isooctane of 544 K means that our highest temperature data near 525 K will show the effect of an increasingly compressible liquid. This effect, which is barely discerned on an enlarged version of Figure 3, is pronounced in Figure 7.

Finally, Figure 8 compares our liquid ethylcyclohexane measurements with those of Huffman et al. (*19*) and of Parks et al. (*20*) below 320 K. While our measurements are at higher temperatures, the alignment appears reasonable with our 20-bar line.

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Isobaric Heat Capacity Data for Liquid HFC-134a

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The isobaric heat capacity, C_p, of liquid HFC-134a, which is a prospective alternative to CFC-12, has been measured by using a flow calorimeter. The values of 31 C_p have been determined at temperatures from 276 to 356 K and pressures from 1.0 to 3.0 MPa. The uncertainty was estimated to be within ±10 mK in temperature, ±3 kPa in pressure, and ±0.3% in C_p, respectively. The C_p of saturated liquid, C_p', has been determined on the basis of the data measured in the compressed liquid phase, and a correlation of C_p' has also been developed.

Introduction

Chlorofluorocarbons (CFCs) have been widely used as working fluids for heat pump systems and refrigerators. The ozone depletion and global warming by CFCs is becoming a very important issue, and it is our urgent task to develop and apply stratospherically safe CFC alternatives. Tetrafluoroethane, CH_2FCF_3 (HFC-134a), is one of the prospective alternatives to CFC-12, which has been widely used as a blowing agent and working fluid of domestic refrigeration systems.

This paper reports the isobaric heat capacity data of liquid HFC-134a and a correlation for the heat capacity of the saturated liquid. The purity of HFC-134a used in this study was 99.97 wt %.

Experimental Section

The detailed description regarding the flow calorimeter has been reported in our previous papers (*1*–*3*). The special features are its highly adiabatic performance, the flow stability of the sample liquid in the closed circulation system, and the reliability of automatically measuring of mass-flow rate.

The isobaric heat capacity, C_p, is defined as follows:

$$C_p = \dot{Q}/(\dot{m}\Delta T) \qquad (1)$$

Flow calorimetry consists of three simultaneous measurements: measurement of energy, $\dot{Q}$, supplied by a microheater to the sample liquid; measurement of the temperature increment, ΔT, which is the difference $T_{out} - T_{in}$, the temperatures of sample liquid before and after heating by the microheater; and measurement of the mass-flow rate, $\dot{m}$. The energy supplied to the sample liquid was determined from the voltage and heating current through the microheater.

The temperature and temperature increment were measured with two 100-Ω platinum resistance thermometers (PRT) calibrated by a standard PRT in accordance with IPTS-68. The mass-flow rate was determined as the mass difference of a vessel before and after a sampling by means of a digital mass balance. The vessel was placed on the digital mass balance and connected to the circulation lines with small-diameter

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Table I. Measured Isobaric Heat Capacity for Liquid HFC-134a[a]

P/MPa	T_{in}/K	T_{out}/K	$\dot{Q}$/W	$\dot{m}$/(g/s)	C_p/[kJ/(kg K)]
1.016	273.143	278.153	0.9037	0.1331	1.355
1.018	273.142	278.153	0.7323	0.1082	1.351
1.018	273.143	278.148	0.6381	0.0939	1.358
1.500	273.143	278.158	0.9045	0.1340	1.346
1.499	273.143	278.146	0.7264	0.1080	1.344
1.983	273.140	278.142	0.8990	0.1335	1.346
1.979	273.142	278.159	0.7293	0.1080	1.346
1.977	273.142	278.148	0.6321	0.0938	1.346
2.490	273.145	278.161	0.8966	0.1331	1.343
2.494	273.144	278.143	0.6474	0.0964	1.344
2.971	273.145	278.166	0.9092	0.1354	1.337
2.969	273.144	278.141	0.7353	0.1098	1.340
1.002	297.497	302.497	0.9659	0.1341	1.441
1.000	297.492	302.450	0.7628	0.1068	1.441
1.004	297.498	302.499	0.6667	0.0925	1.441
1.498	297.492	302.517	0.9622	0.1339	1.430
1.494	297.486	302.492	0.7600	0.1063	1.428
1.498	297.492	302.490	0.6628	0.0927	1.430
1.974	297.488	302.497	0.7555	0.1058	1.426
1.977	297.490	302.510	0.9579	0.1342	1.422
2.522	297.485	302.492	0.9501	0.1335	1.421
2.516	297.483	302.484	0.7560	0.1062	1.423
2.515	297.480	302.495	0.6580	0.0922	1.423
2.968	297.490	302.494	0.9602	0.1354	1.417
2.969	297.492	302.499	0.7772	0.1094	1.419
2.968	297.492	302.494	0.6725	0.0947	1.420
1.002	307.490	312.491	0.9927	0.1327	1.496
1.002	307.492	312.526	0.8029	0.1068	1.494
1.002	307.492	312.526	0.6975	0.0927	1.495
1.511	307.489	312.494	0.9835	0.1337	1.470
1.511	307.490	312.490	0.7829	0.1068	1.466
1.511	307.489	312.497	0.6848	0.0929	1.472
1.513	307.493	312.519	0.8880	0.1204	1.467
2.000	307.484	312.517	0.9915	0.1342	1.468
1.999	307.484	312.526	0.7993	0.1077	1.472
1.998	307.486	312.508	0.6955	0.0943	1.469
2.484	307.479	312.493	0.9922	0.1349	1.467
2.484	307.478	312.502	0.7920	0.1075	1.467
2.484	307.479	312.481	0.6927	0.0942	1.470
2.960	307.490	312.502	0.9820	0.1344	1.458
2.959	307.494	312.467	0.7893	0.1090	1.456
2.959	307.487	312.507	0.6962	0.0951	1.458
1.317	317.505	322.505	1.0312	0.1328	1.553
1.315	317.504	322.522	0.8270	0.1061	1.553
1.313	317.491	322.505	0.7200	0.0926	1.551
1.505	317.492	322.512	1.0355	0.1340	1.539
1.510	317.491	322.513	0.8363	0.1080	1.542
1.513	317.489	322.486	0.7244	0.0941	1.541
1.996	317.494	322.522	1.0266	0.1330	1.535
1.996	317.493	322.507	0.8238	0.1073	1.531
1.996	317.494	322.518	0.7257	0.0941	1.535
2.490	317.493	322.523	1.0337	0.1353	1.519
2.489	317.493	322.480	0.8253	0.1087	1.523
2.489	317.494	322.521	0.7278	0.0950	1.524
2.959	317.488	322.487	1.0148	0.1348	1.506
2.959	317.491	322.478	0.8292	0.1100	1.511
2.955	317.489	322.487	0.7153	0.0949	1.508
1.712	327.491	332.500	1.0842	0.1330	1.628
1.712	327.493	332.501	0.8716	0.1066	1.633
1.713	327.490	332.500	0.7594	0.0928	1.633
1.991	327.487	332.504	1.0811	0.1342	1.606
1.991	327.490	332.510	0.8743	0.1078	1.615
1.991	327.500	332.551	0.7647	0.0940	1.611
2.471	327.486	332.518	1.0749	0.1343	1.591
2.469	327.496	332.538	0.8635	0.1076	1.591
2.469	327.493	332.467	0.7474	0.0944	1.592
2.970	327.496	332.549	1.0729	0.1344	1.580
2.971	327.499	332.521	0.8614	0.1086	1.579
2.971	327.496	332.528	0.7528	0.0947	1.580
2.211	337.496	342.502	1.1730	0.1347	1.739
2.212	337.490	342.500	0.9416	0.1081	1.738
2.209	337.491	342.509	0.8237	0.0944	1.739
2.490	337.485	342.528	1.1648	0.1343	1.720
2.490	337.484	342.489	0.9284	0.1080	1.718
2.490	337.495	342.480	0.8092	0.0943	1.722
2.972	337.487	342.529	1.1209	0.1326	1.676
2.973	337.486	342.480	0.8899	0.1059	1.683
2.973	337.501	342.562	0.7910	0.0929	1.683
2.706	347.487	352.512	1.3054	0.1350	1.925
2.705	347.479	352.498	1.0371	0.1072	1.927
2.701	347.487	352.500	0.9050	0.0938	1.925
2.955	347.496	352.513	1.2665	0.1331	1.897
2.965	347.494	352.491	1.0190	0.1074	1.898
2.962	347.502	352.522	0.8915	0.0941	1.888
2.505	343.988	349.005	1.2438	0.1344	1.844
2.506	343.984	348.996	0.9966	0.1077	1.847
2.507	343.987	348.988	0.8632	0.0938	1.841
2.995	354.486	357.500	0.8656	0.1350	2.128
2.995	354.487	357.491	0.6976	0.1093	2.124
2.995	354.487	357.498	0.6111	0.0955	2.125

[a] T was calibrated in accordance with IPTS-68: $T = (T_{in} + T_{out})/2$; $\Delta T = T_{out} - T_{in}$. T_{in} is the sample temperature before heating; T_{out} is the sample temperature after heating.

stainless steel tubing. We measured the mass-flow rate by measuring the mass difference of the vessel that was connected to the lines. The pressure was measured by using a precise Bourdon-type pressure gauge.

Results

Measurements were performed at temperatures from 276 to 356 K and pressures from 1.0 to 3.0 MPa. All measured values are listed in Table I. The table includes the measured pressure, P, measured temperature, T, energy supplied to the sample fluid, $\dot{Q}$, temperature increment, ΔT, mass-flow rate, $\dot{m}$, and measured heat capacity, C_p. Note that the measured temperature is assigned to the temperature of the arithmetic mean of T_{in} and T_{out}.

In order to know the effect of heat loss on measured C_p values, 90 data measured at various mass-flow rates were plotted against the inverse mass-flow rates in Figure 1. Figure

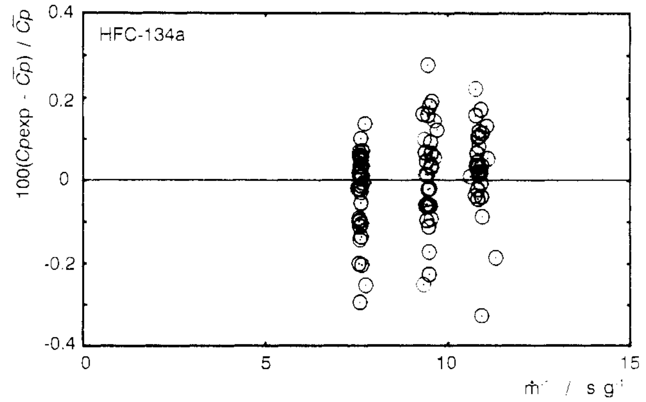

Figure 1. Reproducibility in C_p measurements with various mass-flow rates; $C_{p\,exp}$ denotes the measured value, whereas $\bar{C}_p$ is the averaged value.

Table II. Isobaric Heat Capacity for Liquid HFC-134a

T/K	P/MPa	C_p/[kJ/(kg K)]	T/K	P/MPa	C_p/[kJ/(kg K)]
275.65	1.000	1.355	320.00	1.300	1.552
275.65	1.500	1.345	320.00	1.500	1.541
275.65	2.000	1.346	320.00	2.000	1.534
275.65	2.500	1.344	320.00	2.500	1.522
275.65	3.000	1.339	320.00	3.000	1.508
300.00	1.000	1.441	330.00	1.700	1.631
300.00	1.500	1.429	330.00	2.000	1.611
300.00	2.000	1.424	330.00	2.500	1.591
300.00	2.500	1.422	330.00	3.000	1.580
300.00	3.000	1.419	340.00	2.200	1.739
310.00	1.000	1.495	340.00	2.500	1.720
310.00	1.500	1.469	340.00	3.000	1.681
310.00	2.000	1.470	350.00	2.700	1.926
310.00	2.500	1.468	350.00	3.000	1.894
310.00	3.000	1.457	346.50	2.500	1.844
			356.00	3.000	2.126

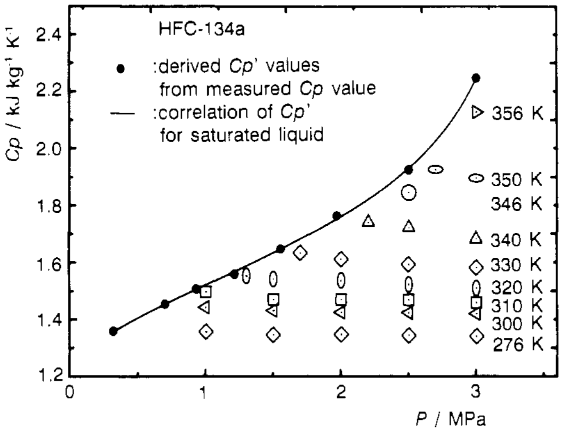

Figure 2. Experimental data and the correlation for specific heat of saturated liquid HFC-134a.

1 shows that measured C_p values do not depend on the mass-flow rate. Thus, it was concluded that the effect of heat loss is small enough not to be compensated. Two to four measurements at a same temperature and pressure but with a different mass-flow rate from other measurements were performed, and a simple correlation for the C_p values along an isobar curve (*4*) was used to get the C_p value at a nominal temperature. Listed in Table II are 31 C_p values at nominal temperatures and pressures determined from 90 measured data listed in Table I.

The uncertainties of the measurements are ±5 mK in temperature increment, ±0.02% in energy supplied, ±0.2% in mass-flow rate, ±10 mK in temperature, and ±3 kPa in pressure, respectively. The overall uncertainty of determined C_p values summarized in Table II is concluded to be less than ±0.3%.

For saturated liquid HFC-134a, 8 heat capacity values, C_p', were also derived on the basis of the data measured in the compressed liquid phase given in Table I. The vapor pressure equation developed by Piao et al. (*5*) was used in this procedure. These C_p' values were correlated with the following temperature function

$$C_p' = (8.2206 \times 10^{-5})(1 - T_r)^{-2.5} - (4.9897 \times 10^{-2})(1 - T_r)^{-0.8} + 1.0036(1 - T_r)^{-0.3} \quad (2)$$

where $T_r = T/T_c$ and C_p' is given in kJ/(kg K). The critical temperature, T_c, is 374.30 K, which has been reported by Kabata et al. (*6*). Equation 2 is effective in a temperature range between 276 and 359 K. The C_p values for compressed liquid and saturated liquid HFC-134a and the correlation of C_p' are shown on a C_p-pressure diagram in Figure 2.

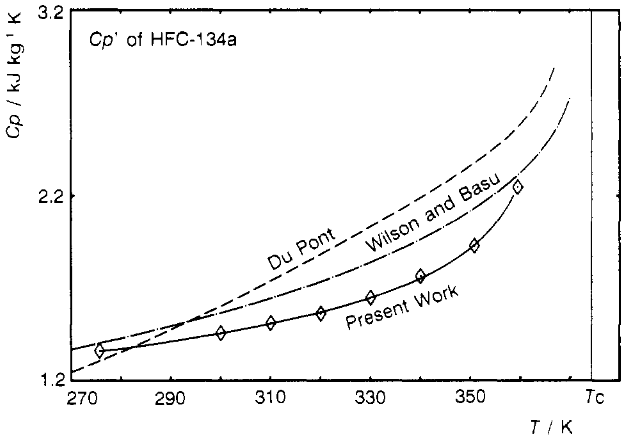

Figure 3. Comparison of three specific heat curves for saturated liquid HFC-134a.

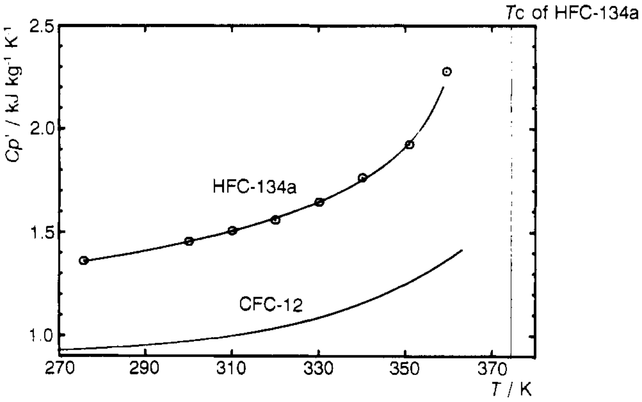

Figure 4. Comparison of specific heat of saturated liquid HFC-134a with that of CFC-12 (*9*).

Discussion

Since no single isobaric heat capacity data have been reported, we have compared the present C_p' values with derived values from equations of state reported by Du Pont (*7*) or Wilson and Basu (*8*). These equations are effective only in the gaseous phase, but they are accompanied by correlations for vapor pressure and saturated liquid density. So, we have applied the Clausius-Clapeyron rule to get the saturated liquid enthalpy values, h', as follows

$$h' = h'' - T(v'' - v')(\mathrm{d}P_s/\mathrm{d}T) \quad (3)$$

where h'', v'', v', and P_s stand for enthalpy, specific volumes of saturated vapor and saturated liquid, and vapor pressure, respectively. Both h'' and v'' have been calculated from the equations of state, while P_s and v' were determined from their correlations. The C_p of saturated liquid was derived from the calculation of $C_p' \approx \Delta h'/\Delta T$.

Figure 3 shows the comparison of present C_p' values with those derived C_p' values. As shown clearly in Figure 3, two curves show larger C_p' values than the present correlation at temperatures up to 360 K. The difference can be considered as the difficulty in the derivation of specific heat from other properties.

For practical applications, the C_p' values of HFC-134a are compared with those of CFC-12 (*9*) in Figure 4. The C_p' of HFC-134a is about 1.5 times larger than that of CFC-12.

Conclusion

The data of 90 C_p in the liquid phase were measured in the temperature range from 276 to 356 K and pressure range from

1.0 to 3.0 MPa with the uncertainty being less than ±0.3%. The C_p' values of saturated liquid HFC-134a were also determined from the measured data, and a correlation of C_p' was also developed.

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Adsorption of Normal Alkanes from Isooctane Solution onto Crystalline Urea

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Experimental data are reported for the adsorption of four *n*-alkanes from isooctane solution onto crystalline urea. Equilibrium isotherms for *n*-dodecane, *n*-tetradecane, and *n*-hexadecane were obtained at 283, 295, and 303 K. The equilibrium adsorption data were correlated by the Langmuir, Freundlich, and BET isotherm equations. The kinetics of the adsorption of *n*-dodecane, *n*-tridecane, and *n*-tetradecane from isooctane solution onto crystalline urea were also studied at 283, 295, and 303 K. The kinetic data were used to calculate the diffusivities and the apparent energies of activation for the urea–*n*-alkane systems.

Introduction

Industrial applications of *n*-paraffins depend on the number of carbon atoms in the *n*-alkane chain. For instance, *n*-paraffins with a chain length of C_8 to C_{20} are used in the manufacture of surfactants and single-cell proteins, C_{10} to C_{17} are used as plasticizers, and C_{20} and higher can be used as additives for lubricating oils. At present, industrial separations of *n*-alkanes from petroleum distillates are accomplished primarily by selective adsorption on molecular sieves and urea adduction techniques. Only a few studies have been reported in which solid urea was used to adsorb *n*-paraffins. Among those studies, McAdie and Frost (*1*), Calderbank and Nikolov (*2*), Patrilyak and Motornyi (*3*), and Zimmerschield et al. (*4*) presented experimental data. Schirmer et al. (*5*) studied the adsorption of *n*-alkanes with medium chain length (C_{10}–C_{12}) on molecular sieve 5A and compared the results with the adsorption on solid urea. They found the dimensions of molecular sieve 5A and urea cavities are similar; both have critical diameters of about 5 Å. Inside the cavities, the molecules of the *n*-alkanes interact during adsorption with the oxygen atoms in the urea channels.

This study presents the adsorption of *n*-dodecane, *n*-tridecane, *n*-tetradecane, and *n*-hexadecane from isooctane solution onto crystalline urea at 283, 295, and 303 K. The data obtained are important for developing a new separation procedure based on the physicochemical aspects of the urea–*n*-alkane systems.

Experimental Section

Materials. All of the chemicals used were high-purity-grade reagents. *n*-Dodecane, *n*-tridecane, *n*-tetradecane, and *n*-hexadecane were used as adsorbates in this study. All four *n*-alkanes were obtained from Alltech Associates, Deerfield, IL, and had a stated purity greater than 99.5%. Isooctane and methanol were obtained from the Matheson Co. with stated minimum purities of 99.5%. The chemicals were used without further purification. The adsorbent used was crystalline urea supplied by Hopkin and Williams Co., Essex, England. Prior to use, the crystalline urea was dried by heating it in a vacuum desiccator for 5 h. It was then placed in a closed container until it was to be weighed for the adsorption study.

Procedure. The adsorption isotherm data were determined by adding 25 mL of sample solutions of initial concentrations ranging from 10 to 50 mol/m^3 to a carefully weighed 1 g of crystalline urea. The solutions were placed in sample bottles and sealed tightly with Teflon-lined caps. The bottles were then placed in a shaker bath, controlled at either 283, 295, or 303 K (±0.2 °C), for 24 h to reach equilibrium. After equilibration, the solutions were withdrawn and filtered twice with Whatman No. 42 filter paper to ensure that all urea crystals were removed from the solution. The filtrate samples were then analyzed with use of a digital density meter (Model DM 240) manufactured by Anton Paar, Graz, Austria.

The batch kinetic data were obtained by mixing 1000 mL of the *n*-alkane solutions (initial concentration 40 mol/m^3) with 10 mL of methanol activator. From the mixture, 25-mL samples were withdrawn and placed in sample bottles each containing a carefully weighted 1 g of crystalline urea. The bottles were tightly sealed with Teflon-lined caps and then placed in a shaker bath controlled to within ±0.2 °C of the desired temperature. Periodically, a sample solution was withdrawn and filtered twice with Whatman No. 42 filter paper to ensure that all urea crystals were removed from the solution. The analysis of the sample filtrate was performed using the digital density meter (DM 240). In order to achieve an accurate measurement, a constant

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