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Vapor Pressures and Vapor−Liquid Equilibria of the 2,2,2-Trifluoroethanol + Quinoline System

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Both vapor pressures and vapor−liquid equilibria (VLE) of the 2,2,2-trifluoroethanol (TFE) + quinoline system, which can be considered as a potential candidate to overcome serious disadvantages of the existing working fluids used for absorption chillers, were measured in order to determine the allowable operation range of this organic mixture. Vapor pressures were measured by using the boiling point method in the temperature range of 293.15 K to 458.55 K and in the concentration range of (0.0 to 100.0) mass percent of TFE and were correlated with an Antoine-type equation. The resulting average absolute deviation (AAD) between the experimental and calculated values was found to be 2.22%. The isobaric VLE data of the 2,2,2-trifluoroethanol (TFE) + quinoline mixture were measured at three different pressures of (13.33, 53.33, and 101.33 kPa), and the thermodynamic consistency was checked by using the point test method.

Introduction

Most commercial absorption heat pumps commonly use water + lithium bromide or the ammonia + water mixture as a working fluid.[1] However, these conventional salt + water and ammonia + water fluids are known to have disadvantages such as corrosion and crystallization problems of the water + lithium bromide mixture and high working pressure and toxicity for the ammonia + water system.[2] Thus, it would be beneficial to examine new organic working pairs that are free of serious corrosion and crystallization problems. In this work, the 2,2,2-trifluoroethanol (TFE) + quinoline system was selected as a new organic pair as a potential replacement for the conventional ones,[1,3] where TFE will act as a refrigerant and quinoline as an absorbent. The most important criteria for this organic pair are its thermal and chemical stability, large boiling point difference, and good solubility of refrigerant in the absorbent.[2,4,5] TFE was found to have high stability and solubility as a refrigerant in quinoline. In addition, the boiling point difference between TFE and quinoline is about 164 K,[4,6] which is a suitable difference.

As a beginning to examine the suitability of the proposed TFE + quinoline pair, the vapor pressure and isobaric vapor−liquid equilibria (VLE) were measured and correlated using the adequate modeling equations. These basic data could be also very useful for developing an optimized absorption chiller cycle.

Experimental Section

Materials. The quinoline (98 mole percent, mol. wt.: 129.16, mp: 257.15 K, bp: 514.15 K) and 2,2,2-trifluoroethanol (99+ mole percent, mol. wt.: 100.04, mp: 229.65 K, bp: 350.15 K) were supplied by Aldrich Chemical Co. and used without any further purification.

Apparatus and Procedure. Vapor Pressure. The vapor pressures were measured by the boiling point method. The apparatus for vapor pressure measurement primarily consisted of an equilibrium vessel with an internal volume of 500 cm^3, a constant-temperature bath, a condenser, a U-tube mercury manometer capable of reading to 0.05 mm, a K-type thermocouple with the accuracy of ±0.05 K of reading, and two stirrers. A schematic diagram is shown in Figure 1. A sample solution of a desired absorbent concentration was prepared. The sample solution with an approximate volume of 250 cm^3 was placed in the vessel and evacuated to a proper degree of pressure. The sample solution was then heated and stirred well with a magnetic stirrer to prevent superheating. After thermal equilibrium was reached, the temperature of the sample solution and the pressure of the apparatus were measured.

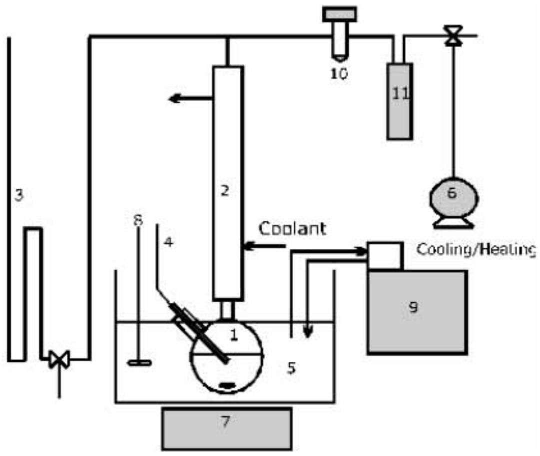

Figure 1. Experimental apparatus for vapor pressure measurements: 1, sample vessel; 2, condenser; 3, mercury manometer; 4, thermocouple; 5, bath; 6, vacuum pump; 7 and 8, stirrer; 9, circulator; 10, needle valve; 11, trap.

VLE Measurements. The apparatus is designed for the measurements of both atmospheric and low pressure VLE. The equipment and procedure were nearly the same as the one used in our previous investigation.[7] It is a recirculation type, in which both liquid and vapor are continuously recirculated, and allows the determination of the equilib-

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Table 1. Vapor Pressures of the TFE + Quinoline System at Various Concentrations and Temperatures

T	*P*	*T*	*P*
K	kPa	K	kPa
0.00 mass % of TFE		20.38 mass % of TFE	
408.35	6.60	343.45	6.93
423.45	11.60	363.85	16.73
434.25	15.60	376.75	29.26
443.65	23.46	390.25	51.06
450.75	26.93	399.15	74.39
458.55	33.06	407.25	97.79
40.40 mass % of TFE		60.65 mass % of TFE	
332.55	11.47	315.25	11.80
350.55	26.20	327.95	22.33
359.65	40.73	336.35	33.46
365.35	52.66	350.55	61.39
374.85	70.73	360.35	91.93
381.95	94.53	362.95	100.59
76.04 mass % of TFE		100.0 mass % of TFE	
312.75	17.53	293.15	7.19
326.95	33.66	297.85	9.52
330.45	42.46	312.15	20.92
338.15	57.26	322.95	36.00
346.45	84.99	328.45	46.60
351.15	100.79	343.15	88.34

rium compositions of both phases. The temperature in the equilibrium cell was measured with a resistance thermometer having an accuracy of ±0.1 K. The pressure was determined by measuring the difference in column height of the mercury in the arms of a mercury U-tube manometer. In the middle part of equilibrium cell, two glass siphon-effect tubes were provided to recirculate the liquid phase. Operating each needle valve above sampling ports of both phases enabled a successful sampling procedure at low pressure. Low-pressure states of the equilibrium cell were obtained with a vacuum pump. The pressure was kept constant by controlling the vacuum pump and needle valves. The accuracy of this control was found to be 2 mmHg.[7,8] Cooling water was continuously circulated through the condenser with a refrigerated bath circulator. The experiment was begun by feeding a liquid solution of approximately 100 mL into the equilibrium cell. The pressure was reduced by using a vacuum pump. When the pressure reached the desired value, the cell was heated by increasing the temperature of silicone oil with a power source. Once the liquid solution in the cell was boiling, the temperature of silicone oil was kept about (2 to 3) K higher than the boiling point in order to maintain steady boiling. When the equilibrium temperature was attained in the cell, the temperature was maintained for 2 h to ensure equilibrium conditions. After the confirmation of equilibrium state, a sample from each phase was taken in a short time under the same pressure with that of the equilibrium cell. The compositions of vapor and liquid phases were determined by gas chromatography on a HP 5890 series II apparatus with a flame ionization detector and capillary column (HP-1) coated with cross-linked methyl silicone gum. The oven, injector, and detector temperatures were held at 533.15 K.

Results and Discussions

Vapor Pressure. In general, the vapor pressure data were needed to analyze an absorption heat pump cycle along with the solubility data. The vapor pressures of the TFE + quinoline system were measured by using a boiling point method in the temperature range from 293.15 K to 458.55 K and in the concentration range from (0.0 to 100.0) mass percent of refrigerant (TFE). The experimental results are listed in Table 1, and these values were correlated with an Antoine-type equation which expresses vapor pressure as a function of temperature and concentration

Table 2. Values of Coefficients for Vapor Pressure at Various Temperatures and Concentrations by Eq

i	A_i	B_i
0	0.55161×10	-0.16778×10
1	0.17650	-0.38664×10^{-1}
2	-0.38964×10^{2}	0.10539×10^{-2}
3	0.23412×10^{-4}	-0.66875×10^{-5}

$$\log P = \sum_{i=0}^{3} [A_i + 1000B_i/(T - 43.15)]X^i \qquad (1)$$

where *P* is the vapor pressure in kPa, A_i and B_i are the regression parameters, *T* is the absolute temperature in K, and *X* is the concentration of refrigerant (TFE). The parameters A_i and B_i were determined by a least-squares method, and the results are shown in Table 2. The AAD between the experimental data and the calculated values was found to be 2.22% for this organic pair. These experimental and calculated results are plotted in Figure 2. This figure shows that the log *P* vs 1000/($T - 43.15$) relation at a given concentration appeared to be linear over the pressure and temperature ranges considered.

VLE Measurement. The vapor−liquid equilibrium data were measured for the TFE + quinoline system at three pressures of (101.33, 53.33, and 13.33) kPa. The experimental results were presented both in Figure 3 and in Tables 3−5. The binary VLE data were correlated using the Wilson[9] and the NRTL[10] models for liquid-phase activity coefficients. Both models can well describe the solutions of two miscible components and therefore predict the corresponding VLE behavior. The fugacity coefficients were calculated from the virial equation of state using the second virial coefficients estimated by the Hayden and O'Connell[11,12] method. The binary interaction parameters of each model were evaluated by a nonlinear regression method based on the maximum-likelyhood principle and summarized in Table 6 with the root-mean-squared deviations in *y* and *T*. Figures 3 shows the comparisons between the experimental and predicted values at each pressure. For all of the experimental data measured at three pressures, it is clear that the relative volatility of TFE increases as the pressure decreases. A thermodynamic consistency

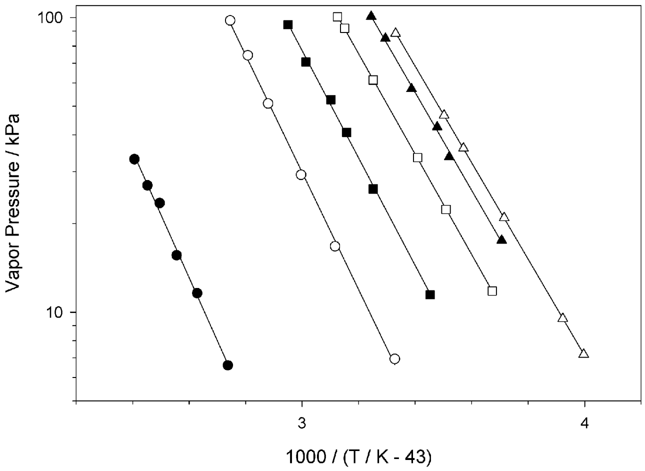

Figure 2. Vapor pressures for the TFE + quinoline system at various temperature and concentration conditions: ●, 0.00% TFE; ○, 20.38% TFE; ■, 40.40% TFE; □, 60.65% TFE; ▲, 76.04% TFE; △, 100.0% TFE.

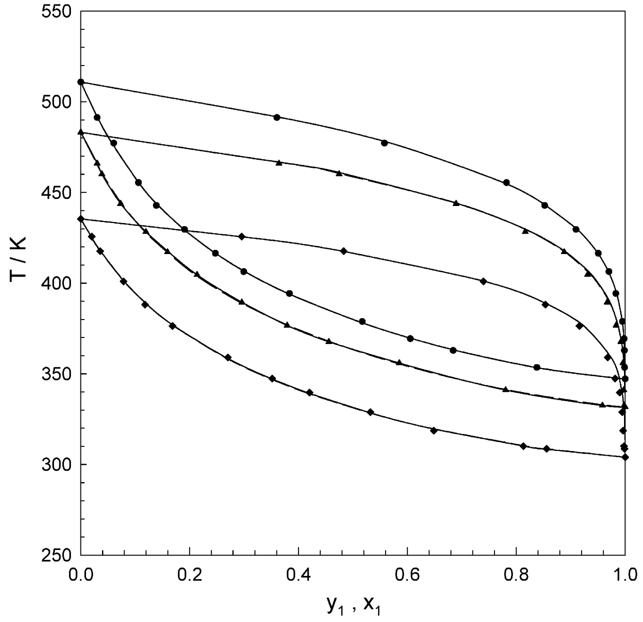

Figure 3. Vapor−liquid equilibria of the TFE (1) + quinoline (2) system: ●, 101.33 kPa; ▲, 53.33 kPa; ◆, 13.33 kPa; - - -, Wilson model; —, NRTL model.

Table 3. Measured VLE Data of TFE (1) + Quinoline (2) System at 101.33 kPa

T / K	x_1	y_1	T / K	x_1	y_1
347.15	1.0000	1.0000	416.45	0.2473	0.9506
353.55	0.8377	0.9990	429.55	0.1907	0.9098
362.85	0.6840	0.9985	442.85	0.1389	0.8521
369.35	0.6054	0.9980	455.45	0.1060	0.7822
378.85	0.5171	0.9951	477.25	0.0604	0.5581
394.25	0.3833	0.9829	491.25	0.0301	0.3602
406.35	0.2994	0.9704	510.85	0.0000	0.0000

Table 4. Measured VLE Data of TFE (1) + Quinoline (2) System at 53.33 kPa

T / K	x_1	y_1	T / K	x_1	y_1
331.75	1.0000	1.0000	404.55	0.2134	0.9310
332.55	0.9584	0.9982	417.15	0.1594	0.8882
341.05	0.7804	0.9974	428.25	0.1197	0.8166
355.95	0.5851	0.9961	443.85	0.0732	0.6893
367.65	0.4557	0.9922	460.15	0.0387	0.4744
376.65	0.3791	0.9834	466.05	0.0301	0.3641
389.45	0.2959	0.9670	483.15	0.0000	0.0000

Table 5. Measured VLE Data of TFE (1) + Quinoline (2) System at 13.33 kPa

T / K	x_1	y_1	T / K	x_1	y_1
304.05	1.0000	1.0000	359.05	0.2701	0.9680
308.65	0.8556	0.9989	376.35	0.1686	0.9159
310.15	0.8133	0.9978	388.15	0.1180	0.8536
318.65	0.6484	0.9965	400.95	0.0784	0.7397
328.85	0.5318	0.9945	417.65	0.0356	0.4829
339.65	0.4201	0.9900	425.65	0.0202	0.2957
347.45	0.3517	0.9817	435.45	0.0000	0.0000

test was applied to the experimental data by using the point test of Fredenslund et al.[11,12] The mean deviations between the experimental and calculated values of the vapor-phase mole fractions were less than 1.5% at all pressure conditions, which confirmed that the present VLE data satisfied the test for thermodynamic consistency.

Table 6. Results of the Correlation with the Wilson and the NRTL Models for TFE + Quinoline System at Three Pressure Conditions of 101.33, 53.33, 13.33 KPa

P / kPa	model	parameters	ΔT_{rms}	Δy_{rms}
101.33	Wilson	$\Delta\lambda 12 = -1.4977 \times 10^3$ $\Delta\lambda 21 = -2.3732 \times 10^3$	4.05×10^{-1}	7.41×10^{-5}
	NRTL	$\Delta g12 = 1.1523 \times 10^1$ $\Delta g21 = -3.9512 \times 10^3$ $\alpha = 0.3$	3.75×10^{-1}	6.60×10^{-5}
53.33	Wilson	$\Delta\lambda_{12} = -1.8557 \times 10^3$ $\Delta\lambda_{21} = -2.4996 \times 10^3$	2.88×10^{-1}	9.75×10^{-5}
	NRTL	$\Delta g_{12} = -2.5469 \times 10^2$ $\Delta g_{21} = -4.2469 \times 10^3$ $\alpha = 0.3$	2.87×10^{-1}	7.32×10^{-5}
13.33	Wilson	$\Delta\lambda_{12} = -1.7645 \times 10^3$ $\Delta\lambda_{21} = -3.4293 \times 10^3$	4.16×10^{-1}	5.05×10^{-5}
	NRTL	$\Delta g_{12} = -1.6676 \times 10^3$ $\Delta g_{21} = -3.8090 \times 10^3$ $\alpha = 0.3$	3.39×10^{-1}	1.64×10^{-4}

Conclusions

The binary organic pair of the TFE + quinoline mixture was proposed as a new potential working fluid for an air-cooled absorption heat pump (cooling or absorption chiller). For the proper cycle analysis, both vapor pressures and VLE were accurately measured over wide concentration and temperature ranges. The data set for vapor pressure was fitted with an Antoine-type equation, and the VLE data were compared with the calculated values using the Wilson and NRTL equations. Both were found to agree with the VLE data.

Acknowledgment

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