j=1}^{2} x_i x_j (a_i a_j)^{0.5}(1 - k_{ij}) \tag{7}$$

$$b = \sum_{i=1}^{2}\sum_{j=1}^{2} x_i x_j \left(\frac{b_i + b_j}{2}\right)(1 - l_{ij}) \tag{8}$$

The parameters k_{ij} and l_{ij} were obtained by minimizing the following objective function:

$$\text{AADP} = \frac{1}{N}\sum_{i=1}^{N}\left[\left|\frac{P_{i,\text{exptl}} - P_{i,\text{calcd}}}{P_{i,\text{exptl}}}\right|\right] \tag{9}$$

where N is the number of experimental points. P_{exptl} is the experimental pressure, and P_{calcd} is the calculated pressure. Because the saturation pressure of squalane is very small under the measurement conditions,[3] the mole fraction of squalane of the gas phase was assumed to be zero. The optimized values of the interaction parameters, k_{ij} and l_{ij}, for each isotherm and the average absolute deviation in estimating the bubble pressure, AADP, are summarized in Table 4. Figures 2 and 3 show the measured data and the correlated results of VLE data curves of the R134a + squalane and propane + squalane systems, respectively. The correlated results fit the data well. The absolute mean deviation and maximum deviation of measured pressures from the correlated results are 0.68 % and 2.8 % for the R134a + squalane system, respectively. For the propane + squalane system, the absolute mean deviation and maximum deviation of measured pressures from the correlated results are 1.0 % and 4.0 %, respectively. Figure 4 shows the pressure deviation of the calculated results of the propane + squalane system at 353.15 K from Diana's[6] data. The comparison shows that data from this work and from Diana's work are in good agreement. This also verifies the validation of this experimental rig. The absolute mean deviation and maximum deviation of correlated pressures in this work from Diana's results are 3.2 % and 7.2 %, respectively.

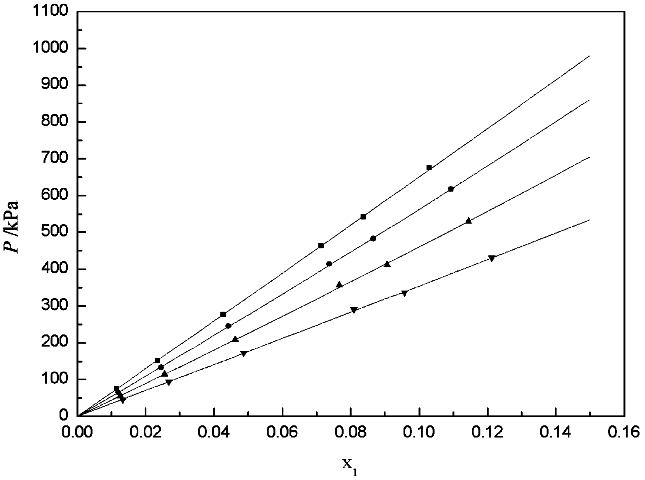

Figure 2. Experimental and calculated pressures for R134a (**1**) in squalane (**3**) at (325 to 400) K: □, 400 K; ●, 375 K; ▲, 350 K; ▼, 325 K; −, calculated with the SRK equation.

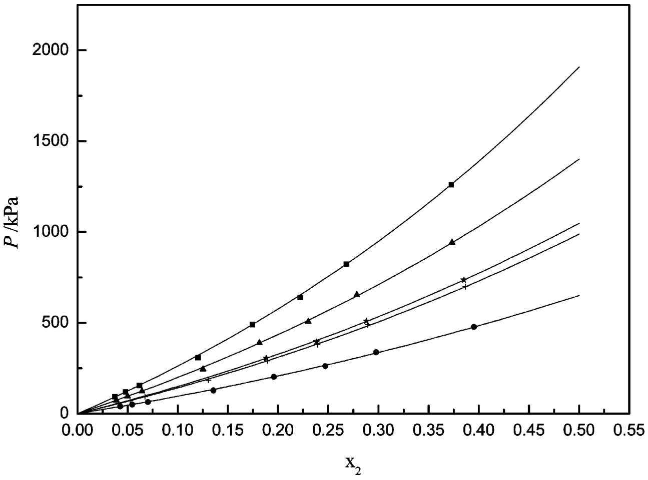

Figure 3. Experimental and calculated pressures for propane (**2**) in squalane (**3**) at (325 to 400) K: □, 400 K; ▲, 375 K; ★, 353.15 K; +, 350K; ●, 325 K; −, calculated with the SRK equation.

Table 4. Modeling Results of the Vapor−Liquid Equilibria

	R134a + squalane			propane + squalane		
T/K	k_{ij}	l_{ij}	AADP/%	k_{ij}	l_{ij}	AADP/%
325	0.1781	−0.0062	0.98	−0.0077	0.0139	1.06
350	0.1886	−0.0021	0.78	−0.0058	0.0156	1.02
353.15				−0.0022	0.01630	0.50
375	0.1718	−0.0043	0.56	−0.0034	0.0168	1.06
400	0.1141	−0.0159	0.42	0.0094	0.0209	1.07

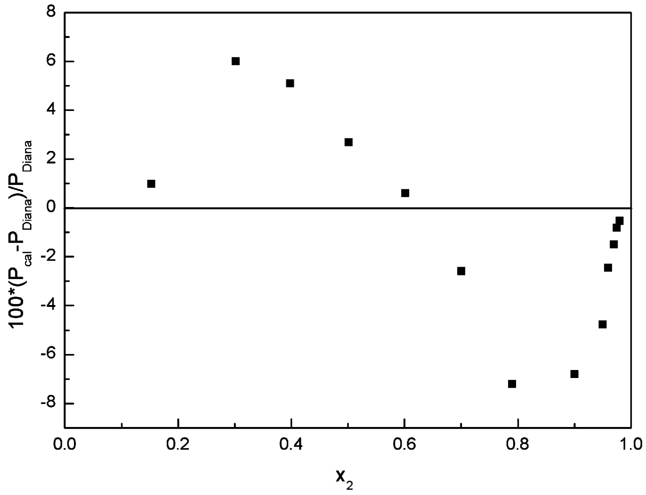

Figure 4. Pressure deviation of the calculated results of the propane (**2**) + squalane (**3**) system at 353.15 K from Diana's data.

Summary

An isochoric apparatus for solubility measurements of refrigerant + lubricant oil systems was designed, fabricated, and verified. The solubilities of R134a and propane in squalane from (325 to 400) K have been measured. The SRK equation of state with the classical van der Waals mixing rule was used to fit all the experimental solubility data with satisfactory accuracy.

Literature Cited

(1) Gong, M. Q.; Wu, J. F.; Luo, E. C.; Qi, Y. F.; Hu, Q. G.; Zhou, Y. Research on the change of mixture compositions in mixed-refrigerant Joule−Thomson cryocoolers. *Adv. Cryog. Eng.* **2002**, *47*, 881−887.

(2) Gong, M. Q.; Zhou, W.; Wu, J. F. *Composition shifts due to different solubility in the lubricant oil for multicomponent mixtures.* Proceedings of ICC14; Annapolis, MD, 2006 (in press).

(3) VonNiederhausern, D. M.; Wilson, G. M.; Giles, N. F. Critical Point and Vapor Pressure Measurements at High Temperatures by Means of a New Apparatus with Ultralow Residence Times. *J. Chem. Eng. Data* **2000**, *45*, 157−160.

(4) Chappelow, C. C.; Prausnitz, J. M. Solubilities of gases in high-boiling hydrocarbon solvents. *AIChE J.* **1974**, *20*, 1097−1104.

(5) Paas, R.; Alwani, Z.; Horvath, E.; Schneider, G. M. Phase equilibria and critical phenomena in fluid binary mixtures of 2,6,10,15,19,23-hexamethyltetracosane with methane and ethane up to 200 MPa. *J. Chem. Thermodyn.* **1979**, *11*, 693−702.

(6) Nanu, D. E.; Poot, W.; Geana, D.; de Loos, T. W. Fluid phase equilibria of binary *n*-alkane + squalane systems. *J. Chem. Eng. Data* **2003**, *48*, 571−575.

(7) Aalto, M.; Liukkonen, S. Bubble point pressure and densities for the binary systems of propane with triacontane, hexatriacontane, tetracontane, pentacontane, and squalane at 353−373 K and 4.00−7.00 MPa. *J. Chem. Eng. Data* **1996**, *41*, 79−83.

(8) Marteau, P.; Tobaly, P.; Ruffier-Meray, V.; de Hemptinne, J. C. High-pressure diagrams of methane + squalane and methane + hexatriacontane mixtures. *J. Chem. Eng. Data* **1998**, *43*, 362−366.

(9) Cukor, P. M.; Prausnitz, J. M. Apparatus for accurate, rapid determinations of the solubilities of gases in liquids at elevated temperatures. *Ind. Eng. Chem. Fundam.* **1971**, *10*, 638−640.

(10) Baruah, S.; Dutta, N. N.; Patil, G. S. Solubility of CO in 1,1,1-Trichloroethane, *N*,*N*-Dimethylacetamide, Dibutyl Phthalate, and Their Mixtures. *J. Chem. Eng. Data* **1992**, *37*, 291−293.

(11) Wahlstrom, A.; Vamling, L. Solubility of HFC32, HFC125, HFC134a, HFC143a, and HFC152a in a pentaerythritol tetrapentanoate ester. *J. Chem. Eng. Data* **1999**, *44*, 823−828.

(12) Zhu, H.; Gong, M.; Zhang, Y.; Wu, J. Isothermal Vapor−Liquid Equilibrium Data for Tetrafluoromethane + Ethane over a Temperature Range from (179.68 to 210.03) K. *J. Chem. Eng. Data* **2006**, *51*, 1201−1204.

(13) Lemmon, E. W.; Mclinden, M. O.; Huber, M. L. *NIST Reference Fluid Thermodynamic and Transport Properties (REFPROP)*, version 7.0; Physical and Chemical Properties Division, National Institute of Standards and Technology: Gaithersburg, MD, 2002.

(14) Fandino, O.; Pensado, A. S.; Lugo, L.; Comunas, M. J. P.; Fernandez, J. Compressed liquid densities of squalane and pentaerythritol tetra-(2-ethylhexanoate). *J. Chem. Eng. Data* **2005**, *50*, 939−946.

(15) Brelvi, S. W.; O'Connell, J. P. Corresponding states correlations for liquid compressibility and partial molar volumes of gases at infinite dilution in liquids. *AIChE J.* **1972**, *18*, 1239−1243.

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