Solubility of 1,1,1,2-Tetrafluoroethane in Triethylene Glycol Dimethyl Ether

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The solubility of 1,1,1,2-tetrafluoroethane in triethylene glycol dimethyl ether was measured by the static method in the temperature range (283.15 to 353.15) K. Triethylene glycol dimethyl ether was completely miscible with 1,1,1,2-tetrafluorethane in the range of temperatures and pressures studied. All experimental solubility data were correlated by the five-parameter NRTL equation with a very small overall average absolute deviation. This binary system exhibited large negative deviations from Raoult's law.

Introduction

At present, few working fluid combinations such as ammonia + water and water + lithium bromide are used in vapor absorption systems. These combinations have a number of inherent drawbacks (e.g. toxicity of ammonia, crystallization, corrosion, and low pressures of LiBr aqueous solutions). With the use of the fluorocarbon-based refrigerant−organic absorbent combinations in vapor absorption systems, most of the above drawbacks can be overcome.

Hydrochlorofluorocarbon-type refrigerants cause atmospheric environment damage, and their uses have been considerably restricted and will be banned. Refrigerant HFC-134a (1,1,1,2-tetrafluoroethane) is currently the leading substitute for CFC-12 and HCFC-22 as a working fluid in refrigeration and heat pump systems. There have been a number of papers published on the thermophysical properties of HFC-134a.[1−4]

However, replacing these refrigerants with HFC-134a does require different lubricants, which are readily miscible with HFC-134a in order to utilize traditional positive displacement-type compressors. As pointed out by Preisegger and Henrici,[5] none of the usual oils are suitable as lubricants with HFC-134a because of poor miscibility. Polyalkylene glycols and polyalkylene glycol dimethyl ethers have been used as lubricants for HFC-134a.[5,6] However, the thermophysical properties of the mixtures HFC-134a + polyalkylene glycol dimethyl ethers are very scarce. Tseregounis and Riley[6] reported solubility data of HFC-134a in tetraethylene glycol dimethyl ether. Phase equilibrium data related to mixtures of HFC-134a + polyalkylene glycol dimethyl ethers are needed to obtain group interaction parameters in the UNIFAC model between the F group and the CH_2O group (including the CH_3O group). In this work, the solubility data of HFC-134a in triethylene glycol dimethyl ether were measured by a static method from (283.15 to 353.15) K. These experimental solubility data were used to determine activity coefficients of HFC-134a in triethylene glycol dimethyl ether. The data were correlated by the five-parameter NRTL activity coefficient model.

Experimental Section

Materials. HFC-134a (1,1,1,2-tetrafluoroethane), CF_3CH_2F (DuPont, >99.9% in mass), and TrEGDME (triethylene glycol dimethyl ether, $CH_3O(CH_2CH_2O)_3CH_3$ (Aldrich, 99+%) were used without further purification. They were carefully degassed by several freezing and thawing cycles. TrEGDME was stored over type 4A molecular sieves before use.

Apparatus. The solubility of HFC-134a in TrEGDME was measured by a static method. The apparatus has been described previously.[7,8] It consists of an equilibrium cell, a double-walled thermostat bath with a 25 L capacity filled with water, a differential pressure null transducer (DPT) (Ruska Model 2439-702), a precise pressure controller (Ruska Model 3891-801), and two Haake proportional temperature controllers (a Haake F6 unit for heating and an immersion cooler Haake EK90 for cooling) for the bath. The temperature in the bath was controlled to better than ±0.01 K. A new cell, designed for measurements at high pressure, was made of stainless steel with a volume of 149 cm^3. The measuring systems are as follows: two digital pressure gauges (Ruska Model 6222 for pressures up to 130 kPa and up to 1 MPa and Ruska Model 6220-750 for pressure above 10 bar), a digital precision thermometer (Anton Paar MKT100), and a Mettler balance (Mettler Toledo PR2003DR). The molar fraction, temperature, and pressure uncertainties were $\Delta x = \pm 0.0001$ mol, $\Delta T = \pm 0.01$ K, and $\Delta P = \pm 0.05$ kPa for pressures lower than 130 kPa, ±0.3 kPa up to 1 MPa, and ±0.6 kPa for higher pressures.

Procedure. The experimental procedure for solubility measurement is also similar to that used in our previous VLE measurements.[7−10] It included the loading of the sample, the measurement of the vapor pressure, and the accurate calculation of the cell volume, as described by Esteve et al.[7] However, due to the HFC-134a nature, the procedure to charge the equilibrium cell differs from that of the usual liquid mixtures. An auxiliary stainless vessel was used for preparing the mixture with a fixed composition. The equilibrium cell was filled with a known mass of TrEGDME and then with a known mass of HFC-134a refrigerant through the auxiliary vessel. By weighing the auxiliary vessel before and after each charging, the exact mass of HFC-134a in the system was determined.

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Table 1. Experimental Vapor Pressure, Solubility (Liquid Mole Fraction), and Activity Coefficients of HFC-134a in TrEGDME at Several Temperatures

x_1	P/kPa	γ_1	x_1	P/kPa	γ_1
T = 283.15 K			T = 323.15 K		
0.1083	24.89	0.6004	0.0927	83.73	0.7885
0.2015	48.33	0.6484	0.1964	186.0	0.8185
0.2952	75.44	0.6993	0.2890	284.5	0.8462
0.3982	112.11	0.7572	0.3670	372.2	0.8697
0.4797	145.7	0.8035	0.4501	476.8	0.8945
0.5440	174.8	0.8394	0.5410	602.6	0.9207
0.5937	198.1	0.8664	0.5919	676.2	0.9346
0.6910	256.1	0.9155	0.6844	821.4	0.9578
0.7962	311.1	0.9597	0.7898	981.7	0.9797
0.9031	363.2	0.9901	0.9004	1136.2	0.9950
T = 293.15 K			T = 333.15 K		
0.1052	36.19	0.6463	0.0887	103.49	0.8376
0.2005	72.12	0.9808	0.1947	239.4	0.8611
0.2941	110.40	0.7365	0.2869	365.3	0.8822
0.3923	160.3	0.7857	0.3562	463.9	0.8981
0.4742	206.2	0.8269	0.4395	595.5	0.9172
0.5434	249.0	0.8608	0.5402	772.3	0.9394
0.5933	281.4	0.8845	0.5915	865.5	0.9501
0.6897	356.0	0.9268	0.6822	1041.5	0.9674
0.7950	429.9	0.9651	0.7874	1245.5	0.9842
0.9026	499.9	0.9914	0.8995	1439.7	0.9961
T = 303.15 K			T = 343.15 K		
0.1016	49.79	0.6929	0.0840	124.52	0.8877
0.1994	101.91	0.7334	0.1928	301.4	0.9038
0.2927	156.6	0.7734	0.2846	459.1	0.9180
0.3852	219.5	0.8138	0.3446	563.6	0.9274
0.4675	281.4	0.8496	0.4280	725.8	0.9405
0.5426	343.5	0.8815	0.5395	969.2	0.9575
0.5928	387.8	0.9018	0.5914	1087.3	0.9650
0.6883	481.3	0.9376	0.6797	1296.0	0.9768
0.7935	578.8	0.9702	0.7848	1547.5	0.9886
0.9020	671.6	0.9927	0.8985	1794.6	0.9972
T = 313.15 K			T = 353.15 K		
0.0976	65.72	0.7403	0.0794	146.3	0.9388
0.1980	140.0	0.7759	0.1908	371.3	0.9465
0.2910	214.2	0.8099	0.2823	565.2	0.9536
0.3767	290.4	0.8417	0.3325	669.2	0.9577
0.4595	371.6	0.8721	0.4157	865.3	0.9647
0.5419	460.8	0.9014	0.5392	1192.6	0.9751
0.5923	517.9	0.9185	0.5917	1335.3	0.9794
0.6865	635.8	0.9479	0.6775	1585.5	0.9860
0.7918	761.6	0.9750	0.7822	1891.8	0.9930
0.9013	882.7	0.9939	0.8976	2203.3	0.9983

Results and Discussion

Data Reduction. The performance of the apparatus along with the new cell were checked by measuring the vapor pressure of HFC-134a from (283.15 to 353.15) K. Our measured vapor pressure data were compared with the very accurate correlation values of Shubert and Ely,[4] yielding an overall absolute average deviation of 0.28%. The data reduction from the initial composition of the sample and measured vapor pressure and temperature was described by Herraiz et al.[9] The liquid molar volumes for each compound were calculated from the density−temperature correlations.[4,11] For HFC-134a, the critical temperature, volume, and pressure and the acentric factor were taken from ref 12. The second virial coefficients of HFC-134a at different temperatures were calculated by the modified Tsonopoulos correlation of Weber.[12] The critical properties for TrEGDME were estimated by the method of Constantinou and Gani.[13] The vapor pressure data for TrEGDME from (273.15 to 473.15) K were taken from Clariant GmbH[14] and were fitted to the following Antoine equation:

$$\ln(P/\text{kPa}) = 16.501 - 5549.4/(T/\text{K} - 24.834) \tag{1}$$

The standard deviation of this fitting is 0.08 kPa.

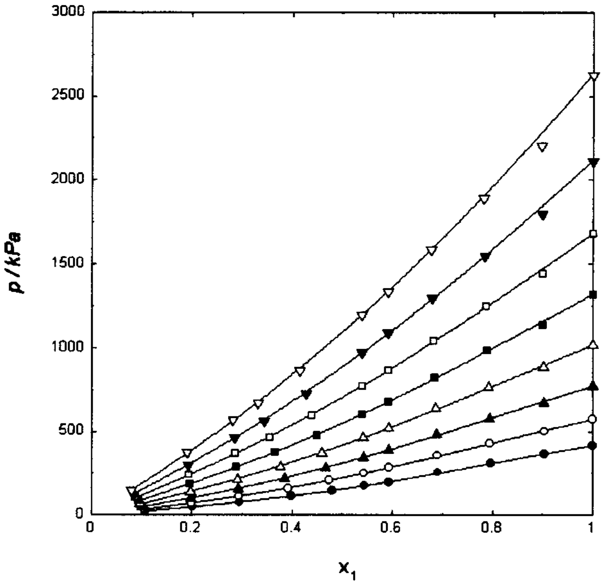

Figure 1. Solubility of HFC134a in TrEGDME as a function of temperature and pressure: (●, 283.15 K; ○, 293.15 K; ▲, 303.15 K; △, 313.15 K; ■, 323.15 K; □, 333.15 K; ▼, 343.15 K; ▽; 353.15 K) experimental data; (—) calculated by the NRTL equation.

For correcting the liquid composition at equilibrium and determining the solubility of HFC-134a in TrEGDME, the following assumptions were made: the vapor phase was assumed to be pure HFC-134a because the vapor pressure of TrEGDME was negligible; the virial equation truncated after the second virial coefficient was used to describe the nonideal behavior of HFC-134a in the vapor phase; the temperature-dependent five-parameter NRTL equation was used to calculate the excess Gibbs free energy function, G^E, from which the activity coefficient of HFC-134a, $\gamma_1(x_1,T)$, was determined.

$$\ln \gamma_i = x_j^2\left[\tau_{ji}\left(\frac{G_{ji}}{x_i + x_j G_{ji}}\right)^2 + \frac{\tau_{ij}G_{ij}}{(x_j + x_i G_{ij})^2}\right] \tag{2}$$

where

$$\tau_{ij} = \frac{C_{ij}}{RT} \tag{3}$$

$$G_{ij} = \exp(-\alpha\tau_{ij}) \tag{4}$$

$$C_{ij} = C_{ij}^{C} + C_{ij}^{T}(T/\text{K} - 273.15) \tag{5}$$

On the basis of the above reduction procedure, the solubility and activity coefficients of HFC-134a in TrEGDME at several pressures were obtained in the temperature range (283.15 to 353.15) K. The solubility, expressed as molar fraction, and the activity coefficients are given in Table 1. Figure 1 shows the solubility of HFC-134a as a function of temperature and pressure.

Data Correlation. Solubility data of HFC-134a in TrEGDME were correlated simultaneously by the NRTL equation. The parameters of the NRTL equation were determined by minimizing the following objective function

$$\text{OF} = \sum_{i=1}^{\text{NP}} \left|\frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}}\right|_i \tag{6}$$

where NP is the number of experimental data points and P is the pressure. The subscripts exp and cal correspond

Table 2. NRTL Parameters for the HFC-134a + TrEGDME System and Objective Function Values

	C^C_{12}	C^T_{12}	C^C_{21}	C^T_{21}		
	J mol^{-1}	J mol^{-1} K^{-1}	J mol^{-1}	J mol^{-1} K^{-1}	α	OF
NRTL	−4042.3	1.8148	1696.3	17.939	−0.12	0.0147

to the experimental and calculated values, respectively. The NRTL equation parameters and the objective function value are given in Table 2. The difference between the experimental and the calculated values from the NRTL equation are shown in Figure 1. The overall average relative deviation for the pressure was less than 1%.

Figure 1 indicates that, at a fixed pressure, the solubility of HFC-134a falls with increase in temperature, while the vapor pressure increases (at a fixed composition) especially in the high solubility region. Table 1 shows that all activity coefficients of HFC-134a under the experimental conditions are less than 1. With the decreases of temperature and solubility of HFC-134a, the logarithm of the activity coefficient of HFC-134a becomes more negative. It indicates that the studied system exhibits a negative deviation from Raoult's law. Figure 1 also shows that there is no phase separation of he HFC-134a + TrEGDME system within the temperature and pressure ranges studied.

Conclusions

The solubility of HFC-134a refrigerant in TrEGDME from (283.15 to 353.15) K has been determined. The five-parameter NRTL temperature-dependent equation was used to fit all the experimental solubility data with a satisfactory accuracy. These data indicate that this binary system has large negative deviations from Raoult's law. The logarithm of activity coefficients of HFC-134a becomes more negative with the decrease in temperature and increase in the mole fraction of TrEGDME.

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