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Measurements of Vapor Pressure, Heat Capacity, and Density along the Saturation Line for Cyclopropane Carboxylic Acid, *N*,*N*-Diethylethanolamine, 2,3-Dihydrofuran, 5-Hexen-2-one, Perfluorobutanoic Acid, and 2-Phenylpropionaldehyde

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This paper reports measurements made for DIPPR Research Project 821 in the 1997 Project Year. Vapor pressures were measured to a pressure limit of 270 kPa or lower decomposition point for all six compounds using a twin ebulliometric apparatus. Liquid-phase densities along the saturation line were measured for each compound over a range of temperatures (ambient to a maximum of 448 K). A differential scanning calorimeter was used to measure two-phase (liquid + vapor) heat capacities for each compound in the temperature region ambient to the critical temperature or lower decomposition point. The results of all the measurements were combined to derive a series of thermophysical properties including critical temperature, critical density, critical pressure, acentric factor, enthalpies of vaporization [within the temperature range (±50 K) of the vapor pressures], solubility parameter, and heat capacities along the saturation line. Wagner-type vapor-pressure equations were derived for each compound. In addition, the liquid-phase densities were compared with values derived using a four-term power series in $[(1 - T_r)^{n/3}]$. All measured and derived values were compared with those obtained in a search of the literature.

Introduction

The papers[1−7] previously published in this Journal detail the background, equipment used, and so forth for measurements made within the DIPPR 821 Vapor Pressures of Industrial Interest Research Program at Bartlesville, OK. With the demise of the Thermodynamics Research Group at Bartlesville, the DIPPR 821 Project is now accomplished within the Physical Properties Research Facility in the Chemical Engineering Division at Oak Ridge National Laboratory. The objectives of the ongoing research program can be summarized as follows: to obtain, analyze, and purify (to a minimum purity level of 99.9 mol %) each of the compounds chosen for vapor-pressure studies; to measure the vapor pressure of each sample in the pressure region 2−270 kPa or from the triple point to the decomposition temperature, if the corresponding pressure is less than 270 kPa; to use the DSC method, developed within our Group at Bartlesville, to experimentally measure two-phase (liquid + vapor) heat capacities for each compound in the temperature region ambient to the critical temperature or lower decomposition point; to determine, if possible, the critical temperature and critical density for each compound; to determine liquid-phase densities along the saturation line over a wide temperature range (up to 548 K if possible) for each compound; to fit the measured vapor pressures to a Wagner-form vapor-pressure equation;[8] to use fitting procedures to determine heat capacities along the saturation line and derive the critical pressure; to derive an acentric factor for each compound; to derive enthalpies of vaporization for each compound, using the Clapeyron equation (extrapolations are restricted to within ±50 K of the temperature region of the experimentally determined vapor pressures); and to derive the solubility parameter for each compound.

Figure 1 lists the structural formulas, names, and Chemical Abstracts Service registry numbers (CAS No.) for each of the compounds studied in the 1997 Project Year for DIPPR Project 821.

Experimental Section

The apparatus and procedures used in obtaining the experimental data have been previously described in the literature and in various DOE reports. In addition, the earlier papers published in this Journal under the DIPPR auspices[1−7] give detailed references to the experimental techniques and fitting procedures. Therefore, in this paper no details are given and the reader is referred to refs 1−7 and the earlier publications referenced therein.

Materials. To minimize errors due to impurities, care was taken to ensure only samples of high purity (>99.9 mol % purity) were subjected to the thermophysical property measurements. All compounds were purchased from Aldrich Chemical Co. Gas−liquid chromatographic (GLC) analyses on the purchased samples gave an average purity of 98 mol %, in agreement with Aldrich specifications. The purchased compounds were purified by repeated distillations using a spinning-band column. GLC analyses of those samples used in the measurements gave purities of at least 99.95 mol % for each compound. The high purity of each sample was confirmed subsequently by the small differences between the boiling and condensation temperatures in the ebulliometric vapor-pressure measurements listed in Table 1.

All transfers of the purified samples were done under nitrogen or helium or by vacuum distillation. The water

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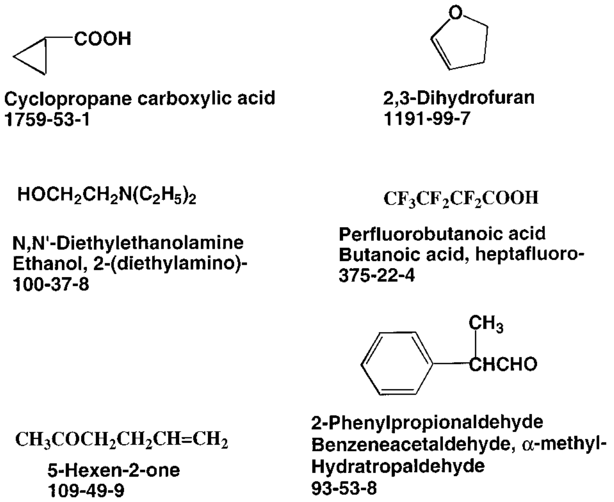

Figure 1. Structural formulas, common names, Chemical Abstracts Service names (provided by the authors), and Chemical Abstracts Service Registry Numbers (provided by the authors) for the compounds studied in this research.

used as a reference material in the ebulliometric vapor-pressure measurements was deionized and distilled from potassium permanganate. The *n*-decane used as a reference material for the ebulliometric measurements was purified by urea complexation, two recrystallizations of the complex, decomposition of the complex with water, extraction with ether, drying with $MgSO_4$, and distillation at 337 K and 1 kPa pressure. GLC analysis of the *n*-decane sample failed to show any impurity peaks.

Physical Constants. Molar values are reported in terms of the 1991 relative atomic masses[9] and the gas constant, $R = 8.314\,51\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, adopted by CODATA.[10] The platinum resistance thermometers used in these measurements were calibrated by comparison with a standard platinum resistance thermometer whose constants were determined at the National Institute of Standards and Technology (NIST). All temperatures were measured in terms of IPTS-68 and converted to ITS-90 with published increments.[11,12] Measurements of mass, time, electric resistance, and potential difference were made in terms of standards traceable to calibrations at NIST.

Results

Vapor Pressures. Measured vapor pressures for cyclopropane carboxylic acid, *N*,*N*-diethylethanolamine, 2,3-dihydrofuran, 5-hexen-2-one, perfluorobutanoic acid, and 2-phenylpropionaldehyde are listed in Table 1. The vapor pressures, the condensation temperatures, and the differences between the condensation and boiling temperatures for the samples are reported. The small differences between the boiling and condensation temperatures in the ebulliometric measurements indicated correct operation of the equipment and the high purity of the samples studied. In Table 1 significant increases in the difference between the boiling and condensation temperatures are specially noted. This phenomenon normally indicates sample decomposition. Onset of sample decomposition was probable for cyclopropane carboxylic acid above 465 K and for 2-phenylpropionaldehyde above 509 K.

Differential Scanning Calorimetry. Two-phase heat capacities $C^{II}_{x,m}$ were determined by DSC for each of the compounds.[13] Heat capacities were determined at 20 K intervals with a heating rate of 0.083 $\mathrm{K{\cdot}s^{-1}}$ and a 120 s equilibration period between additions of energy. For each compound the upper temperature bound of the measurements was set by the critical region or earlier sample decomposition.

For all the compounds studied, extensive sample decomposition precluded attainment of heat-capacity measurements above the highest listed temperatures. Only in the cases of 2,3-dihydrofuran and 5-hexen-2-one was the range of temperature sufficient to distinguish between $C^{II}_{x,m}$ and $C_{sat,m}$, and for those compounds the results obtained for each cell filling are listed in Table 2. For each of cyclopropane carboxylic acid, *N*,*N*-diethylethanolamine, perfluorobutanoic acid, and 2-phenylpropionaldehyde, an equation representing the variation of $C_{sat,m}$ with temperature is listed in Table 2. (Note: the heat-capacity equations should only be used to derive values within the temperature ranges specified in Table 2; extrapolation outside the temperature range will produce erroneous values.)

Densitometry. Measured densities for each of the compounds in the liquid phase along the saturation line obtained using a vibrating tube densimeter are listed in Table 3. The temperatures are precise to ±0.005 K. As derived by Chirico and Steele,[14] the expected accuracy of the densities is $\pm 0.1\ \mathrm{kg{\cdot}m^{-3}}$.

Fitting Procedures. For both 2,3-dihydrofuran and 5-hexen-2-one, careful scrutiny of the DSC traces during the heat-capacity measurements allowed a guess of the critical temperature. Values of 2,3-dihydrofuran, 525 K, and 5-hexen-2-one, 594 K, were "guesstimated". For both compounds, a simultaneous nonlinear least-squares fit of the vapor pressures listed in Table 1 and the two-phase heat capacities $C^{II}_{x,m}$ given in Table 2 was completed using the "guesstimated" values for T_c. The fitting procedure has been described in detail by Steele,[13] and hence, only a summary of the procedure follows.

The Wagner vapor-pressure equation[8] in the formulation highlighted by Ambrose and Walton,[15]

$$\ln(p/p_c) = (1/T_r)[AY + BY^{1.5} + CY^{2.5} + DY^{5}] \qquad (1)$$

where $T_r = T/T_c$ and $Y = (1 - T_r)$ was fitted to the measured vapor pressures (Table 1) using the respective approximated critical temperature and with the critical pressure, p_c, included in the variables. The approximated T_c values were fixed. They were not included "in the variables." The vapor-pressure fitting procedure including the minimization equation and the relative weightings is detailed in ref 13.

For fitting the two-phase heat capacities obtained in a cell of volume V_x, the experimental $C^{II}_{x,m}$ values (Table 2) were converted to $C^{II}_{V,m}$ by means of the equation

$$V_x(T)/V_x(298.15\ \mathrm{K}) = 1 + ay + by^2 \qquad (2)$$

where $y = (T - 298.15)$ K, $a = 3.216 \times 10^{-5}\ \mathrm{K}^{-1}$, and $b = 5.4 \times 10^{-8}\ \mathrm{K}^{-2}$ for the cell expansion and the vapor-pressure fit for $(\partial p/\partial T)_{sat}$,

$$C^{II}_{V,m} = C^{II}_{x,m} - T/n\{(\partial V_x/\partial T)_x(\partial p/\partial T)_{sat}\} \qquad (3)$$

The values of $C^{II}_{V,m}$ were used to derive functions for $(\partial^2 p/\partial T^2)_{sat}$ and $(\partial^2\mu/\cdot T^2)_{sat}$ (see eq 2 of ref 13). The functional form chosen for variation of the second derivative of the chemical potential with temperature was

$$(\partial^2\mu/\partial T^2)_{sat}/(\mathrm{J{\cdot}K^{-2}{\cdot}mol^{-1}}) = \sum_{i=0}^{3} b_i(1 - T/T_c)^i \qquad (4)$$

Table 1. Summary of Vapor-Pressure Results[a]

method	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K	method	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K
					Cyclopropane Carboxylic Acid						
d	357.605	1.9999	0.0000	0.0003	0.031	w	419.363	31.171	0.002	0.004	0.007
d	370.945	3.9894	0.0000	0.0005	0.017	w	425.316	38.554	0.002	0.004	0.008
d	376.922	5.3310	0.0003	0.0007	0.014	w	431.288	47.367	0.005	0.005	0.009
d	385.745	8.0117	−0.0004	0.0010	0.009	w	437.268	57.796	0.006	0.006	0.010
d	392.271	10.6727	0.0002	0.0012	0.008	w	443.286	70.108	−0.010	0.007	0.010
d	397.543	13.338	−0.001	0.002	0.007	w	449.305	84.511	−0.013	0.008	0.014
d	402.982	16.662	−0.001	0.002	0.005	w	455.340	101.293	−0.009	0.009	0.015
d	407.506	19.935	0.000	0.002	0.005	w	461.393	120.77	0.02	0.01	0.021
d	413.437	25.032	0.002	0.003	0.005	w	467.463[c]	143.21	0.03	0.01	0.027
w	413.419[b]	25.015	0.001	0.003	0.006	w	473.560[c]	168.97	0.02	0.01	0.034
					N,*N*′-Diethylethanolamine						
d	332.500	2.0022	−0.0001	0.0003	0.048	w	409.277	47.366	0.002	0.005	0.015
d	346.094	4.0031	0.0004	0.0005	0.032	w	415.709	57.801	0.003	0.006	0.016
d	352.159	5.3331	−0.0002	0.0007	0.027	w	422.189	70.099	0.001	0.007	0.017
d	361.220	8.0029	0.0002	0.0010	0.024	w	428.716	84.517	0.002	0.008	0.017
d	368.003	10.6642	0.0000	0.0012	0.022	w	435.281	101.296	−0.002	0.009	0.018
d	373.496	13.325	0.000	0.002	0.020	w	441.890	120.75	0.00	0.01	0.018
d	379.233	16.669	−0.001	0.002	0.017	w	448.548	143.21	0.00	0.01	0.019
d	383.986	19.937	0.000	0.002	0.016	w	455.247	169.00	0.01	0.01	0.018
d	390.254	25.037	0.001	0.002	0.016	w	461.988	198.45	0.00	0.02	0.019
w	390.227[b]	25.011	−0.001	0.003	0.015	w	468.775	231.99	0.00	0.02	0.020
w	396.546	31.178	−0.001	0.003	0.014	w	475.597	269.96	0.00	0.02	0.021
w	402.902	38.576	−0.001	0.004	0.013						
					2,3-Dihydrofuran						
w	301.860	38.553	0.000	0.005	0.006	w	332.907	120.77	0.00	0.01	0.006
w	306.949	47.370	−0.001	0.005	0.005	w	338.209	143.22	0.00	0.01	0.006
w	312.068	57.811	0.000	0.006	0.004	w	343.539	168.96	0.00	0.02	0.006
w	317.222	70.109	0.000	0.007	0.005	w	348.916	198.42	−0.01	0.02	0.006
w	322.409	84.503	−0.001	0.009	0.005	w	354.333	231.98	0.00	0.02	0.007
w	327.647	101.32	0.00	0.01	0.005	w	359.775	269.95	0.00	0.02	0.008
					5-Hexen-2-one						
d	317.324	3.9922	0.0000	0.0005	0.019	w	383.650	57.797	0.000	0.006	0.004
d	323.152	5.3312	−0.0001	0.0007	0.012	w	389.815	70.103	−0.001	0.007	0.004
d	331.762	7.9906	0.0002	0.0010	0.012	w	396.016	84.509	−0.002	0.008	0.005
d	338.264	10.6671	0.0000	0.0012	0.009	w	402.262	101.307	−0.001	0.009	0.006
d	343.470	13.315	0.000	0.002	0.006	w	408.541	120.75	0.00	0.01	0.006
d	348.941	16.662	0.000	0.002	0.006	w	414.868	143.20	0.00	0.01	0.008
d	353.445	19.915	0.000	0.002	0.005	w	421.236	168.99	0.00	0.01	0.008
d	359.427	25.024	0.000	0.003	0.004	w	427.643	198.45	0.01	0.02	0.007
w	365.427	31.182	0.001	0.004	0.005	w	434.088	231.95	−0.01	0.02	0.008
w	371.468	38.573	0.001	0.004	0.004	w	440.573	269.94	0.00	0.02	
w	377.545	47.382	0.001	0.005	0.004						
					Perfluorobutanoic acid						
d	310.883	2.0006	0.0001	0.0003	0.027	w	373.916	47.371	−0.002	0.005	0.013
d	322.259	3.9934	0.0000	0.0006	0.022	w	379.058	57.793	−0.004	0.006	0.014
d	327.331	5.3274	−0.0008	0.0008	0.021	w	384.231	70.104	−0.005	0.007	0.015
d	334.848	8.0013	−0.0003	0.0011	0.019	w	389.410	84.493	−0.002	0.009	0.017
d	340.416	10.6540	0.0004	0.0014	0.018	w	394.628	101.318	−0.005	0.010	0.019
d	344.952	13.333	0.000	0.002	0.016	w	399.854	120.79	0.00	0.01	0.021
d	349.616	16.662	0.001	0.002	0.016	w	405.091	143.22	0.01	0.01	0.026
d	353.480	19.924	0.002	0.002	0.015	w	410.352	168.98	0.01	0.02	0.027
d	358.572	25.023	0.001	0.003	0.014	w	415.632	198.41	0.01	0.02	0.029
w	363.666	31.171	−0.001	0.004	0.013	w	420.940	231.97	0.00	0.02	0.031
w	368.782	38.560	0.000	0.005	0.014	w	426.264	269.98	−0.02	0.02	0.032
					2-Phenylpropionaldehyde						
d	363.733	2.0012	0.0003	0.0003	0.110	w	443.126	38.558	0.001	0.004	0.044
d	379.111	4.0008	−0.0002	0.0005	0.083	w	450.310	47.359	−0.001	0.005	0.045
d	385.971	5.3323	−0.0007	0.0006	0.079	w	457.545	57.795	−0.002	0.006	0.047
d	396.201	8.0020	−0.0014	0.0009	0.071	w	464.837	70.101	−0.010	0.006	0.046
d	403.863	10.6691	−0.0006	0.0011	0.066	w	472.169	84.503	−0.018	0.008	0.048
d	410.057	13.334	0.001	0.001	0.060	w	479.544	101.307	0.009	0.009	0.053
d	416.505	16.671	0.001	0.002	0.055	w	486.976	120.77	0.00	0.01	0.055
d	421.875	19.953	0.002	0.002	0.051	w	494.456	143.22	0.00	0.01	0.060
d	428.893	25.024	0.003	0.002	0.047	w	501.966	168.97	0.01	0.01	0.071
w	428.883[b]	25.014	0.002	0.003	0.048	w	509.523[c]	198.43	0.08	0.02	0.084
w	435.976	31.163	0.001	0.003	0.045	w	517.116[c]	231.93	0.18	0.02	0.108

[a] Water (w) or *n*-decane (d) refers to which material was used in the reference ebulliometer. T is the condensation temperature of the sample. The pressure p was calculated from the condensation temperature of the reference substance. Δp is the difference of the value of pressure, calculated with eq 1 and the parameters listed in Table 4, from the observed value of pressure ($\Delta p = p - p_{\mathrm{Wagner}}$). σ is the propagated error calculated using $\sigma(p) = (0.001)\{(\mathrm{d}p_{\mathrm{ref}}/\mathrm{d}T)^2 + (\mathrm{d}p_x/\mathrm{d}T)^2\}^{1/2}$, where p_{ref} and p_x are the vapor pressures of the reference substance and compound under study, respectively. ΔT is the difference between the boiling and condensation temperatures ($T_{\mathrm{boil}} - T_{\mathrm{cond}}$) for the sample. [b] Values at this temperature were not included in the fit of the Wagner equation. The measurement was an overlap point between the use of *n*-decane and water as pressure measurement standards. [c] Values at this temperature were not included in the fit of the Wagner equation because sample decomposition was indicated by the increase in the ΔT values.

Table 2. Experimental Two-Phase Heat Capacities, Derived Saturation Heat-Capacity Equations, and Phase-Transition Enthalpies Derived from DSC Measurements

Cyclopropane Carboxylic Acid (liquid)
$C_{\mathrm{sat,m}}/R = 0.06T - 1.55$ (in temperature range 293 K to 458 K)

N,N'-Diethylethanolamine (liquid)
$C_{\mathrm{sat,m}}/R = 0.052T + 19.25$ (in temperature range 293 K to 458 K)

2-Phenylpropionaldehyde (liquid)
$C_{\mathrm{sat,m}}/R = 0.053T + 12.34$ (in temperature range 293 K to 513 K)

Perfluorobutanoic Acid (liquid)
$C_{\mathrm{sat,m}}/R = 0.088T + 5.65$ (in temperature range 293 K to 398 K)

	$C^{\mathrm{II}}_{\mathrm{X,m}}/R$		
T/K	m/g = 0.010 918 $V_c{}^a = 0.0522$	m/g = 0.013 460 $V_c{}^a = 0.0522$	m/g = 0.019 095 $V_c{}^a = 0.0522$
	2,3-Dihydrofuran		
308.15	15.2	15.7	15.5
328.15	16.1	16.6	16.3
348.15	17.2	17.5	17.1
368.15	18.5	18.7	17.9
388.15	19.8	20.0	18.8
408.15	21.1	21.0	19.9
428.15	22.3	22.1	20.8
448.15	23.9	23.3	21.5
468.15	25.5	24.2	21.3
488.15	27.5	25.4	23.4
508.15	28.2	28.0	25.6
528.15[b]	22.7	28.4	26.1
548.15[b]	14.8	13.8	15.6
	$C^{\mathrm{II}}_{\mathrm{X,m}}/R$		
T/K	m/g = 0.008 778 $V_c{}^a = 0.0522$	m/g = 0.014 994 $V_c{}^a = 0.0522$	m/g = 0.018 015 $V_c{}^a = 0.0522$
	5-Hexen-2-one		
308.15	25.3	24.9	24.9
328.15	26.0	25.6	25.6
348.15	27.0	26.4	26.3
368.15	27.9	27.0	27.1
388.15	29.0	27.8	27.9
408.15	30.1	28.8	28.8
428.15	31.7	29.7	29.6
448.15	33.0	30.9	30.6
468.15	34.9	32.0	31.7
488.15	36.4	32.5	32.6
508.15	37.9	33.4	33.3
528.15	39.5	34.7	34.0
548.15	42.8	36.2	35.7
568.15	44.3	38.1	38.3
588.15[b]	43.6	44.8	41.4
608.15[b]	32.2	15.2	26.5

[a] Volume of cell (V_c) is given in cubic centimeters for 298.15 K. [b] Values not used in fitting procedures since at least some of the 20 K heating cycle (see text) is above the critical temperature.

Details of the weighting procedures and so forth are given by Steele in ref 13.

For the remaining four compounds, estimates were made for the critical temperature using literature techniques such as those due to Joback[16] and Ambrose[17] to guide the selection of values. All four compounds decomposed well removed from the critical region, and measured vapor pressures covered a relatively narrow range of temperatures (Table 1). The measured $C^{\mathrm{II}}_{x,\mathrm{m}}$ values were virtually independent of cell filling. Hence, fitting procedures were restricted to include the Wagner vapor-pressure equation only. Corresponding critical pressures were selected with Waring's criterion for $T_r = 0.85$.[18] Application of this criterion was discussed recently by Steele.[13]

Derived Results. Table 4 lists the parameters derived using the procedures outlined above. Details of the fits using the vapor-pressure results are given in Table 1 (column 4 labeled $\Delta p = p - p_{\mathrm{Wagner}}$ with p_{Wagner} calculated using the parameters listed in Table 4).

Values of $C^{\mathrm{II}}_{\mathrm{V,m}}(\rho = \rho_{\mathrm{sat}})$ were derived for both 2,3-dihydrofuran and 5-hexen-2-one from the parameters listed in Table 4, and corresponding $C_{\mathrm{sat,m}}$ values were obtained using eq 6 of ref 13. The results for $C_{\mathrm{sat,m}}/R$ are reported in Table 5. The estimated uncertainty in these values is 1%.

Table 3. Measured Liquid-Phase Densities along the Saturation Line[a]

T/K	ρ/kg·m^{-3}	$100(\rho - \rho_{\mathrm{calc}})/\rho$	T/K	ρ/kg·m^{-3}	$100(\rho - \rho_{\mathrm{calc}})/\rho$
Cyclopropane Carboxylic Acid[b]			N,N'-Diethylethanolamine[c]		
323.135	1058.2	−0.07	323.136	855.9	0.11
348.130	1033.2	−0.09	348.128	830.7	−0.11
373.124	1007.9	−0.07	373.124	806.3	−0.12
398.113	983.2	0.13	398.115	782.6	0.12
423.115	957.4	0.35	423.118[d]	758.3	0.50
			448.111[d]	731.3	0.78
5-Hexen-2-one[e]			2,3-Dihydrofuran[f]		
323.135	813.2	0.07	313.151	900.8	0.01
348.131	788.2	−0.07	333.139	875.5	0.00
373.122	763.5	−0.08	353.129	849.2	0.01
398.113	739.1	0.04	373.124	822.0	0.00
423.116	713.5	0.14			
448.110	684.3	−0.08			
2-Phenylpropionaldehyde[g]			Perfluorobutanoic Acid[h]		
323.133	976.25	0.01	313.152	1606.2	0.00
348.132	952.97	−0.01	333.131	1559.9	0.01
373.123	930.59	0.01	353.130	1511.3	−0.02
398.114	908.25	0.00	373.125	1461.7	0.01
423.115	887.23	0.07	393.117	1409.0	0.00
448.110[d]	862.62	−0.31			

[a] ρ_{calc} values were calculated using eq 7 and the parameters listed below. [b] $\rho_{\mathrm{calc}} = 324.0 + 570.9(1 - T/671)^{1/3} + 428.1(1 - T/671)^{2/3}$. [c] $\rho_{\mathrm{calc}} = 277.0 + 454.3(1 - T/616)^{1/3} + 366.7(1 - T/616)^{2/3}$. [d] Possible compound decomposition. [e] $\rho_{\mathrm{calc}} = 273.0 + 760.6(1 - T/594)^{1/3} - 544.6(1 - T/594)^{2/3} + 607.2(1 - T/594)$. [f] $\rho_{\mathrm{calc}} = 327.0 + 764.9(1 - T/525)^{1/3} - 368.4(1 - T/525)^{2/3} + 519.8(1 - T/525)$. [g] $\rho_{\mathrm{calc}} = 307.0 + 1781.2(1 - T/680)^{1/3} - 2867.3(1 - T/680)^{2/3} + 2092.2(1 - T/680)$. [h] $\rho_{\mathrm{calc}} = 503.7 + 1497.3(1 - T/530)^{1/3} - 736.0(1 - T/530)^{2/3} + 969.4(1 - T/530)$.

Table 4. Parameters for Eqs 2 and 4, Critical Constants, and Acentric Factors[a]

Cyclopropane Carboxylic Acid				N,N'-Diethylethanolamine			
A	−10.074 69			A	−7.646 78		
B	5.099 50			B	0.383 01		
C	−7.784 28			C	−2.334 87		
D	−1.273 82			D	−7.009 89		
T_c	671	p_c	5995	T_c	616	p_c	2650
ρ_c	324	ω	0.5953	ρ_c	277	ω	0.4662
5-Hexen-2-one				2,3-Dihydrofuran			
A	−8.076 72	b_0	−0.402 14	A	−7.081 51	b_0	−0.249 24
B	2.217 72	b_1	−0.646 76	B	1.557 44	b_1	−0.658 35
C	−3.291 59	b_2	0.772 80	C	−1.995 25	b_2	1.265 21
D	−3.791 33	b_3	−1.224 61	D	−3.363 31	b_3	−1.368 73
T_c	594	p_c	3550	T_c	525	p_c	5575
ρ_c	273	ω	0.3836	ρ_c	327	ω	0.2254
2-Phenylpropionaldehyde				Perfluorobutanoic acid			
A	−8.632 93			A	−10.184 47		
B	2.716 67			B	3.349 51		
C	−4.303 70			C	−7.828 68		
D	−3.254 58			D	−3.005 72		
T_c	680	p_c	2720	T_c	530	p_c	2650
ρ_c	307	ω	0.4664	ρ_c	504	ω	0.7981

[a] The parameters listed in this table are those derived from the fitting procedures.

Table 5. Values of $C_{\mathrm{sat,m}}/R$ (R = 8.314 51 J·K^{-1}·mol^{-1})

T/K	$C_{\mathrm{sat,m}}/R$	T/K	$C_{\mathrm{sat,m}}/R$	T/K	$C_{\mathrm{sat,m}}/R$	T/K	$C_{\mathrm{sat,m}}/R$
2,3-Dihydrofuran				5-Hexen-2-one			
300.0	14.8	420.0	18.9	300.0	24.6	460.0	30.2
320.0	15.5	440.0	19.7	320.0	25.3	480.0	30.9
340.0	16.1	460.0	20.5	340.0	26.0	500.0	31.8
360.0	16.8	480.0	21.6	360.0	26.7	520.0	32.7
380.0	17.5	500.0	23.9	380.0	27.3	540.0	34.0
400.0	18.2	520.0	38.1	400.0	28.0	560.0	36.2
				420.0	28.7	580.0	42.3
				440.0	29.4		

Enthalpies of vaporization $\Delta_l^g H_m$ were derived from the Wagner-equation parameters (Table 4) using the Clapeyron equation

$$\mathrm{d}p/\mathrm{d}T = \Delta_l^g H_m/(T\Delta_l^g V_m) \qquad (5)$$

where $\Delta_l^g V_m$ is the increase in molar volume from the liquid to the real vapor. In earlier work in this project the liquid-phase density estimates were made with the extended corresponding-states equation of Riedel[19] as formulated by Hales and Townsend[20]

$$(\rho/\rho_c) = 1.0 + 0.85Y + (1.6916 + 0.9846\omega)Y^{1/3} \qquad (6)$$

with $Y = (1 - T/T_c)$, ρ_c = critical density, and ω = acentric factor. The acentric factor, ω, is defined as $[-\log(p/p_c) - 1]$, where p is the vapor pressure at $T/T_c = 0.7$ and p_c is the critical pressure. However, often eq 6 was not a good representation of the measured densities. A power series of the type

$$\rho = \rho_c + A(1 - T_r)^{1/3} + B(1 - T_r)^{2/3} + C(1 - T_r) + ... \qquad (7)$$

has proved to be a better representation of the measured densities for a wide range of compound types from alkanes through compounds containing highly polar groups[21] with the exception of alcohols. (Alcohols and other strongly hydrogen-bonding compounds are best represented by a power series in T over the temperature range from the triple point to approximately 400 K.)

Estimates of the liquid-phase volumes were made using eq 7 and the parameters listed in the footnotes to Table 3 and/or in Table 4. Vapor-phase volumes were calculated with the virial equation of state truncated at the third virial coefficient. Second virial coefficients were estimated with the corresponding-states equation of Pitzer and Curl,[22] and third virial coefficients were estimated with the corresponding-states method of Orbey and Vera.[23] This formulation for third virial coefficients was applied successfully in analyses of the thermodynamic properties of benzene and toluene.[14] Third virial coefficients are required for accurate calculation of the gas volume for pressures greater than 1 bar. Uncertainties in the virial coefficients are assumed to be 10%. Derived enthalpies of vaporization are reported in Table 6. For p > 1 bar, the uncertainties in the virial coefficients are the dominant contributions to the uncertainties in the derived enthalpies of vaporization.

Solubility parameters are listed in Table 7. The solubility parameter is defined as $\delta = [(\Delta_l^g H_m - RT)\rho]^{1/2}$, where $\Delta_l^g H_m$ is the enthalpy of vaporization at 298.15 K (or the melting point if above 298.15 K), R is the gas constant, T = 298.15 K (or the melting point), and ρ = the saturation liquid density at 298.15 K (or the melting point).

Discussion

General Comments. This section emphasizes comparison of the measured properties of this research with experimentally determined values reported in the literature. Only passing reference is made to correlated values available in the literature, mostly those abstracted in the DIPPR Project 801 Database.[24]

Table 6. Enthalpies of Vaporization Obtained from the Wagner and Clapeyron Equations[a]

T/K	$\Delta_l^g H_m$/kJ·mol^{-1}	T/K	$\Delta_l^g H_m$/kJ·mol^{-1}
Cyclopropane Carboxylic Acid			
298.15[b]	62.14 ± 0.30	420.0	52.39 ± 0.23
300.0[b]	62.00 ± 0.30	440.0	50.64 ± 0.27
320.0[b]	60.44 ± 0.27	460.0	48.78 ± 0.37
340.0	58.88 ± 0.25	480.0[b]	46.82 ± 0.48
360.0	57.30 ± 0.23	500.0[b]	44.73 ± 0.65
380.0	55.71 ± 0.22	520.0[b]	42.52 ± 0.85
400.0	54.08 ± 0.22		
N,*N'*-Diethylethanolamine			
280.0[b]	54.44 ± 0.25	400.0	43.29 ± 0.25
298.15[b]	52.50 ± 0.22	420.0	41.55 ± 0.35
300.0[b]	52.31 ± 0.22	440.0	39.72 ± 0.48
320.0[b]	50.34 ± 0.20	460.0	37.75 ± 0.67
340.0	48.48 ± 0.18	480.0[b]	35.63 ± 0.86
360.0	46.72 ± 0.18	500.0[b]	33.3 ± 1.1
380.0	45.00 ± 0.20	520.0[b]	30.7 ± 1.4
2,3-Dihydrofuran			
260.0[b]	33.04 ± 0.10	340.0	28.55 ± 0.25
280.0[b]	31.94 ± 0.10	360.0	27.30 ± 0.37
298.15[b]	30.94 ± 0.12	380.0[b]	25.96 ± 0.48
300.0	30.84 ± 0.12	400.0[b]	24.48 ± 0.65
320.0	29.72 ± 0.17	420.0[b]	22.85 ± 0.81
5-Hexen-2-one			
280.0[b]	44.90 ± 0.17	400.0	36.64 ± 0.33
298.15[b]	43.61 ± 0.15	420.0	35.13 ± 0.45
300.0[b]	43.48 ± 0.15	440.0	33.49 ± 0.60
320.0	42.12 ± 0.13	460.0[b]	31.72 ± 0.78
340.0	40.78 ± 0.15	480.0[b]	29.8 ± 1.0
360.0	39.44 ± 0.17	500.0[b]	27.7 ± 1.2
380.0	38.07 ± 0.23		
Perfluorobutanoic Acid			
260.0[b]	56.17 ± 0.30	380.0	43.53 ± 0.35
280.0[b]	54.11 ± 0.27	400.0	40.99 ± 0.53
298.15[b]	52.27 ± 0.23	420.0	38.15 ± 0.76
300.0[b]	52.09 ± 0.23	440.0[b]	35.0 ± 1.1
320.0	50.07 ± 0.22	460.0[b]	31.4 ± 1.4
340.0	48.02 ± 0.22	480.0[b]	27.3 ± 1.9
360.0	45.85 ± 0.25		
2-Phenylpropionaldehyde			
298.15[b]	56.78 ± 0.25	460.0	45.01 ± 0.37
360.0	52.25 ± 0.18	480.0	43.39 ± 0.48
380.0	50.84 ± 0.18	500.0	41.67 ± 0.63
400.0	49.44 ± 0.18	520.0[b]	39.82 ± 0.81
420.0	48.02 ± 0.22	540.0[b]	37.8 ± 1.0
440.0	46.55 ± 0.27	560.0[b]	35.7 ± 1.3

[a] Uncertainty intervals are twice the standard deviation. [b] The value at this temperature was calculated with extrapolated vapor pressures derived from the fitted Wagner equation.

Table 7. Solubility Parameters[a,b]

compound	ρ	$\Delta_l^g U_m$	$10^{-4}\delta$
	mol·m^{-3}	J·mol^{-1}	(J·m^{-3})$^{1/2}$
cyclopropane carboxylic acid	1082	59 660	2.74
N,*N'*-diethylethanolamine	877.3	50 020	1.94
2,3-dihydrofuran	919.3	28 460	1.93
5-hexen-2-one	836.1	41 130	1.87
perfluorobutanoic acid	1640	49 790	1.95
phenylpropionaldehyde	999.8	54 300	2.01

[a] Densities at 298.15 K (listed to an extra significant figure to prevent round-off errors) were estimated by extrapolation of the equations listed in the footnotes to Table 4. [b] $\Delta_l^g U_m = (\Delta_l^g H_m - RT)$ obtained using the values for the enthalpy of vaporization at 298.15 K.

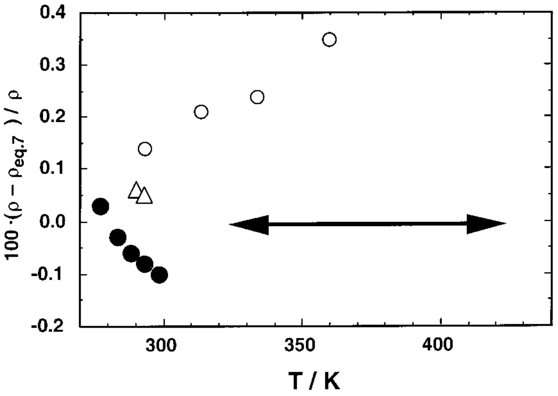

Figure 2. Comparison of literature saturation liquid densities for cyclopropane carboxylic acid with values obtained using eq 7 and the parameters listed in footnote *b* of Table 3. The double-headed arrow represents the temperature span of the density measurements obtained in this research (see Table 3). Key: (●) Bone and Perkin, Jr.;[25] (△) Brühl;[26] (○) Jeffery and Vogel.[27]

Table 8. Relative[25] and Absolute Densities[a] of Cyclopropane Carboxylic Acid

T/K	relative density	absolute density/kg·m^{-3}
277	1.1024	1102.4
283	1.0966	1096.3
288	1.0923	1091.4
293	1.0884	1086.7
298	1.0848	1081.6

[a] Absolute densities calculated using the values of Haar et al.28 as reference points (see text).

Comparison with Literature Values. Cyclopropane Carboxylic Acid. Sample decomposition prevented measurement of critical properties for this compound. Values of $T_c = (671 \pm 10)$ K, $p_c = (5995 \pm 500)$ kPa, and $\rho_c = (324 \pm 20)$ kg·m^{-3} were used in this research.

Extensive decomposition occurred above 470 K during the heat-capacity measurements. Scrutiny of the differences between the boiling and condensation temperatures listed in Table 1 points to possible decomposition at as low a temperature as ~460 K.

Only single-temperature point values for the vapor pressure of cyclopropane carboxylic acid were found in a search of the literature through June 1997. The datum corresponded to either values of the normal boiling point ($T_{bp} = 457 \pm 3$ K) or reduced pressure values obtained during preparation of samples as organic reaction intermediates.

Figure 2 compares saturated density, ρ_{sat}, values for cyclopropane carboxylic acid found in the literature[25-27] with values calculated using eq 7 and the parameters listed in the footnotes to Table 4. Note that the values listed by Bone and Perkin, Jr., are relative to the corresponding density of water at the given temperature and were measured by W. H. Perkin, Sr. Table 8 lists both the values given in the Bone and Perkin, Jr., reference and the corresponding absolute density obtained using modern literature values for pure water[28] as the reference point.

N,N-Diethylethanolamine. For *N*,*N*-diethylethanolamine, extensive decomposition occurred above 460 K during the heat-capacity measurements. Scrutiny of the differences between the boiling and condensation temperatures listed in Table 1 does *not* point to possible decomposition at temperatures below 476 K in this mainly glass apparatus. Density measurements above 423 K also showed the possible onset of decomposition (see Table 3). Interaction with the exposed metal surfaces during both the DSC and density measurements is a possible explanation of the differing decomposition onset points.

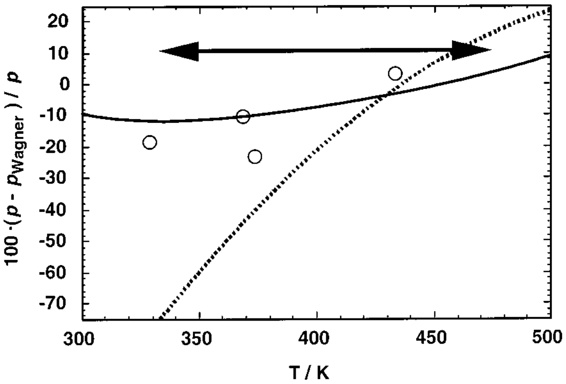

Figure 3. Comparison of literature saturation vapor pressures for *N*,*N*-diethylethanolamine with values obtained using the Wagner equation (eq 1) and the parameters listed in Table 4. The double-headed arrow represents the temperature span of the vapor-pressure measurements obtained in this research (see Table 1). The solid line represents the deviations obtained using the DIPPR 801 Project Database[24] correlation equation. The dashed line represents the deviations from an equation derived using the values listed in Engineering Sciences Data Item 79030.[29] Key: (○) Headlee et al.[30]

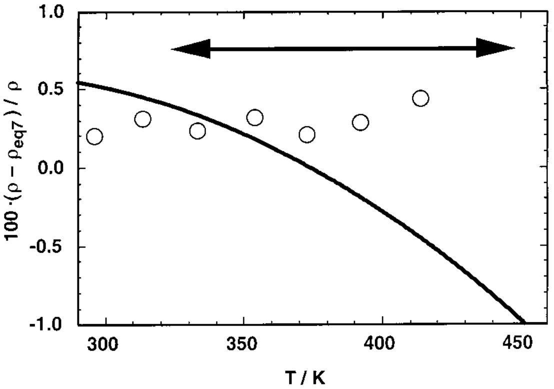

Figure 4. Comparison of literature saturation liquid densities for *N*,*N′*-diethylethanolamine with values obtained using eq 7 and the parameters listed in footnote *c* of Table 3. The double-headed arrow represents the temperature span of the density measurements obtained in this research (see Table 3). The solid line represents the deviations obtained using the DIPPR 801 Project Database.[24] Key: (○) DiGulllo et al.[31]

The sample decomposition prevented measurement of critical properties for this compound. For the fitting, values of $T_c = (616 \pm 10)$ K, $p_c = (2650 \pm 500)$ kPa, and $\rho_c = (277 \pm 20)$ kg·m^{-3} were used in this research. The 1997 version of the DIPPR 801 Database[24] recommends the following critical properties for *N*,*N*-diethylethanolamine: $T_c = (592 \pm 30)$ K, $p_c = (3180 \pm 320)$ kPa, and $\rho_c = (292 \pm 75)$ kg·m^{-3}. The DIPPR 801 Database lists predicted values of $T_c = 616$ K and $p_c = 4650$ kPa attributed to an Engineering Sciences Data Item.[29]

Figure 3 compares literature values for the vapor pressure of *N*,*N*-diethylethanolamine[24,29,30] with values obtained using the Wagner equation (eq 1) and the parameters listed in Table 4. Below 400 K, the Engineering Sciences[29] data are in serious disagreement with the measured values. The DIPPR 801 Project Database equation[24] is in reasonable agreement with the values obtained in this research.

Figure 4 compares ρ_{sat} values for *N*,*N*-diethylethanolamine found in the literature[31] and values obtained using

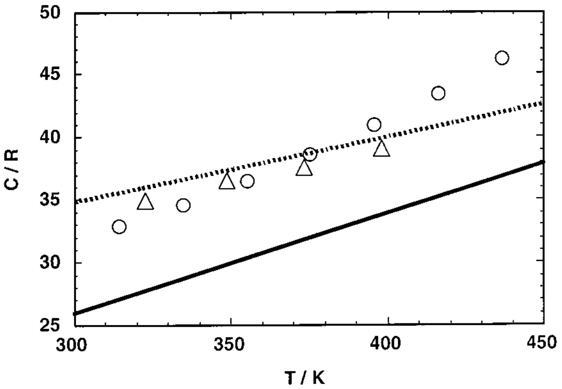

Figure 5. Comparison of literature saturation liquid-phase heat capacities for *N*,*N*-diethylethanolamine with values obtained using the equation listed in Table 2. The dashed line represents the equation. The solid line represents the saturated-heat-capacity equation listed in the 1997 version of the DIPPR 801 Project Database.[24] Key: (○) values calculated at representative temperatures using the group-additivity method of Ruzicka and Domalski;[33] (△) Maham et al.[32]

the DIPPR 801 Project Database[24] correlated equation with values calculated using eq 7 and the parameters listed in footnote *c* of Table 3. The values obtained by the Georgia Tech. group[31] are ~0.4% higher across the temperature range of the measurements than those obtained in this research. The DiGulllo et al.[31] sample was used as obtained from Aldrich Chemical Co. and may have contained dissolved water. However, the quantity of water necessary for agreement between their measurements and those listed in Table 3, 2 mole %, would seem large for a sample listed as 99 mole % pure.

Liquid-phase heat capacities for *N*,*N*-diethylethanolamine were obtained by Maham et al.[32] As shown in Figure 5, their results and values obtained using the saturation-heat-capacity equation given in Table 2 agree within the combined uncertainty intervals ($0.02C_{\mathrm{sat}}$). Also given in Figure 5 are a solid line representing the saturated-heat-capacity equation recommended in the DIPPR 801 Project Database[24] and values obtained at representative temperatures using the group-additivity method of Ruzicka and Domalski.[33] The Ruzicka and Domalski[33] correlation equation has the wrong temperature dependence of the heat capacity.

2,3-Dihydrofuran. Thermophysical property measurements on this compound were made by our group as part of the DIPPR 871 Project for 1987.[34] However, the sample used was not of the highest purity, as seen by the CO_2 recoveries averaging 100.11 mole %. Also, the difference between the boiling and condensation temperatures in the ebulliometric vapor-pressure measurements ranged from 0.013 K at the 70 kPa point to 0.029 K at 270 kPa. Because of these problems, a new sample was obtained for the measurements reported in this research.

Rapid decomposition in the region of the critical point prevented measurement of the critical temperature and density using the DSC method.[13] The onset of sample decomposition occurred so close to the critical point that careful scrutiny of the DSC traces during the heat-capacity measurements allowed an approximate value of the critical temperature to be determined. A simultaneous nonlinear least-squares fit of the vapor pressures listed in Table 1 and the two-phase heat capacities $C_{x,\mathrm{m}}^{\mathrm{II}}$ given in Table 2 was completed using the approximated value for T_c. The fitting procedures used[13] provide values of $T_c = (525 \pm 5)$ K, $p_c = (5575 \pm 300)$ kPa, and $\rho_c = (327 \pm 10)$ kg·m^{-3}. The 1997 version of the DIPPR 801 Database[24] recommends the following critical properties for 2,3-dihydrofuran: $T_c = (524 \pm 30)$ K, $p_c = (5500 \pm 550)$ kPa, and $\rho_c = (342 \pm 40)$ kg·m^{-3}.

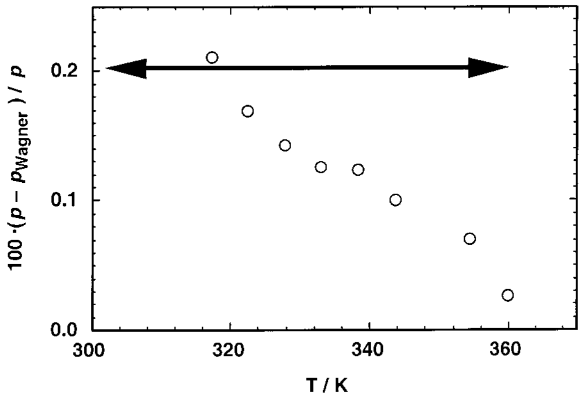

Figure 6. Comparison of the previous ebulliometric saturation vapor pressures for 2,3-dihydrofuran[34] with values obtained using the Wagner equation (eq 1) and the parameters listed in Table 4. The double-headed arrow represents the temperature span of the vapor-pressure measurements obtained in this research (see Table 1).

Figure 6 compares the earlier ebulliometric vapor-pressure measurements[34] with values obtained using the Wagner equation (eq 1) and the parameters listed in Table 4. Differences are of the order of tenths of a percent and are probably due to the greater purity of the sample used in this research. [Note: differences between boiling and condensation temperatures (Table 1, column 6) average 0.006 K.] The derived enthalpies of vaporization (Table 6) are slightly different from those listed in Table 27 of the 1989 reference.[34] The differences, always within the listed error limits (2 times the standard deviation from the mean), arise from both the differing vapor pressures and also the methods of determination. The earlier work employed the Cox equation to represent the vapor-pressure variation with temperature, and the equation of state used was truncated at the second virial coefficient.

The earlier DIPPR 871 work[34] lists values for the heat capacity and saturation liquid-phase density at 298.15 K of 14.7*R* and 927 kg·m^{-3}, respectively. The corresponding values calculated using the relevant equations derived in this research are 14.7*R* and 919 kg·m^{-3}. No further references to thermophysical property determinations for 2,3-dihydrofuran were located in a search of the literature through June 1997.

5-Hexen-2-one. A literature search produced, with one exception, no references containing measured thermophysical properties for 5-hexen-2-one. The exception is a paper by Kobe et al.,[35] which contained vapor-pressure measurements in the region 450 K to 560 K that corresponds to pressures between 370 kPa and 2220 kPa. These measurements are in the region between the upper bound of the ebulliometric equipment used in this research and the critical point.

Rapid decomposition in the region of the critical point prevented measurement of the critical temperature and density using the DSC method.[13] The onset of sample decomposition occurred so close to the critical point that careful scrutiny of the DSC traces during the heat-capacity measurements allowed an approximation of the critical temperature. Kobe et al.[35] noted in their measurements that: “With 5-hexen-2-one the vapor pressure values were significantly lower after heating for some time. This was taken to indicate polymerization of this compound.” A simultaneous nonlinear least-squares fit of the vapor

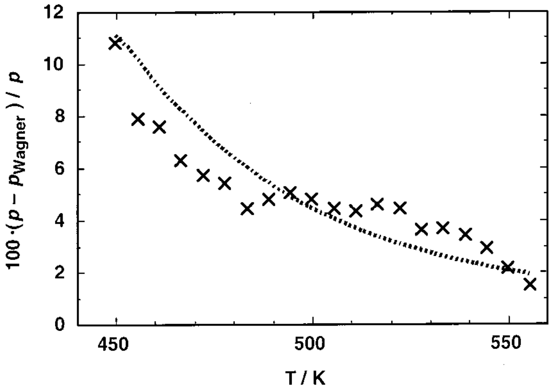

Figure 7. Comparison of the vapor-pressure measurements of Kobe et al.[35] for 5-hexen-2-one with values obtained using the Wagner equation (eq 1) and the parameters listed in Table 4. The dashed line represents a positive deviation of 41 kPa (6 pounds per square inch absolute). Key: (×) Kobe et al.[35]

pressures listed in Table 1 and the two-phase heat capacities $C^{\mathrm{II}}_{x,\mathrm{m}}$ given in Table 2 was completed using the approximate value for T_c. The fitting procedures used[13] provide values of $T_c = (594 \pm 5)$ K, $p_c = (3550 \pm 300)$ kPa, and $\rho_c = (273 \pm 10)$ kg·m^{-3}. The paper by Kobe et al.[35] recommended correlation equations for the critical temperatures and pressures of ketones. Using those correlations, values of $T_c = 589$ K and $p_c = 3456$ kPa are obtained, in excellent agreement with those derived here.

Figure 7 compares the vapor pressures obtained by Kobe et al.[35] with values derived using the Wagner equation and the parameters listed in Table 4. Note there is no overlap between the Kobe et al. measurements and those obtained in this research (Table 1). Also shown in the figure is a dashed line representing a positive deviation of 41.4 kPa (6 pounds per square inch absolute). Kobe et al. "considered" the uncertainty interval in vapor pressures of 5-hexen-2-one to be "4 pounds per square inch absolute." No polymerization of the sample used in this research was seen either by careful inspection of the sample after completion of the measurements or in the difference between the boiling and condensation temperatures (Table 1, column 6).

Perfluorobutanoic Acid. The only reference to the thermophysical properties of perfluorobutanoic acid obtained in a literature search through June 1997 was a paper by Kauch and Diesslin in 1951.[36] Kauch and Diesslin note the perfluorocarboxylic acids of their study were completely ionized in water solution and "are equivalent to mineral acids in strength." They also note that the perfluoro acids "are highly thermally stable" and "can be heated to 400 °C in borosilicate glass without significant decomposition."

The ebulliometric vapor-pressure measurements reported in Table 1 show the thermal stability of perfluorobutanoic acid in borosilicate glass to at least 426 K. However, in the DSC measurements, decomposition was noted above 400 K with extensive pitting of the 321 stainless steel cell. Additionally, in the vibrating-tube densimeter measurements, the sample colored above 400 K with accompanying pitting of the containment tubing.

A critical temperature of (530 ± 5) K, a corresponding critical pressure of (2650 ± 250) kPa, and a critical density of (504 ± 15) kg·m^{-3} derived using the fitting procedures were used in this research for corresponding states and other estimations for perfluorobutanoic acid (Table 4). No literature references to measurements of these properties were located. Figure 8 compares the vapor-pressures

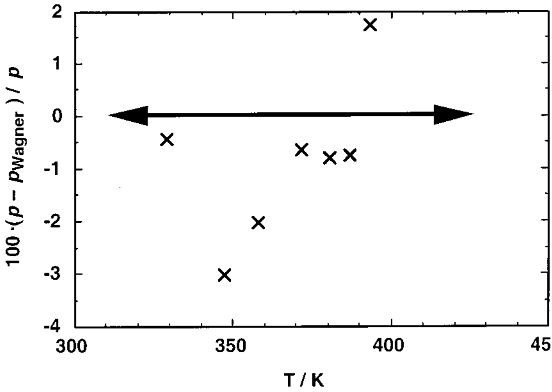

Figure 8. Comparison of the vapor-pressure measurements of Kauck and Diesslin[36] for perfluorobutanoic acid with values obtained using the Wagner equation (eq 1) and the parameters listed in Table 4. The double-headed arrow represents the temperature span of the vapor-pressure measurements obtained in this research (see Table 1). Key: (×) Kauck and Diesslin.[36]

measurement of Kauck and Diesslin[36] for perfluorobutanoic acid with values obtained using the Wagner equation eq 1 and the parameters listed in Table 4. Agreement is not as good as would be expected using "highly purified specimens." Kauck and Diesslin[36] listed a density of 1651 kg·m^{-3} at 293 K and an enthalpy of vaporization of 46.86 kJ·mol^{-1} at the normal boiling point. A density of 1652 kg·m^{-3} at 293 K is obtained by extrapolation of the results of this research, using the equation given in footnote *h* of Table 3. At 394.65 K (normal boiling point), an enthalpy of vaporization of (41.7 ± 0.6) kJ·mol^{-1} is interpolated using the values listed in Table 6. The lower enthalpy of vaporization in turn lowers the Trouton's ratio for perfluorobutanoic acid from 28.5 to 25.3, close to that listed for perfluoroacetic acid by Kauck and Diesslin,[36] namely, 24.1.

2-Phenylpropionaldehyde. This compound has optical isomers. The sample used in the measurements reported in this research had no optical activity. In Chemical Abstracts Service Collective Indices 6−8, references to it can be found under the name "hydratropaldehyde". From Collective Index Number 9 to date, it is indexed under the name "benzeneacetaldehyde, α-methyl". A literature search produced, with one exception, no references containing measured thermophysical properties for 2-phenylpropionaldehyde. The exception is a paper by Daubert[37] which contained vapor-pressure measurements in the region 375.4 K to 511 K (pressures between 3.81 kPa and 235.1 kPa).

For 2-phenylpropionaldehyde extensive decomposition occurred above 513 K during the heat-capacity measurements. Scrutiny of the differences between the boiling and condensation temperatures listed in Table 1 also points to extensive decomposition at temperatures above 517 K. Density measurements above 440 K also showed the possible onset of decomposition (see Table 3). Daubert[37] also noticed decomposition at the top end of his measurements (>511 K).

A critical temperature of (680 ± 15) K, a corresponding critical pressure of (2720 ± 500) kPa, and a critical density of (307 ± 30) kg·m^{-3} derived using the fitting procedures were used in this research for corresponding states and other estimations for 2-phenylpropionaldehyde (Table 4). No literature references to measurements of these properties were located. Figure 9 compares the vapor-pressure measurements of Daubert[37] for 2-phenylpropionaldehyde with values obtained using the Wagner equation (eq 1) and the parameters listed in Table 4. In Figure 9 the solid curve

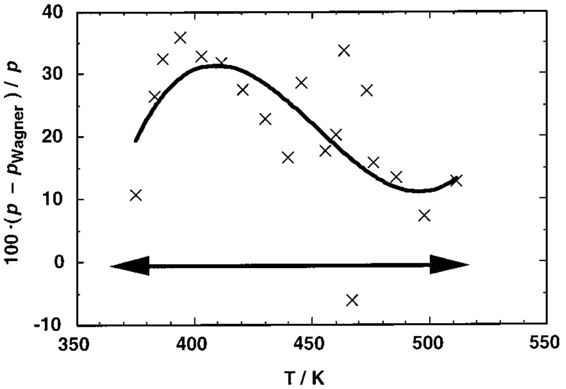

Figure 9. Comparison of the vapor-pressure measurements of Daubert[37] for 2-phenylpropionaldehyde with values obtained using the Wagner equation (eq 1) and the parameters listed in Table 4. The double-headed arrow represents the temperature span of the vapor-pressure measurements obtained in this research (see Table 1). The solid line shows a third-order fit of the individual deviations noted on the plot. Key: (×) Daubert.[37]

is a smoothed representation with temperature of the individual differences also plotted in the figure. Agreement is poor and is larger than what would be expected for such measurements. Daubert did use a sample which was stated to be 98 mol % pure. In addition, he notes that "Scatter in the high-pressure data near the normal boiling point could not be eliminated although three experiments were run."

Decomposition Points and Bond Dissociation Energies. In the 1992 Project Report,[1] a "Rule-Of-Thumb", which applies *only* in cases where thermal decomposition is initiated by bond scission and radical formation, was derived to estimate bond dissociation energies. The rule was

$$\mathrm{BDE} = 64.7RT \qquad (9)$$

where BDE = bond dissociation energy, R = the gas constant, and T = the temperature of the onset of thermal decomposition. The onset of extensive decomposition was noted for cyclopropane carboxylic acid at ~470 K during the ebulliometric vapor-pressure measurements with the possibility of initial decomposition at ~460 K. Applying that rule in this case leads to a bond dissociation energy in the range 247 to 252 $\mathrm{kJ \cdot mol^{-1}}$ for cyclopropane carboxylic acid.

The decomposition temperature for 2-phenylpropionaldehyde (509 K) is too low to signify radical formation being the initial step in the decomposition reaction. In that case, a concerted condensation reaction mechanism[38] is the probable initial pathway.

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