Solid−Liquid Equilibria for the Carbon Dioxide + 1,1-Tetrafluoroethane and Nitrous Oxide + 1,1-Tetrafluoroethane Systems

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A recently built experimental setup was employed for the estimation of the solid−liquid equilibria of alternative refrigerant systems. The behavior of two binaries, i.e., carbon dioxide + 1,1-tetrafluoroethane (CO_2 + R134a) and nitrous oxide + 1,1-tetrafluoroethane (N_2O + R134a), was measured down to temperatures of 142 K. The triple points of CO_2 and N_2O were measured to confirm the reliability of the apparatus. The triple point of R134a was also measured; however, the pressure at the triple point for this fluid was too low to be accurately measured with the current apparatus. All triple point data measured revealed a generally good consistency with the literature. The results obtained for the mixtures were interpreted by means of the Schröder equation.

Introduction

Natural gases such as carbon dioxide and nitrous oxide are considered interesting options as refrigerants for low-temperature applications. In addition, their combination with hydrofluorocarbons (HFCs) offers a possible solution as working fluids for cascade cycle units. The main limitation of these binary systems lies on the lowest-temperature limit at which the refrigerant may circulate in the fluid state.

The data on solid−liquid equilibria (SLE) are important in defining the lowest application limit of the systems. In addition, SLE provide theoretical information on the behavior of studied systems at low temperatures in terms of activity coefficients. However, in fact, the SLE for HFC refrigerants are extremely scarce in the literature.

At very low temperatures (down to about 142 K), SLE measurements generally create difficulties in the visual observation of the disappearance of the last amount of solid phase. Hence, a setup was specifically built[1] avoiding the need for the visual observation of phase behavior. Recently, the SLE of the CO_2 + R125 (pentafluoroethane) and N_2O + R125 systems,[1] CO_2 + N_2O, CO_2 + R32 (difluoromethane) and N_2O + R32 systems,[2] and CO_2 + R152a (1,1-difluoroethane) and N_2O + R152a[3] were studied. In this paper, the system's behavior was measured down to temperatures of 142 K for two binaries, i.e., CO_2 + R134a and N_2O + R134a. No information on the SLE of both systems is available in the literature.

Description of the Apparatus

Measurement Cell. The experimental setup is shown in Figure 1. It is the same as that already described elsewhere,[1,2] so it will be only shortly described here. The measuring cell (1), with a volume of approximately 47 cm^3, was made out of a stainless steel cylinder. A stirrer (3), consisting of a stainless steel rod having a rounded end with two steel blades welded onto it, was placed in the cell. The purpose of the stirrer was to prevent any premature stratification of the fluids comprising the various mixtures, while also assuring a greater homogeneity during the liquefaction and crystallization of the mixture. The stirrer inside the cell was turned by a magnet (4), which drives the plate welded onto the lower end of the rod and shaped so as to follow the bottom of the cell as faithfully as possible. Two holes were made in the cover, and a stainless steel tube was inserted through and welded to the first hole for charging the cell with gas. The second hole was used to contain the thermometer (2). The magnet was housed in a seat made of brass, which was connected to the shaft of an electric engine (5) driving the rotation of the magnet and thus also of the stirrer inside the cell.

The cooling system globally included four parts:

1. A coil consisting of a copper tube, placed inside a Dewar filled with liquid nitrogen (6), which absorbs heat from the carrier fluid (compressed air) flowing inside it.
2. A coil with the same structural features as above, wrapped around the measuring cell and removing heat from the cell by surface contact due to the cold air circulating inside it. The assembly consisting of the coil and the cell, suitably coated with neoprene, was placed inside a second Dewar (7) so as to increase its thermal isolation.
3. A double pipe heat exchanger (8): the diameter of the tubes was 6 mm for the inner tube and 16 mm for the outer tube. A flow of air at room temperature entered the exchanger's inner tube, and as it moved through the tube, it was cooled by the backflow heat exchange with the cold air leaving the coil wrapped around the measuring cell. The carrier fluid can thus be precooled, enabling a considerable saving of liquid nitrogen consumption.
4. An ice trap (9) consisting of a copper base to ensure the stratification on the inside walls of the ice that forms after the liquefaction and subsequent solidification of the humidity in the carrier fluid circulating in the first coil.

A dry air supplier (10) was installed to overcome any problems relating to air humidity, which would have interfered with its free flow inside the coils, especially at the low temperatures.

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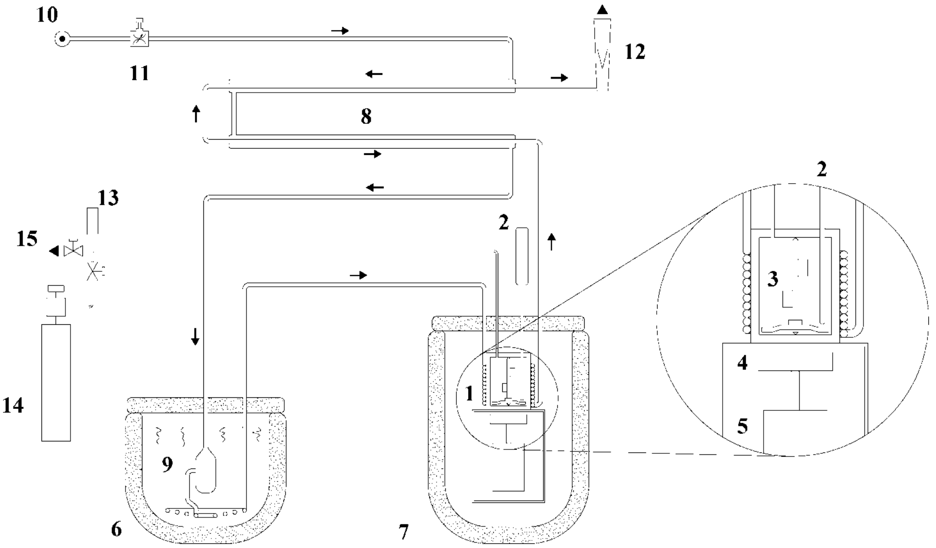

Figure 1. Schematic illustration of the apparatus. Notation: 1, measurement cell; 2, platinum resistance thermometer; 3, stirrer; 4, magnet; 5, electric engine; 6, Dewar with liquid nitrogen; 7, Dewar containing the measurement cell; 8, double pipe heat exchanger; 9, ice trap; 10, dry air supplier; 11, mass flow controller; 12, rotameter; 13, pressure trasducer; 14, charging bottle; 15, vacuum pump system.

A mass flow control was installed upstream from the dehumidifier (11). The airflow was also measured by a rotameter (12).

An absolute pressure transducer (HBM, model P8A) (13) was installed in the charging tube.

Temperature Measuring Systems. To monitor the temperatures, the apparatus was equipped with one thermoresistance put in the measuring cell. The system parameters and the efficiency of the regenerative exchanger and of the coil immersed in the liquid nitrogen were assessed using thermocouples at specific points on the copper tube. The platinum resistance thermometer used in the apparatus (100 Ω, Minco, model S7929) was calibrated by comparison with a 25 Ω platinum resistance thermometer (Hart Scientific, model 5680 SN1083).

Experimental Procedure and Uncertainties

Experimental Procedure. The charging procedure consisted of the following steps: the bottle containing the first fluid was weighed on the electronic balance; then the bottle was connected to the apparatus and a vacuum was created inside the measuring cell and the charging tube; then the fluid was charged by opening the valve on the gas bottle; the temperature of the cell was brought down by a flow of compressed air cooled with liquid nitrogen so as to insert the whole mass in the cell, leaving as little as possible in the charging tube; a suitable time interval was allowed so that the pressure, being lowered by the temperature reduction, could drop to below atmospheric pressure; then the on/off valve was closed; the gas bottle was disconnected and weighed again to establish the actual mass charged in the cell. The same procedure was repeated for the second fluid.

The air was cooled by putting the coil inside a Dewar filled with liquid nitrogen. The coil was then wrapped around the measuring cell. During the measurement procedure, the temperature of the sample inside the cell was carefully controlled to fall at a uniform rate by the air flowing inside the coil. Monitoring the time dependence of the temperature, a cooling curve was obtained for each sample concentration. While the change of phase occurs, the heat removed by cooling is compensated by the latent heat of the phase change. The arrest in cooling during solidification allows the melting point of the material to be identified on the time−temperature curve. To give a phase diagram, the melting points can be plotted versus the composition.

Uncertainties. All the uncertainties were calculated using the law of error propagation, as reported elsewhere.[1] Here, the previously reported results will be briefly summarized.

The total uncertainty of the mass of a sample mixture was less than ± 0.01 g. The uncertainty in composition measurements was estimated to always be lower than 0.005 in mole fraction.

The total uncertainty for the temperature, using the law of error propagation, was calculated to be less than ± 0.023 K.

Experimental Results

Chemicals. Carbon dioxide and nitrous oxide were supplied by Sol SpA. Their purity was checked by gas chromatography, using a thermal conductivity detector, and was found to be 99.99 % for both fluids, basing all estimations on an area response. R134a was donated by Ausimont Spa of Italy, and its purity was found to be 99.98 % on an area response.

Pure Fluids. For carbon dioxide and nitrous oxide, results are presented elsewhere.[2] The tests conducted showed that a faster cooling rate coincided with a greater supercooling effect. The cooling rate that seemed to guarantee the greatest repeatability of the results was approximately $-0.01\ \mathrm{K \cdot s^{-1}}$, corresponding to an air flow rate of approximately $0.17\ \mathrm{dm^3 \cdot s^{-1}}$. For both pure fluids, a metastable phase appeared. Triple-point measurements presented a good agreement with literature sources, in terms of both temperature and pressure.[2]

For R134a, the metastable phase was not appearing during the measurements, and only a change of slope was evident in the temperature−time diagram. The triple-point temperature was measured to be 169.7 K, in agreement with the literature data[4] that report a triple point of 169.85 K.

Results for Mixtures. Measurements were taken using different concentrations of the two components, obtaining a satisfactory number of points, which were then recorded on a concentration/temperature graph (T−x).

Conducting several tests on the same sample, we noted that we obtained better, more reliable results by switching off the

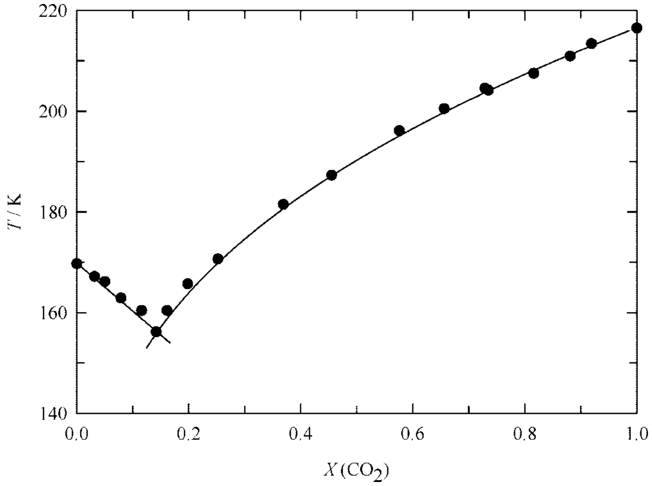

Figure 2. SLE for the CO_2 + R134a system. Black symbols denote the experimental points, while the lines denote the Schröder equation.

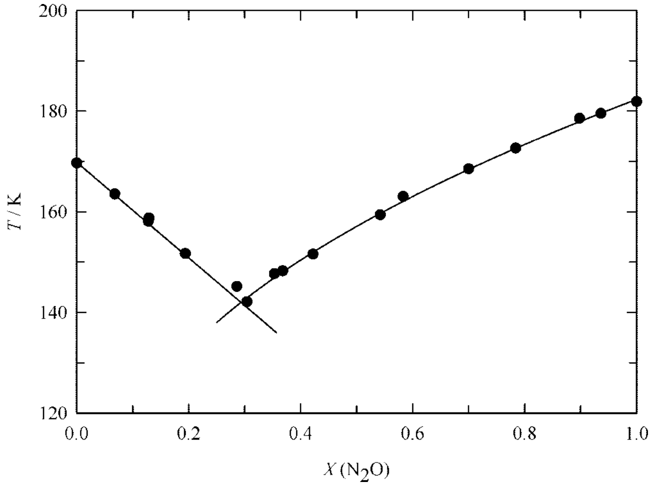

Figure 3. SLE for the N_2O + R134a system. Black symbols denote the experimental points, while the lines denote the Schröder equation.

stirrer before reaching the triple-point temperature, at least about (20 to 40) K.

The $T-x$ measurements for the two mixtures considered (CO_2 + R134a and N_2O + R134a, respectively) are given in Figures 2 and 3. The results were also summarized in Table 1. From the $T-x$ data, it is evident that both systems form eutectics ($x(CO_2) = 0.14$ at $T = 156$ K for CO_2 + R134a and $x(N_2O) = 0.30$ at $T = 142$ K for N_2O + R134a).

Since the measured vapor pressure data were not accurately measured at very low temperatures within the declared precision of the used instrument (the pressure values were acquired by an absolute pressure transducer HBM, model P8A, and the global uncertainty of the pressure measurements was estimated to be less than ± 3 kPa),[3] the vapor pressure data were not reported in the present paper.

Rossini Method Corrections. The results of the temperature data acquisitions were corrected using the Rossini method[5] because a constant cooling rate is not indispensable and was not guaranteed by our experimental method. This graphic method is illustrated elsewhere.[1-3] The entity of the corrections takes into account the fact that the fluid is still in a liquid state during the metastable state (supercooling) that precedes proper solidification. In this phase, the temperature is distinctly lower than the one characterizing the instant when crystallization begins, its amplitude depending mainly on the rate at which the temperature is lowered. The resulting corrections were nonetheless always very limited, of the order of a few tenths of a Kelvin in the majority of cases, and always well below 1 K.

Table 1. $T-x$ Measurements for the CO_2 + R134a and N_2O + R134a Binary Systems

CO_2 (1) + R134a (2)		N_2O (1) + R134a (2)	
x_1	T/K	x_1	T/K
0.000	169.70	0.000	169.70
0.032	167.18	0.068	163.52
0.050	166.18	0.128	158.13
0.079	162.91	0.129	158.76
0.116	160.43	0.194	151.71
0.142	156.18	0.286	145.17
0.161	160.43	0.304	142.15
0.198	165.70	0.353	147.69
0.252	170.66	0.368	148.25
0.369	181.50	0.422	151.59
0.455	187.29	0.542	159.41
0.576	196.14	0.583	163.05
0.656	200.52	0.700	168.54
0.729	204.56	0.784	172.65
0.735	204.19	0.898	178.57
0.816	207.54	0.936	179.55
0.881	210.93	1.000	181.90
0.919	213.41		
1.000	216.52		

Interpretation of the Results

As both systems formed eutectics, the solubility of the solid solute (CO_2 and N_2O in our case) in the solvent (here, R134a) can be described by the Schröder equation, known since the end of the 19th century.[6] The present equation takes the following form

$$\ln \gamma_2 x_2 = -\frac{\Delta h_m}{RT}\left(1 - \frac{T}{T_m}\right) \qquad (1)$$

where the subscript 2 denotes the solute and the subscript m denotes property at the melting point. Assuming as a first approximation that the solute's activity coefficient $\gamma_2 = 1$, we can write

$$\ln x_2 = -\frac{\Delta h_m}{RT}\left(1 - \frac{T}{T_m}\right) \qquad (2)$$

This simplification leads to the consideration that the solubility of the solid solute is independent of the solvent as far as the assumptions hold. The enthalpies at melting point (Δh_m) were assumed to be $9020\ \text{J}\cdot\text{mol}^{-1}$[7] and $6540\ \text{J}\cdot\text{mol}^{-1}$,[7] for CO_2 and N_2O, while for R134a, since no data were available in the open literature, the enthalpy was estimated fitting the experimental data. Adopting both binary system results, the optimal value of the enthalpy at melting point for R134a was estimated to be $(2500 \pm 500)\ \text{J}\cdot\text{mol}^{-1}$.

The course of the liquidus calculated with the Schröder equation is included in Figures 2 and 3. Both systems well followed the Schröder equation. For the CO_2 + R134a system, a good agreement with the equation prediction was evident. For this binary system, the equation prediction was generally lower than the experimental data of about (1 to 2) K, especially near the eutectic. For the N_2O + R134a system, a good agreement with the Schröder equation was evident.

Conclusion

The SLE behavior of CO_2 + R134a and N_2O + R134a was measured down to temperatures of 142 K. The triple points of the R134a were measured to check the reliability of the new apparatus, revealing a good consistency with the literature. The apparatus enabled us to record temperature and composition data. The CO_2 + R134a and N_2O + R134a systems showed the presence of a eutectic ($x_1 = 0.14$ at $T = 156$ K for CO_2 + R134a and $x_1 = 0.30$ at $T = 142$ K for N_2O + R134a) and of a generally good agreement with Schröder equation prediction.

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